Electronic Supplementary Information for "Self-limiting temperature window for thermal atomic layer etching of HfO_2 and ZrO_2 based on the atomic scale mechanism"

Rita Mullins,† Suresh Kondati Natarajan,†,‡ Simon D. Elliott,†,¶ and Michael Nolan†

†*University College Cork, Tyndall National Institute, Lee Maltings, Dyke Parade, Cork, T12 R5CP, Ireland.*

‡*Department of Electrical Engineering and Automation, Aalto University, Espoo 02150, Finland*

¶*Schrödinger Inc., 120 West 45 th Street, 17 th Floor, New York, NY 10036-4041, USA.*

E-mail:

S1. Self-limiting surface models

We model by hand the self-limiting surfaces for the thermochemical calculations by removing a surface oxygen and replacing it with two fluorine atoms on HfO_2 and ZrO_2. The top layer of HfO_2 and ZrO_2 in Figures 1 and 2 have 16 Hf/Zr and 16 O atoms that can be used to model a fluorinated self-limiting surface. Self-limiting models are created for three different O:F product states by removing 16, 12 and 8 O and replacing with 32, 24 and 16 F atoms, Figures 3 and 4.

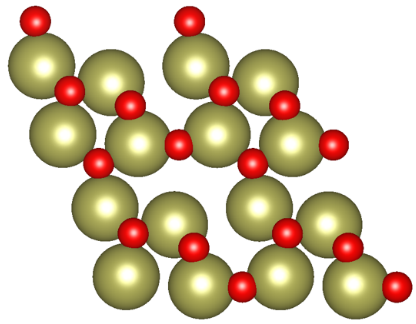


Figure 1: Top surface of bare HfO_2. The colour coding is: yellow = Hf and red = O.

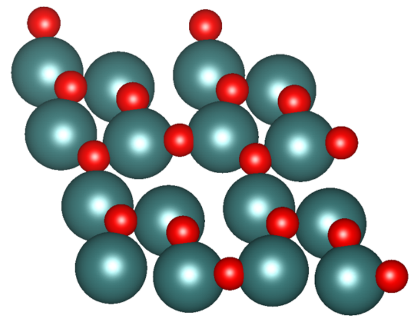


Figure 2: Top surface of bare ZrO_2. The colour coding is: green = Zr and red = O.

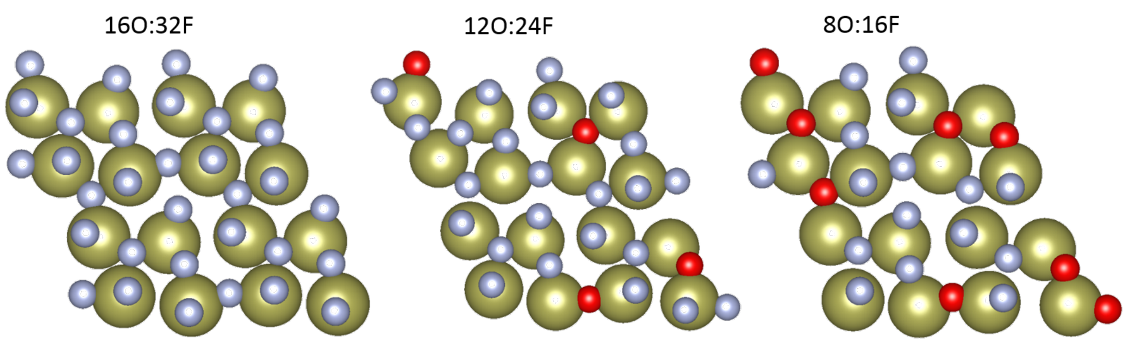


Figure 3: HfO_2 O:F. The colour coding is: yellow = Hf, red = O and blue = F.

