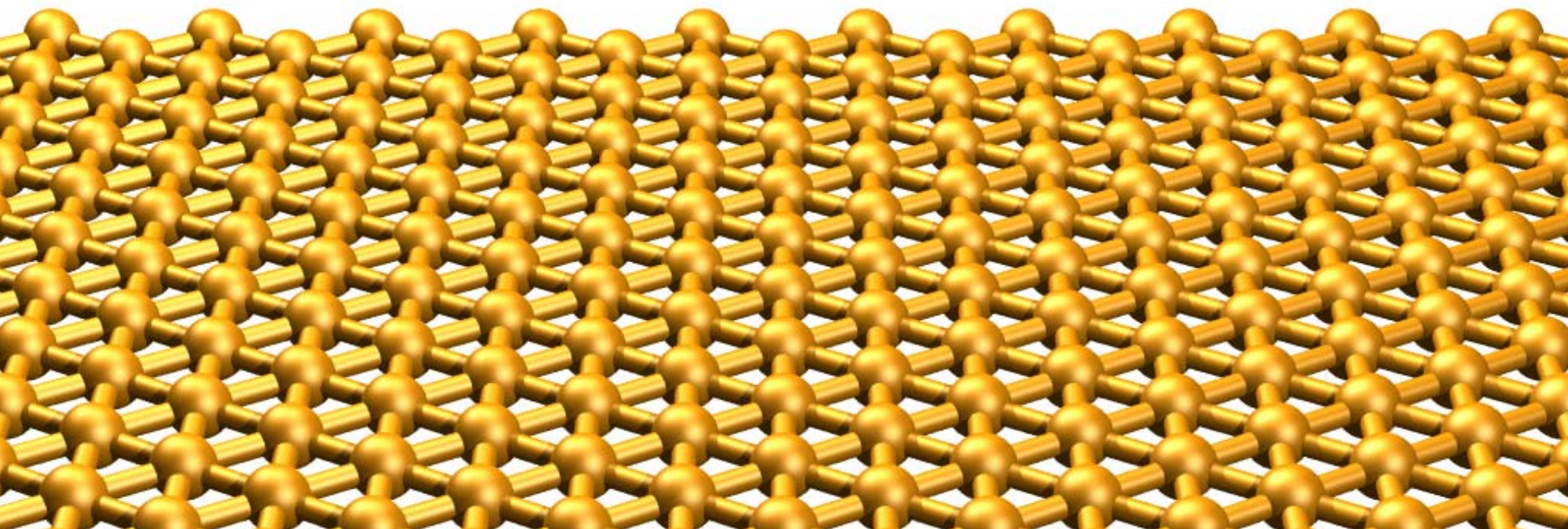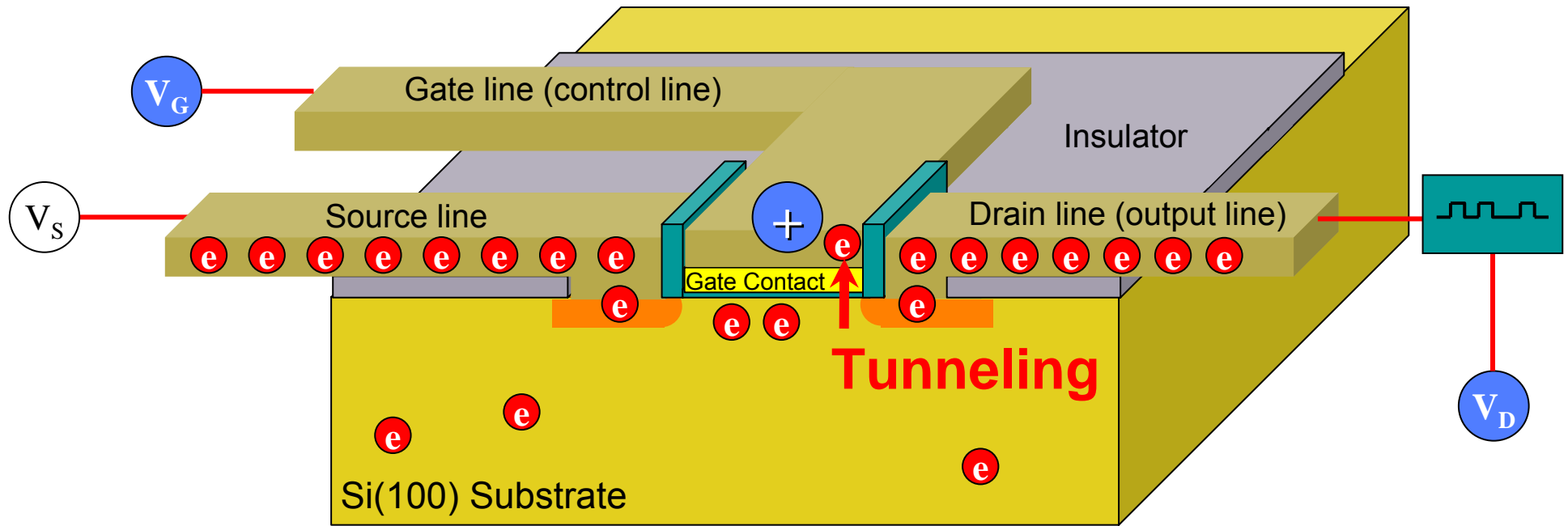# Quantum Chemical Simulation of ALD of HfO$_2$

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Current Technology:

- Leakage current from electron tunneling increasing exponentially as gate dielectric thickness decreases.

High-K Choices

Dielectric Materials		κ
silicon oxide	SiO_2	3.5
silicon nitride	Si_3N_4	7
aluminum oxide	Al_2O_3	9
zirconium oxide	ZrO_2	25
hafnium oxide	HfO_2	30 - 40

- ZrO_2 , HfO_2 , and Al_2O_3 are favorable candidates for the gate dielectric
  - High-k
  - Stable with respect to SiO_2 and silicate formation
- Problem: Process for producing uniform deposition with good dielectric properties needs to be developed.
 - Possible solution: Atomic Layer Deposition (ALD)

The ALD Process

1. Clean substrate
2. Chemically prepare substrate
3. Vaporize precursors

Substrate

Substrate

Functionalized Substrate

First Half-Cycle

A1. Transport vapor of first precursor to substrate

A2. Self-limiting reaction of first precursor with surface

A3. Transport excess reactant and volatile byproduct out of reactor
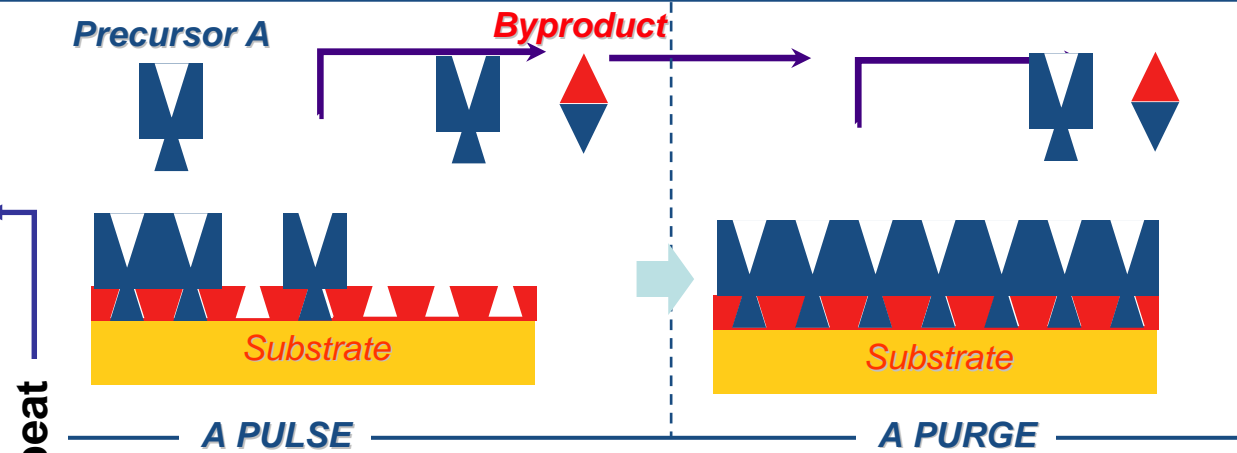
Second Half-Cycle