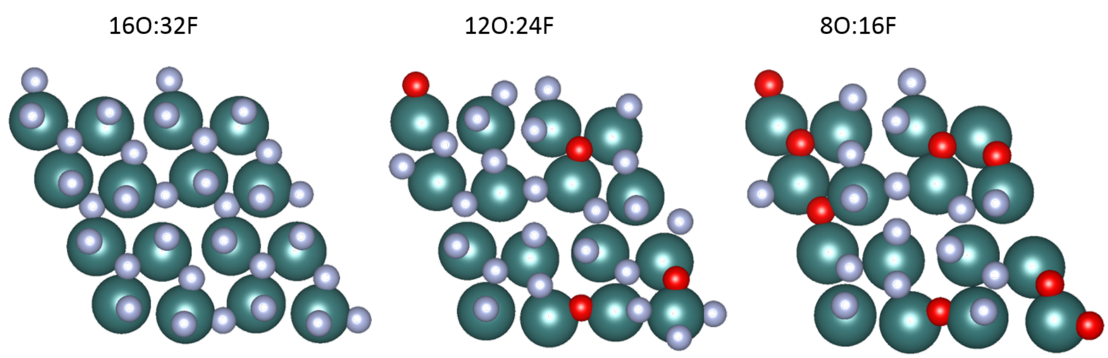


Figure 4: ZrO_2 O:F. The colour coding is: green = Zr, red = O and blue = F.

S2. Binding sites of 1 HF Molecule at HfO_2 and ZrO_2

We introduced one HF molecule approximately 3 Å from the bare surfaces of HfO_2 and ZrO_2 at three different binding sites. In Figures 5 and 6 we see binding sites A a, B b and C c where the uppercase letter represents the Hf/Zr-F bond and the lowercase latter represents the O-H bond. From the relaxed geometries of HF adsorption at the A, B and C sites of HfO_2, the coordination number (c.n) of each oxygen atom, which forms the O-H bond, is 2 (excluding the H bond) and of each hafnium atom, which forms Hf-F bond, is 6 (excluding the F bond). Similarly, at the A and B sites of ZrO_2, the c.n of each oxygen atom is 2 (excluding the H bond) and at site C it is 3 (excluding the H bond). Also the c.n for each zirconium atom bonded to fluorine is 6 (excluding the F bond). For site C of HfO_2 and ZrO_2 the resulting relaxation geometries for the O-H bond are at different surface oxygen due to the HF molecules having different orientations at the initial geometry before relaxation.

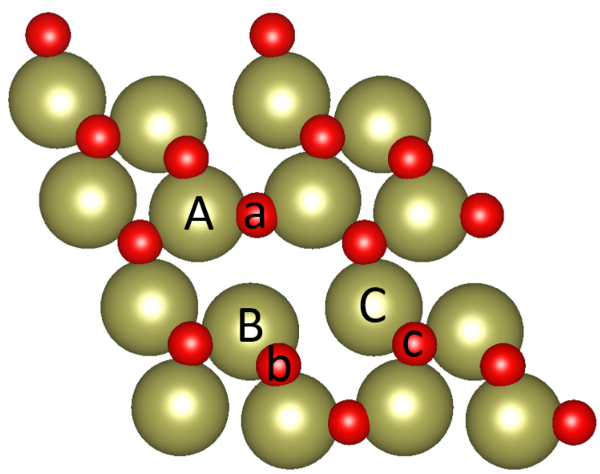


Figure 5: Binding sites for 1 HF on HfO_2.

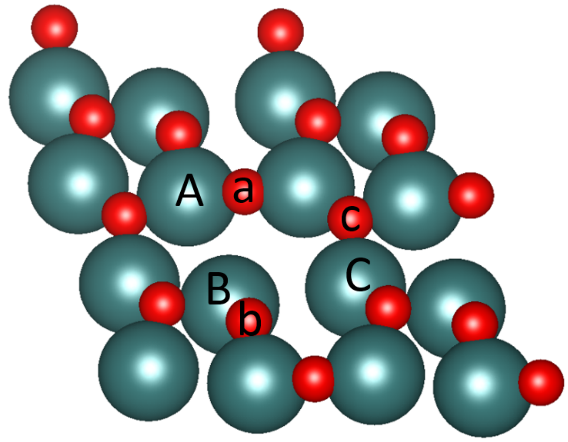


Figure 6: Binding sites for 1 HF on ZrO_2.