B1. Transport vapor of second precursor to substrate

B2. Self-limiting reaction of second precursor with surface

B3. Transport excess reactant and volatile byproduct out of reactor

Repeat

Precursor A

Byproduct

Substrate

A PULSE

Substrate

A PURGE

Precursor B

Substrate

B PURGE

Substrate

B PULSE

4
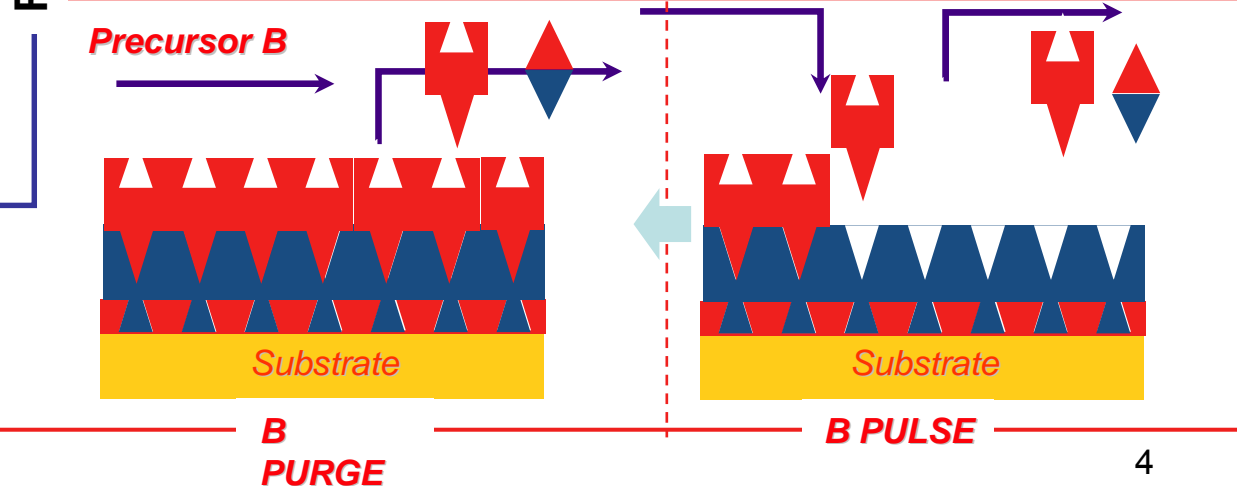
Questions:

- What causes submonolayer growth?
  - Steric effects?
- What causes Cl contamination when metal chloride precursors are used?
- What determines the ALD process temperature?
- How to select an ALD precursor?
- What are the ALD chemical mechanisms?
- How do you prepare a surface for ALD?
- Can an ALD process be transferred to different substrates?
- Can ALD be done selectively?

$H_2O(g)$

$HfCl_4(g)$

Hf-Cl*

Hf-OH*

HfO_2
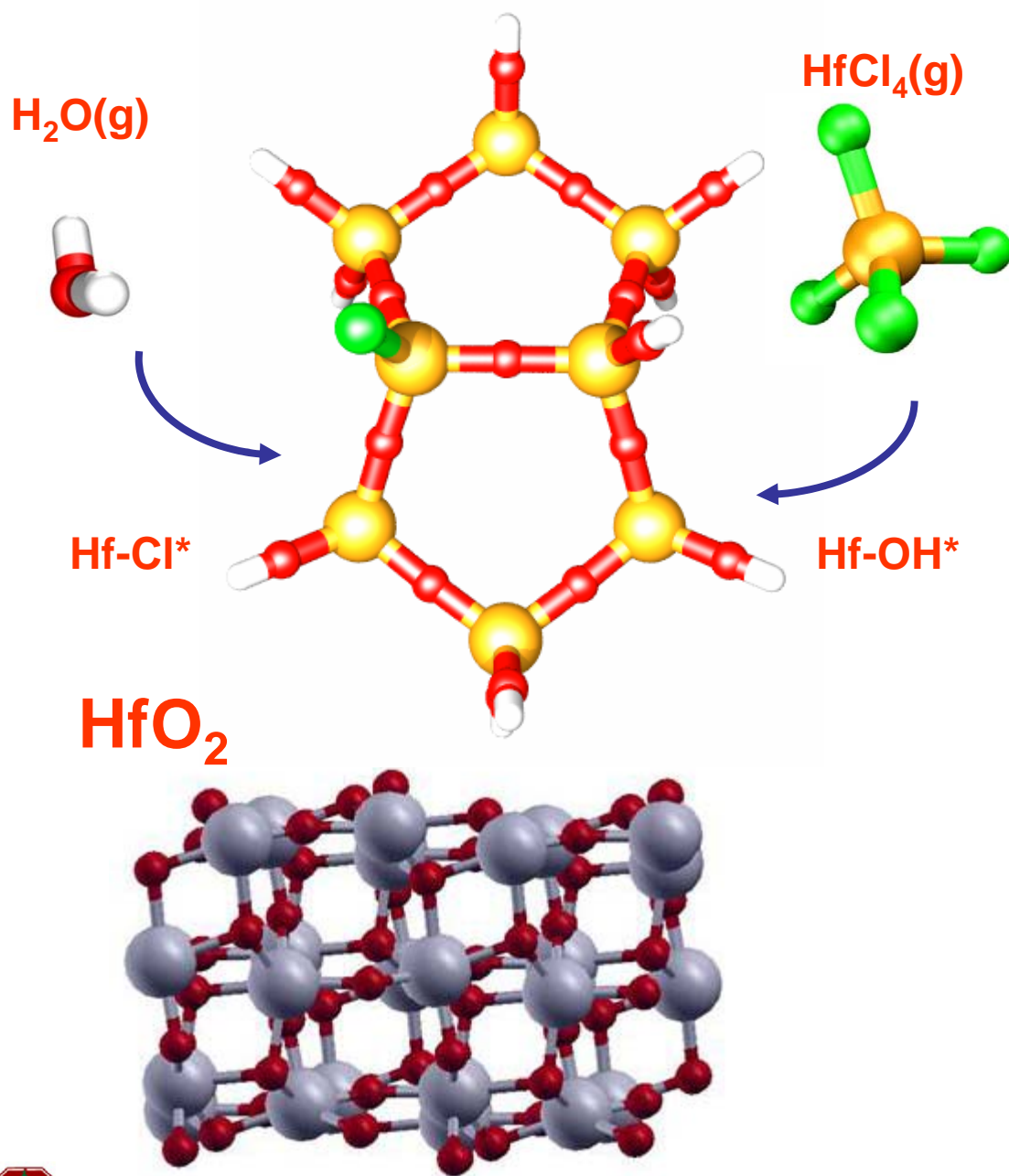
Computational Methods:

Slab Models
- **VASP**
- **PW91-DFT Method**
- **Projected augmented wave**
- **450 eV Cutoff**
- **Slab thicknesses chosen so that energies and displacements converged**
- **Semicore with 5p, 5d and 6s electrons treated explicitly**
- **10x10x1 k-point sampling (chosen using the Monkhorst-Pack method)**
- **Born-Oppenheimer MD**

Bulk Properties

	Present GGA	Previous LDA	Previous GGA	Expt.
Cubic				
Energy/HfO$_2$ Unit	-30.45	-	-	-
V	32.11	31.95	36.15	32.77
a	5.045	5.248	5.04	5.08
Tetragonal				
Energy/HfO$_2$ Unit	-30.51	-	-	-
V	32.69	32.77	37.74	
a	3.565	5.056	5.299	
c	5.146	5.127	5.373	
Monoclinic				
Energy/HfO$_2$ Unit	-30 .69	-	-	-
V	34.10	34.35	38.01	34.58
a	5.079	5.106	5.291	5.117
b	5.177	5.165	5.405	5.175
c	5.250	5.281	5.366	5.220
β	99.24	99.35	97.92	99.22

ΔH_f= 1070.54 kJ/mol (1144 kJ/mol) (7% error)

Excellent agreement with experiment
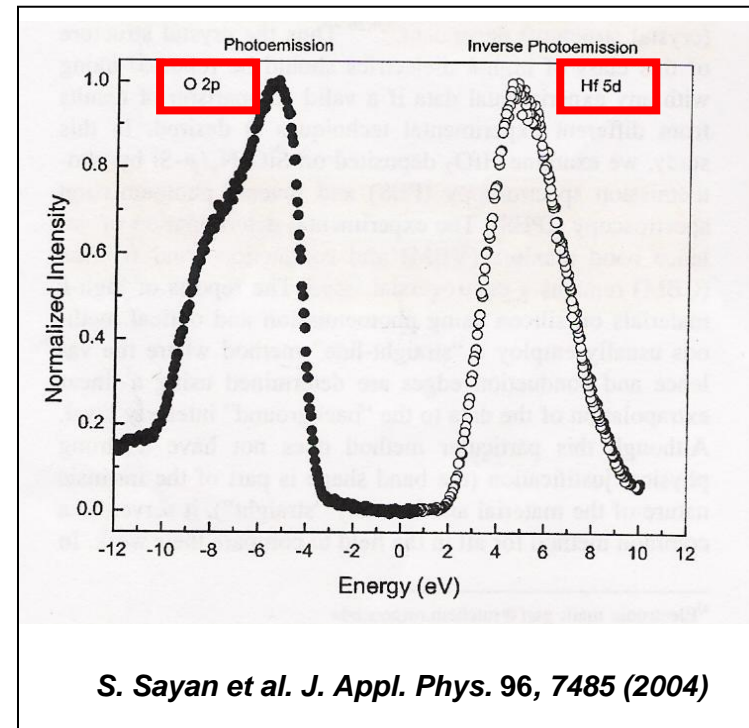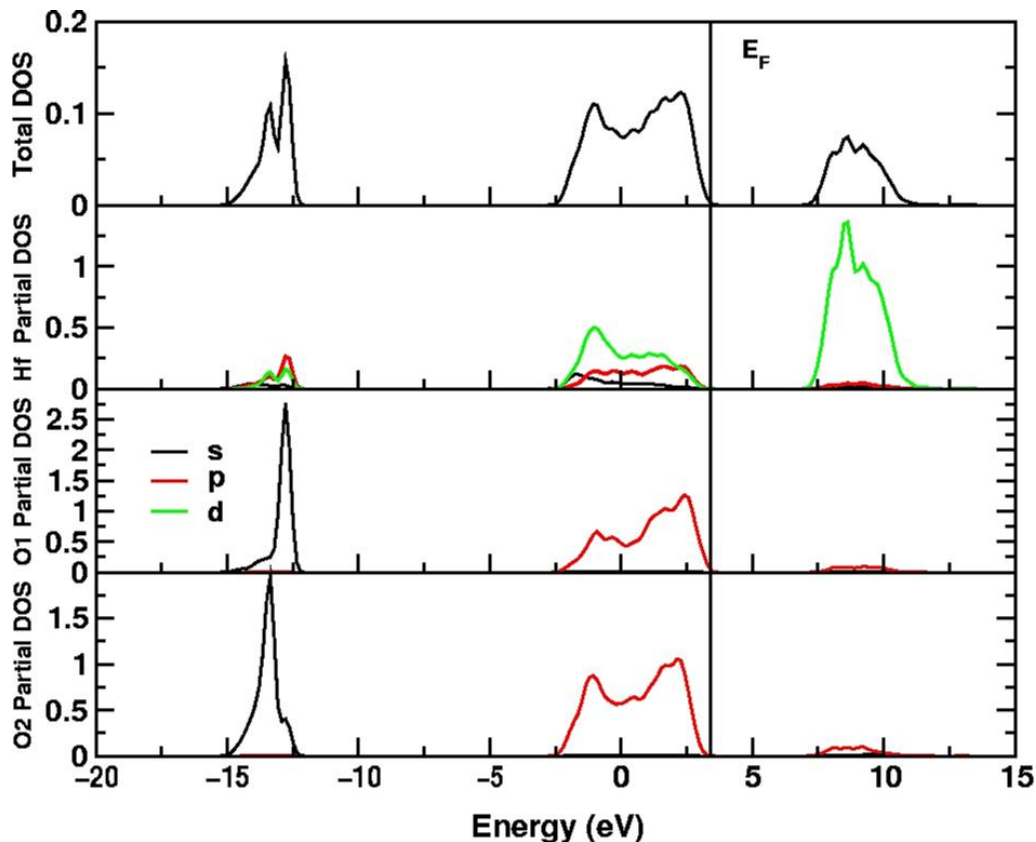
*S. Sayan et al. J. Appl. Phys. 96, 7485 (2004)*

- Band gap: 3.76 eV
- Good agreement of the character of the valence band with photoemission data
- Covalency of Hf-O bond

Mukhopadhyay, A., J. Sanz and C. Musgrave, "First-Principles Calculations of Structural and Electronic Properties of Monoclinic Hafnia Surfaces," *Phys. Rev. B*, 73, 115330-115337 (2006).

The Monoclinic HfO$_2$ Surfaces

Why Calculate Surface Properties? Because interface properties partially depend on substrate surface upon which films are deposited.

- The electronic structure of metal-high-K interfaces will depend upon the surface structure of the high-K upon which the metal is deposited
- High-K films are amorphous or polycrystalline and so interface properties will be an average over the interface configurations present.
- Although experimental data for HfO$_2$ surfaces like XRD, RHEED exist, they only provide indirect and incomplete information about the surface structure
- Interpretations of experiment is complicated by finite-size effects
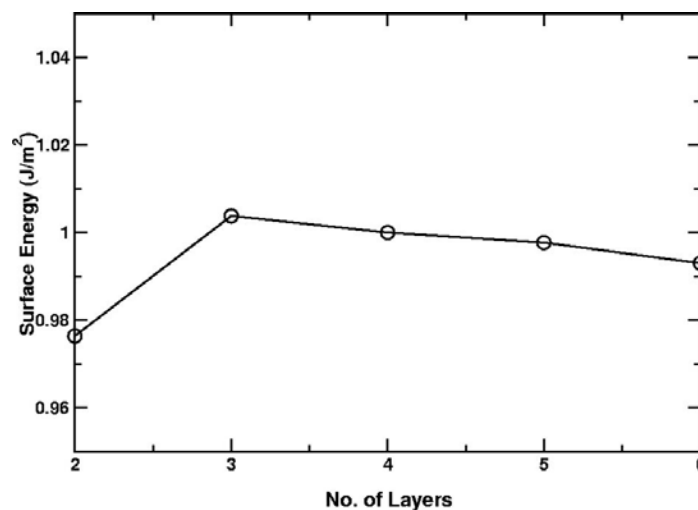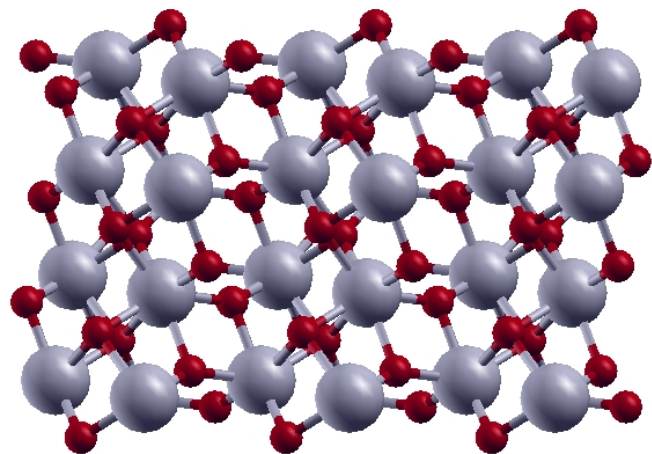- Comparisons are often difficult and dependent on experimental conditions

Lee et al. Eur. Phys. J. B 39, 273 (2004)