S3. Summary of Bond Dissociation Energies

Bond Type	Bond dissociation Energy (eV)
H-F	5.9
Hf-F	6.7
Zr-F	6.5
Hf-O	8.3
Zr-O	7.9

Table 1: Summary of bond dissociation energies.[1]

S4. Mixed molecular and dissociative adsorption of the HF molecules.

Figures 7 and 8 show for HfO_2 and ZrO_2 the geometries that did not result in complete dissociation of the HF molecules.

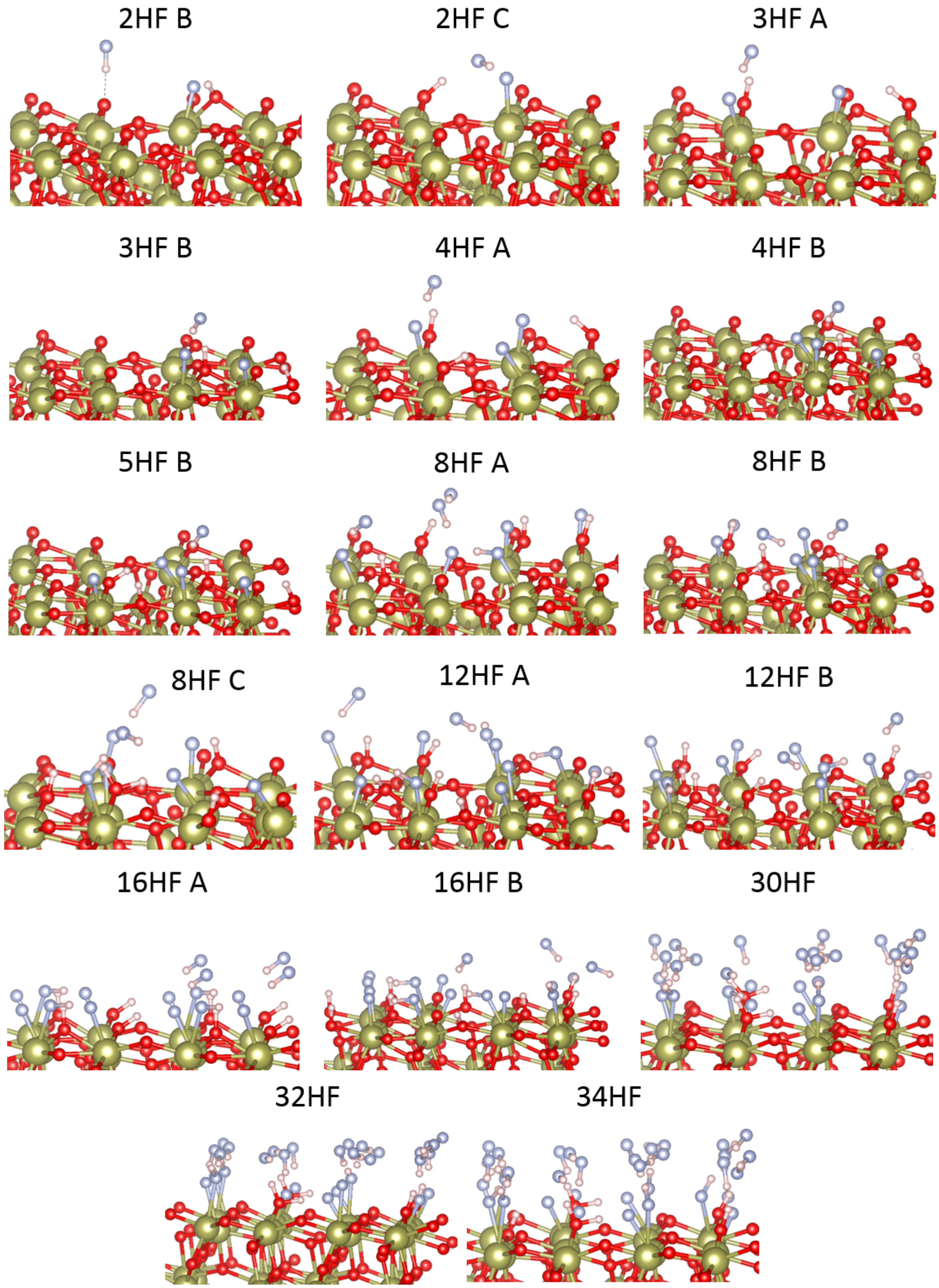
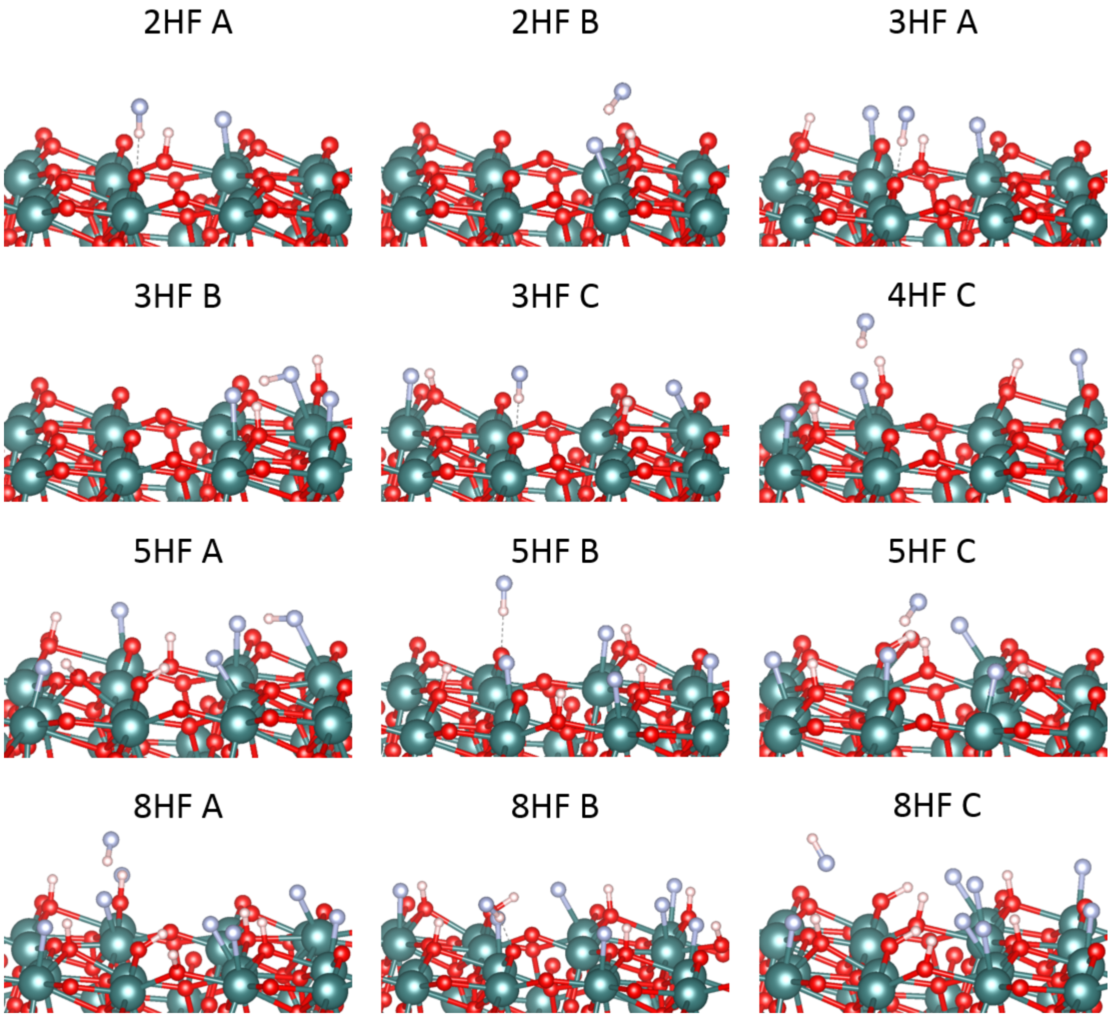