J. Aarik Thin Solid Films 466, 41 (2004)
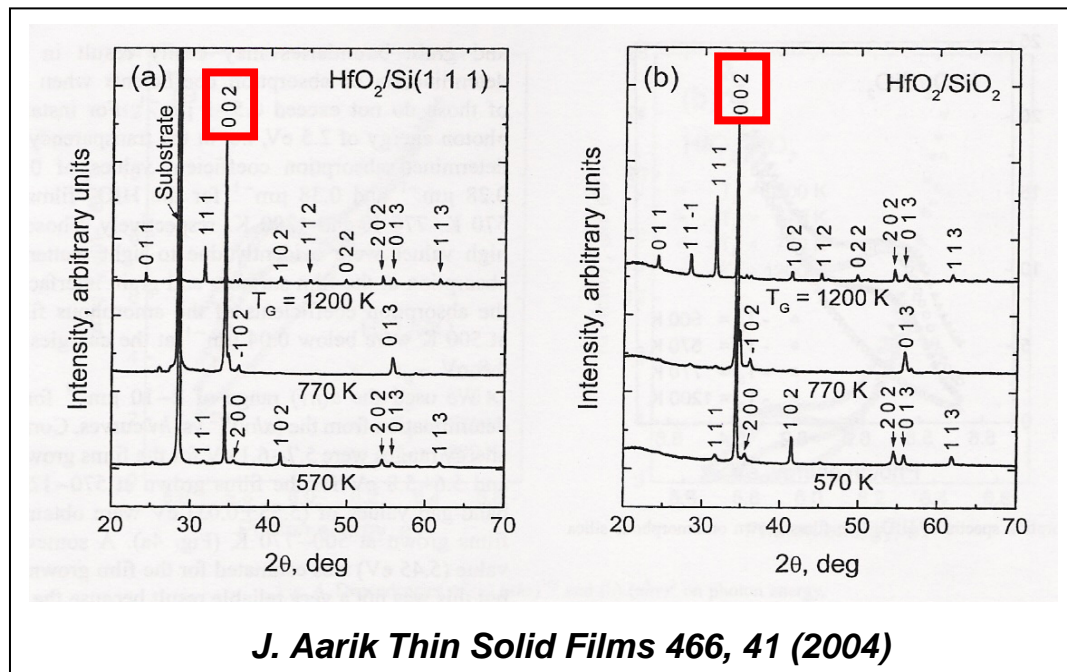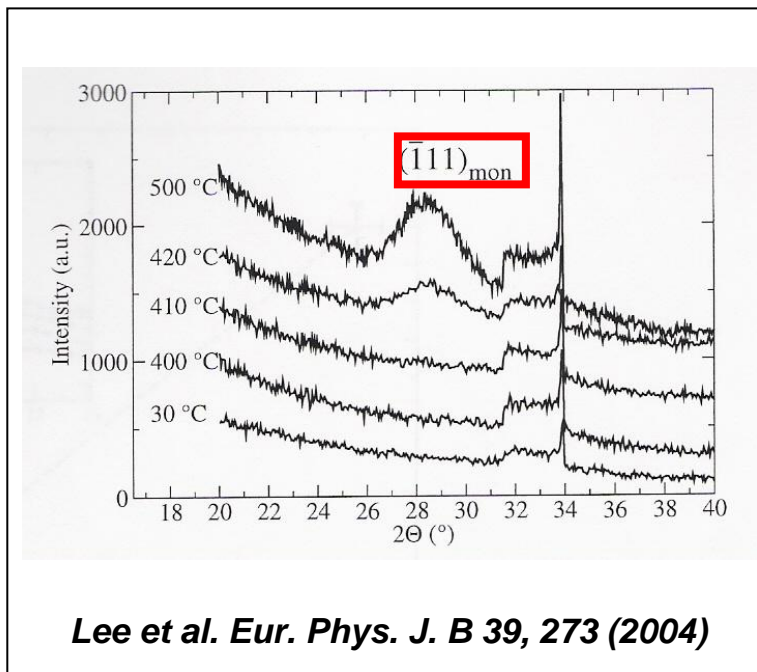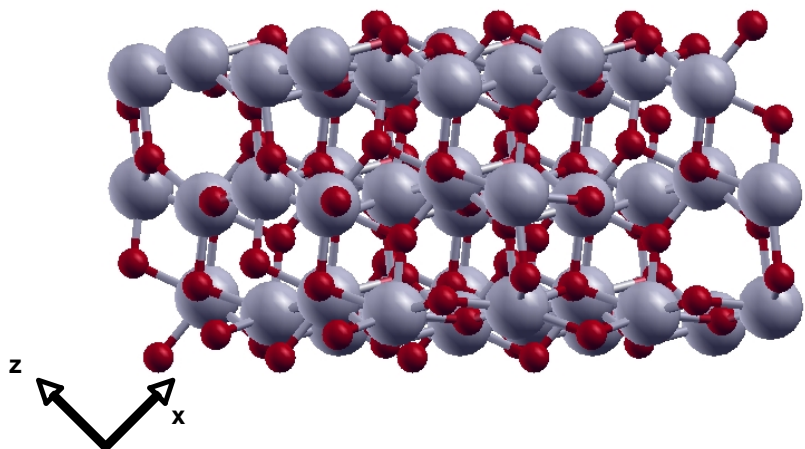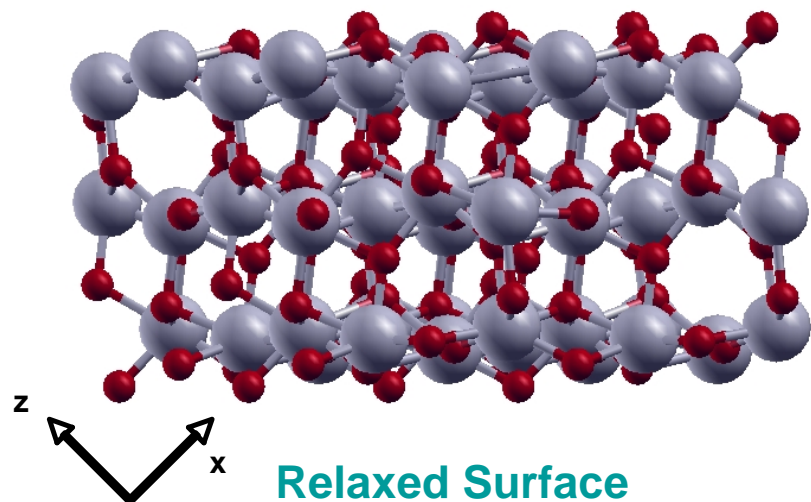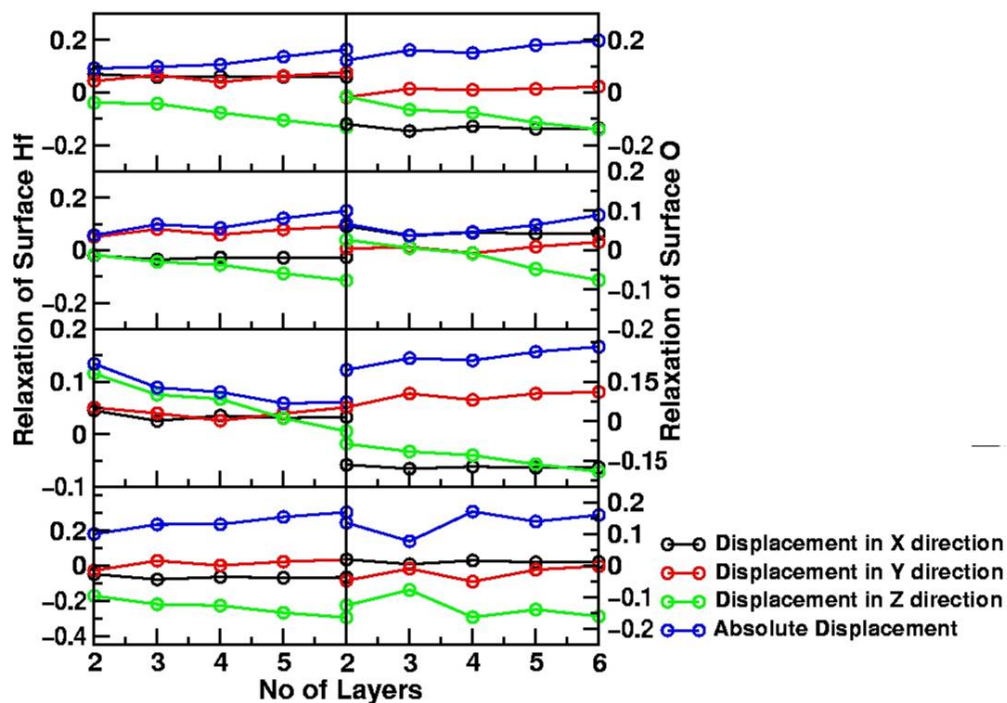
Unrelaxed Surface
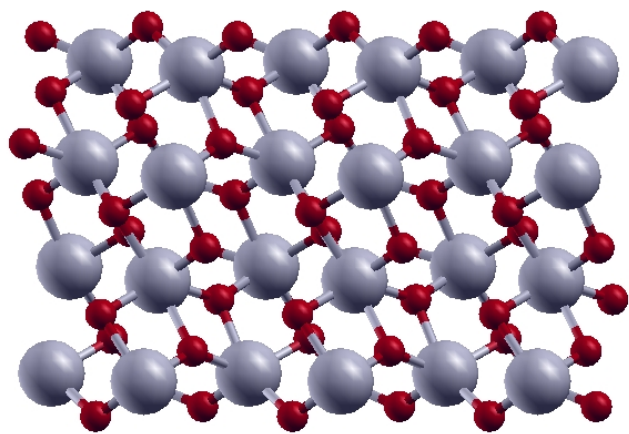
Relaxed Surface

HfO₂ Surface Stability and Relaxation

Unrelaxed Surface

Relaxed Surface

| Face	Surface Energy (J/m²)		% Relaxation Energy	RMS ionic relaxation Å
	Relaxed	Unrelaxed		
($\overline{1}$11)	0.993	1.460	32	0.026
(111)	1.199	1.562	23	0.023
($\overline{1}$01)	1.322	1.858	29	0.033
(110)	1.388	2.043	32	0.030
(001)	1.416	2.169	35	0.060
(011)	1.484	2.100	29	0.024
(101)	1.550	2.412	36	0.047
(100)	1.667	2.165	23	0.021
(010)	1.878	2.782	33	0.040

- *Although m-(-111) has the lowest surface energy, the m-(001) surface is observed experimentally and is kinetically stable during processing.*

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Mukhopadhyay, Sanz and Musgrave
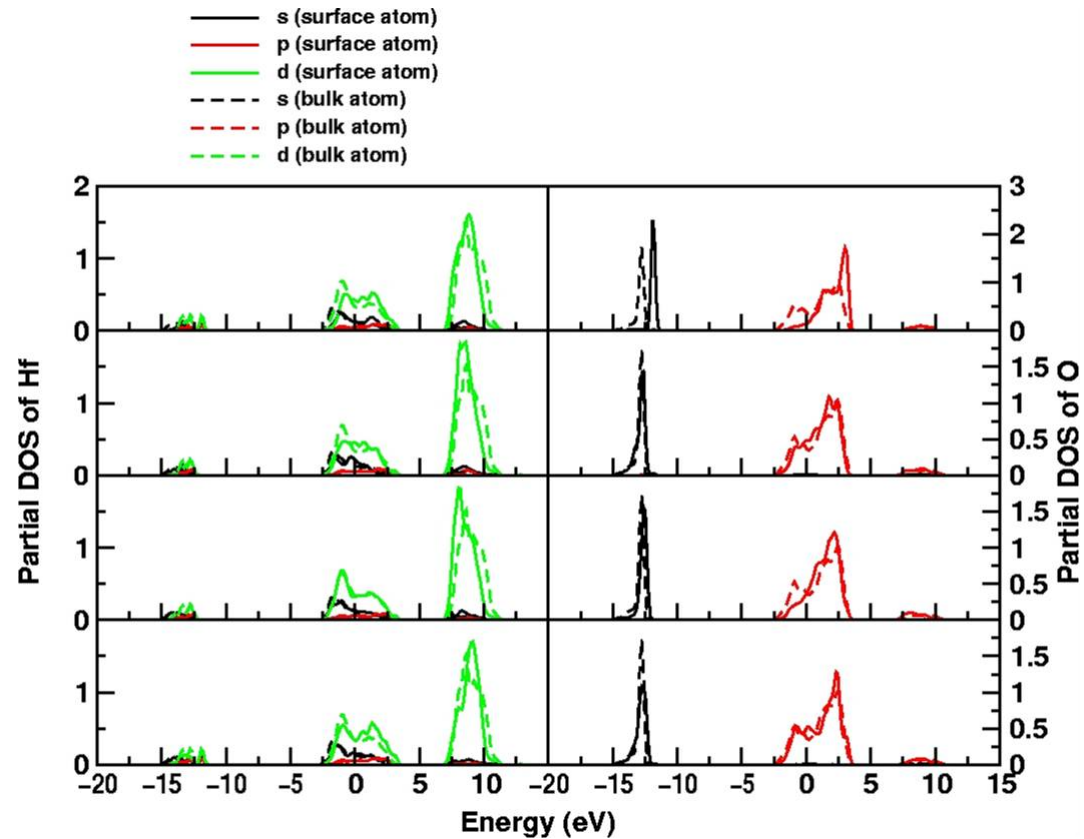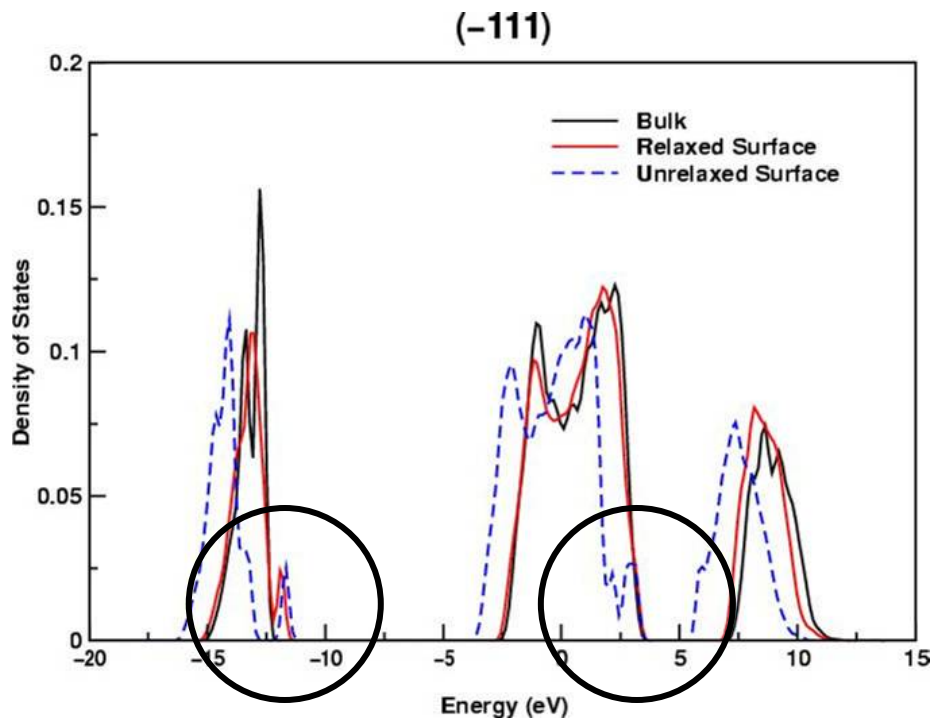
- DOS of unrelaxed surface is shifted towards lower energy
- Bandgap smaller than bulk, as expected
- Two surface states at -12 eV (O-2s) and 3 eV (O-2p)
- Relaxation causes the surface oxygen 2p state to become 'bulk-like'
- Surface state generated by surface O-2s

12
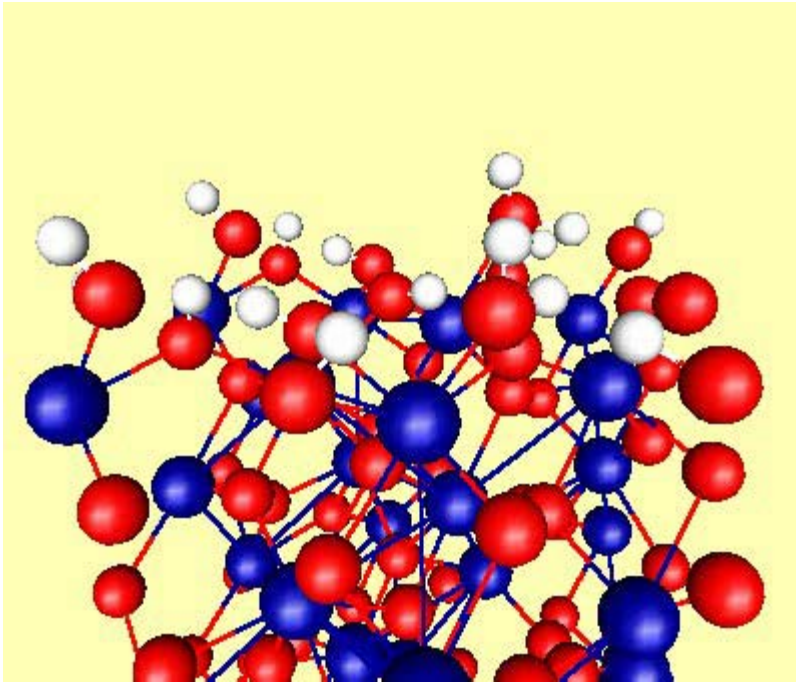
- Surface –OH groups play an important role as reactive species
- Metal precursor form a surface bound product
- Hydroxyl group formed may condense and librate water
- Dehydroxylation process is a function of temperature and pressure
- GPC will strongly depend on concentation of surface hydroxyl group.

Ab initio Born-Oppenheimer MD of water adsorbed on the monoclinic (001) HfO₂ surface (450 K)

Department of Chemical Engineering, Stanford University   **Mukhopadhyay, Sanz and Musgrave**

SURFACE ENERGY:

$$A_{hkl}\Gamma_{hkl} = G(surf_{hkl} + nH_2O) - G(bulk) - n\mu_{H2O,}$$

Neglecting for the condensed phase the varaition of internal energies

$$\Gamma_{hkl} = \Gamma^0_{hkl} + \Theta_{hkl}(E_{ads} + \Delta\mu_{H2O}),$$

Where,

$$\Gamma^0_{hkl} = \frac{G(surf_{hkl}) - G(bulk)}{A_{hkl}} \qquad E_{ads} = \frac{G(surf_{hkl} + nH2O) - G(surf_{hkl})}{n}$$

$$\approx \frac{E_{0K}(surf_{hkl}) - E_{0K}(bulk)}{A_{hkl}} \qquad \approx \frac{E_{0K}(surf_{hkl} + nH2O) - E_{0K}(surf_{hkl})}{n}$$

$$\Delta\mu_{H2O} = h^0_{H2O} - Ts^0_{H2O} + RT\ln\left(\frac{p_{H2O}}{P_0}\right) - e_{H2O}$$

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	(-111) face	(001) face
SE before relaxation (J m^{-2})	1.460	2.169
SE after relaxation (J m^{-2})	0.993	1.416
Hf (atom. nm^{-2})	9.2	7.6
μ_2-O (atom. nm^{-2}) [a]	1.8	7.6
μ_3-O (atom. nm^{-2}) [b]	6.9	-
N_{Hf-O} (nm^{-2}) [c]	20.6	22.8

(001) Surface has higher concentration of under-coordinated centers and hence, a higher surface energy

Effect of Hydration

Coverage (H_2O molecule.nm^{-2})	(-111) face		
	Molecular	Dissociative	Combination
2.3	-106.6	-60.5	-76.9
4.6	-87.6	-86.4	-101.3
6.9	-75.6	-60.3	-91.6
9.2	-78.8	-	-86.4
	(001) face		
1.9	-94.8	-183.0	-
3.8	-85.0 (107)	-148.5 (150.0)	-111.5
5.7	-98.4	-130.5	-105.7
7.6	-92.7	-108.6 (91)	-101.6
9.5	-	-	95.9

The mode of adsorption is dependent on nature of surface, especially at low coverage.

QM molecular dynamics used to determine possible configurations of H$_2$O on m-(001)HfO$_2$
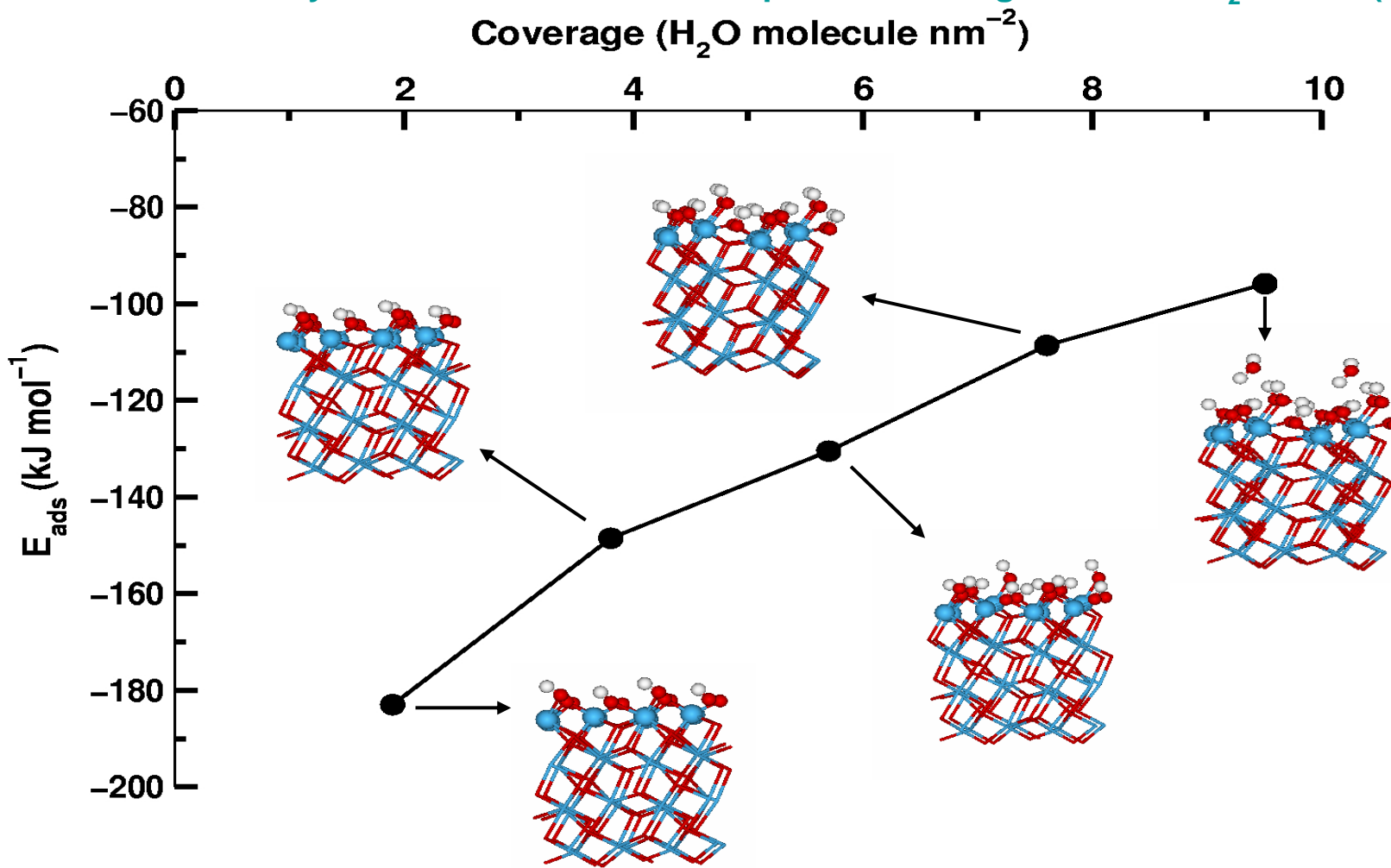
- *H$_2$O dissociatively adsorbs at low coverages*
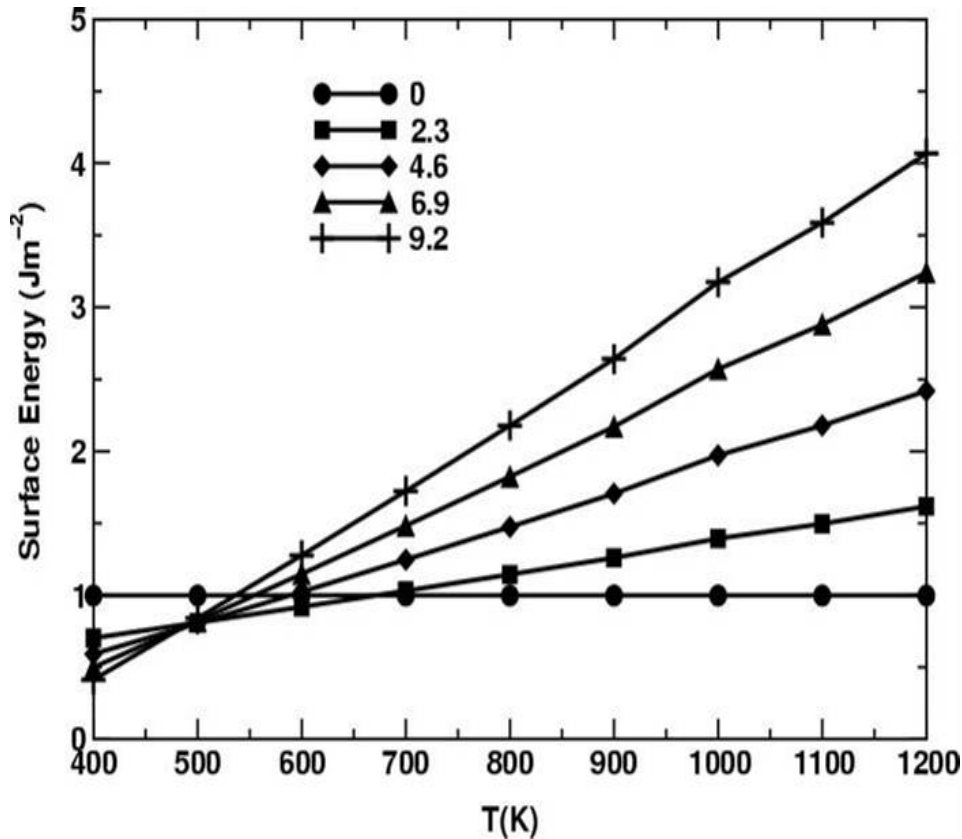- *Hydroxylated m-(001) surface is more stable than m-(-111) at low H$_2$O coverages.*

Mukhopadhyay, A., J. Sanz and C. Musgrave, "First-Principles Investigation of Hydroxylated Monoclinic HfO$_2$ Surfaces," Chem. Mater., 18, 3397-3403, 2006

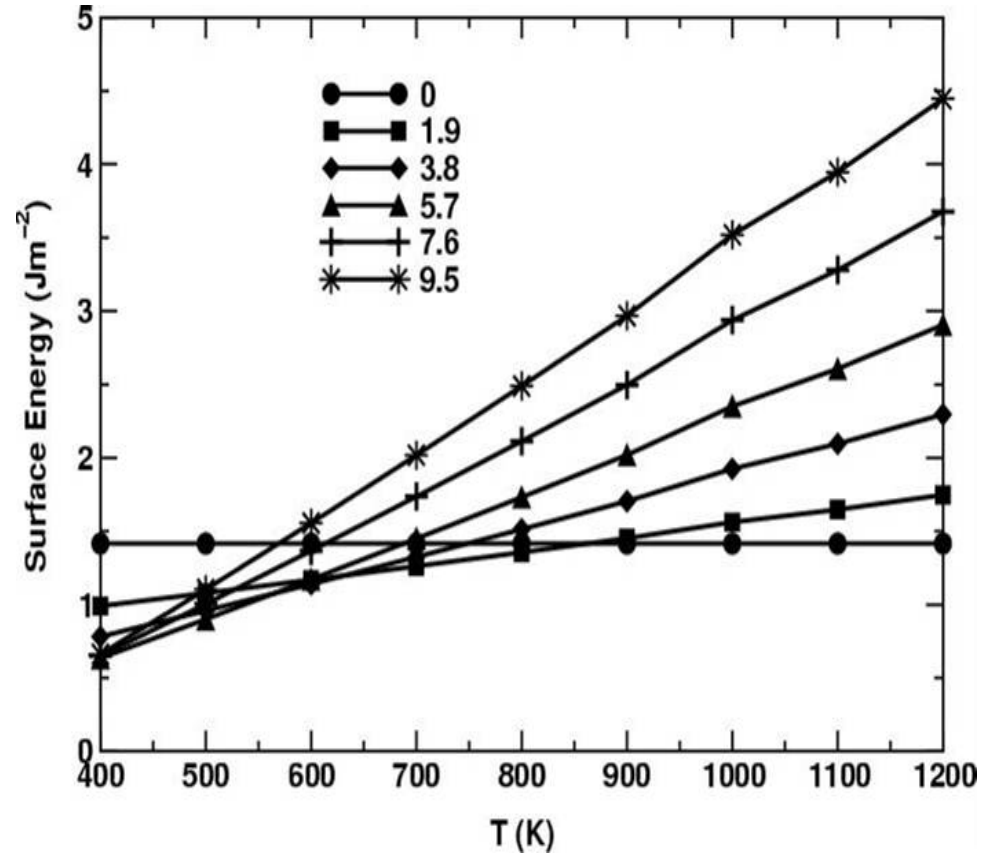17

Hydration of m-(-111) HfO$_2$ Surface
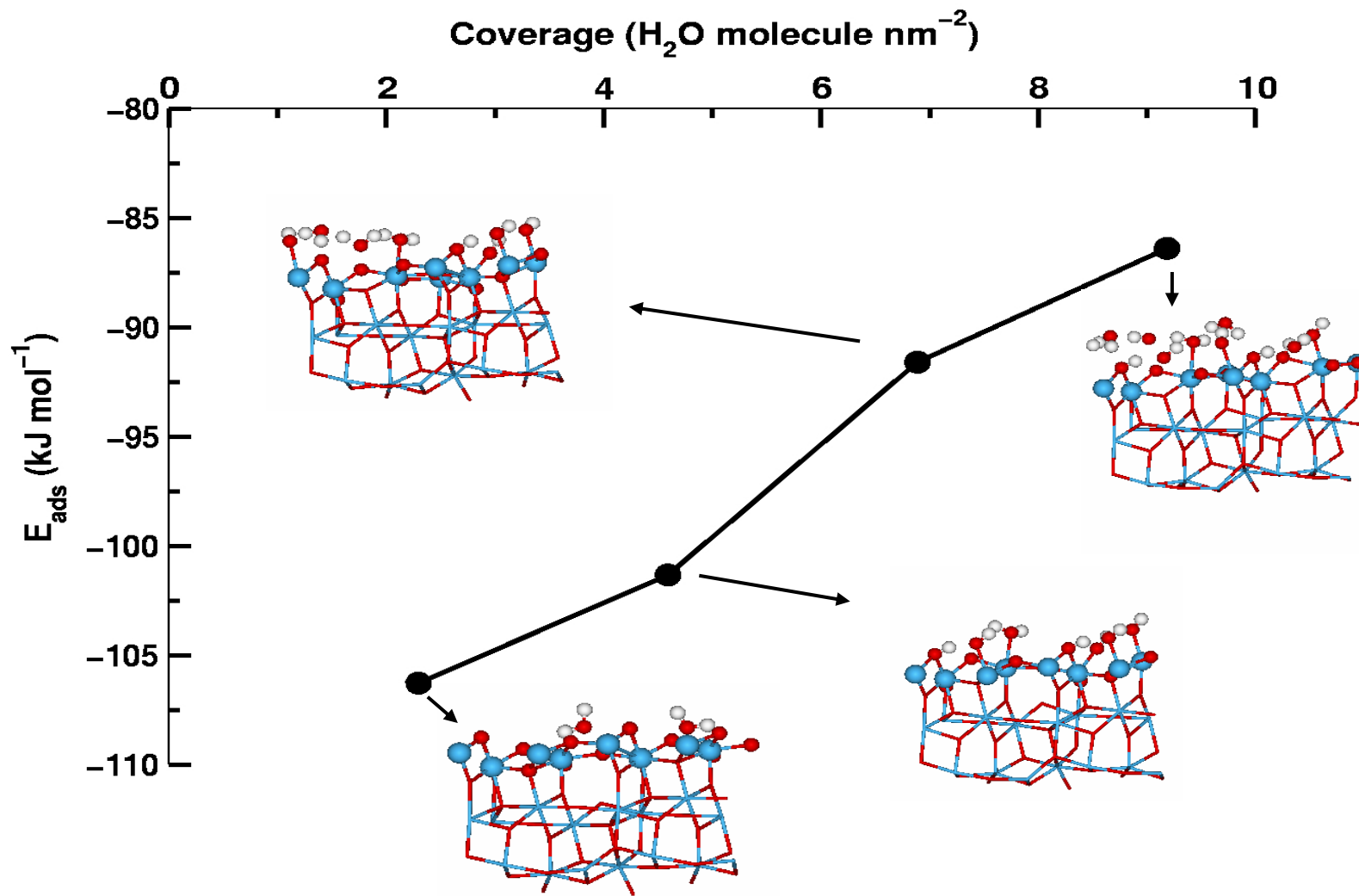
- Lower H$_2$O adsorption energies on m-(-111) than on m-(001) surface.

(-111)　　　　　　　　　**(001)**

(001) has greater ability to retain water compared to (-111) surface
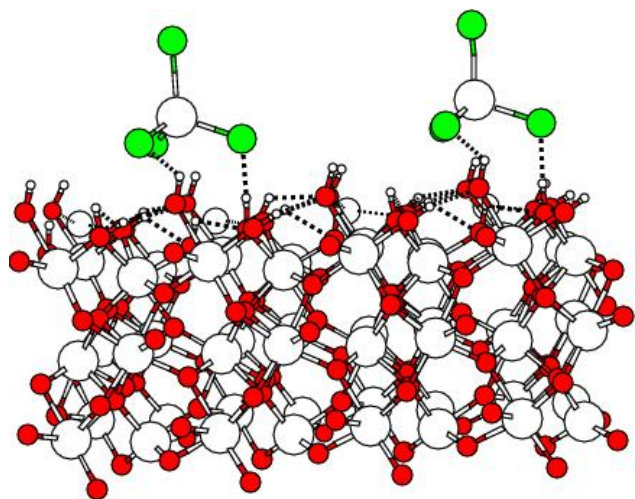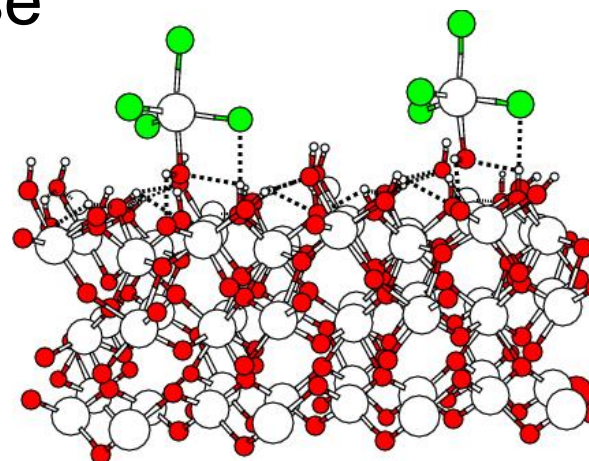
m-(-111)
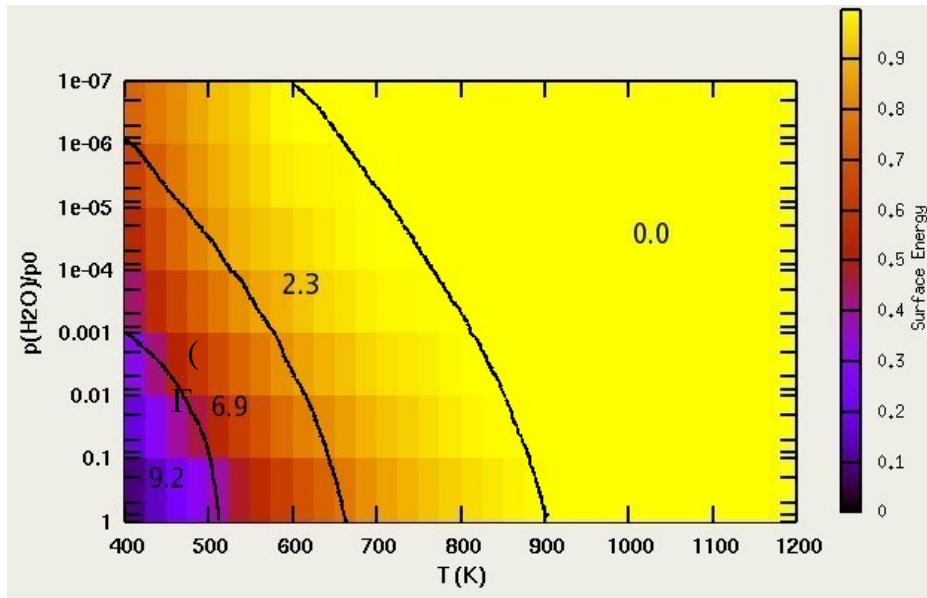
m-(001)
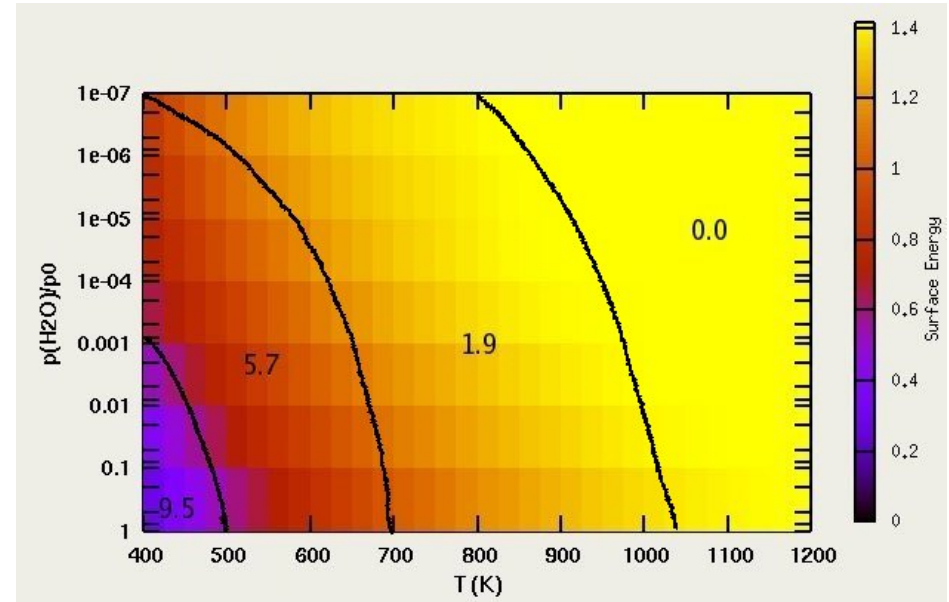
- Phase diagrams representing the surface energy as a function of T and P_{H2O}.
- (-111) face with lower dehydration temperature mainly exhibits Lewis acid-base properties under ALD growth conditions, however the (001) surface retains a significant amount of Brønsted acid sites.
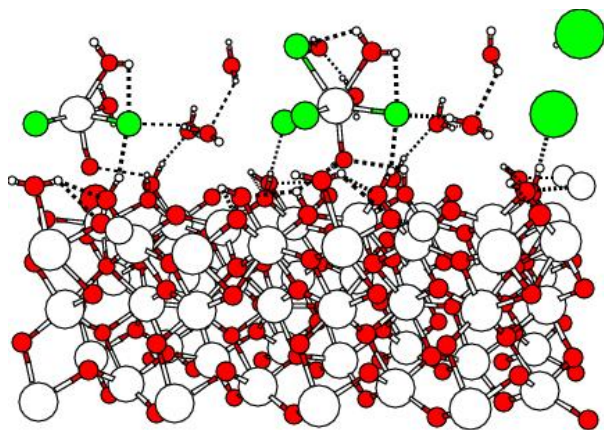
20

HfCl$_4$ Pulse

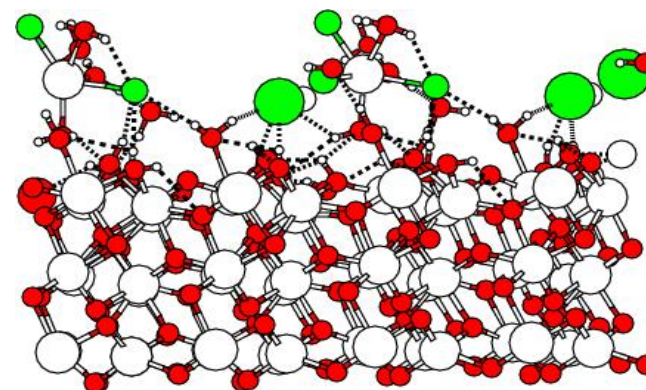Initial Interaction through H-bonding

Formation of precursor complex on surface

H$_2$O Pulse

Formation of 7-coordinated surface complex

Precursor dissociation and stabilization of Cl ion by neighboring protons

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Conclusions

- m-(-111) most stable surface

- PDOS of bulk indicates hybridization of O 2p and Hf 5d states

- Predominate surface state at -12 eV due to surface O 2s states

- m-(001) surface kinetically stable, probably because of H_2O stabilization

- Water adsorption energies generally decreases with increasing coverage

- Mode of adsorption at low coverage is dependent on nature of surface

- (001) surface can retain higher concentration of OH sites compared to (-111) face

- QMD providing more detailed information of ALD surface chemistry