Figure 7: Relaxed geometries for different HF coverages of HfO_2 where a mixture of molecular and dissociative adsorption of HF is observed. The colour coding is: yellow = Hf, red = O, white = H and blue = F.


2HF A
2HF B
3HF A
3HF B
3HF C
4HF C
5HF A
5HF B
5HF C
8HF A
8HF B
8HF C

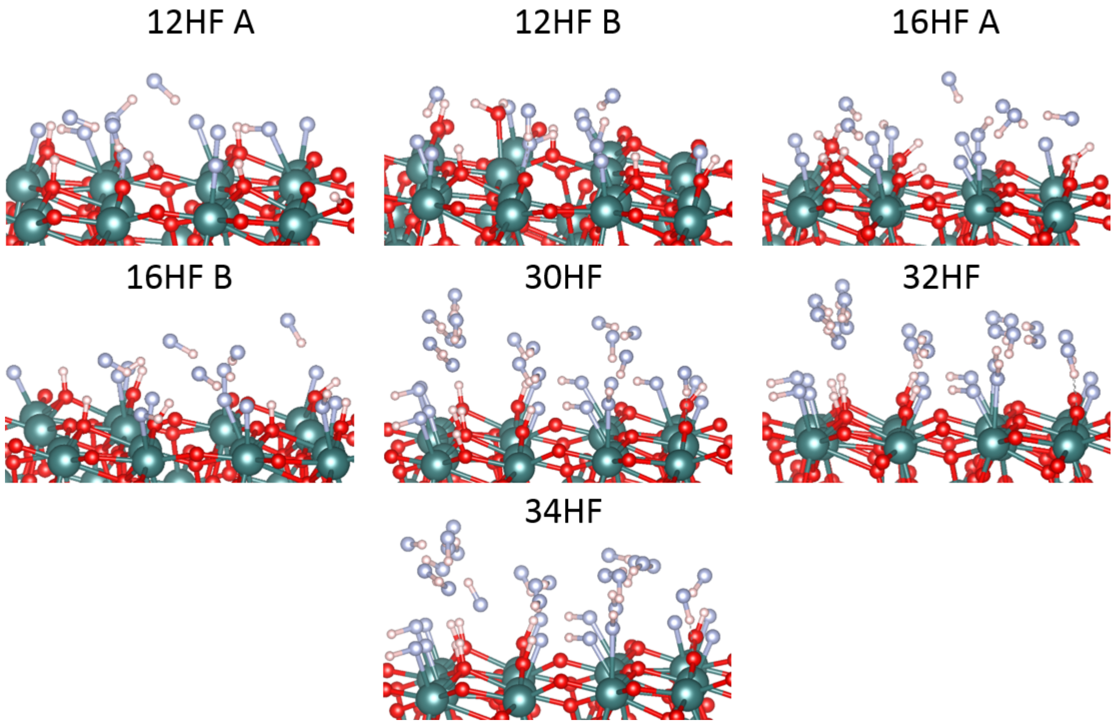


Figure 8: Relaxed geometries for different HF coverages of ZrO_2 where a mixture of molecular and dissociative adsorption of HF is observed. The colour coding is: green = Zr, red = O, white = H and blue = F.

S5. Summary of experimental etch rates

A summary of experimental etch rates for HfO_2 and ZrO_2 using HF and a metal precursor are shown in Tables 2 and 3.

Material	Precursors	Etch Rate (Å/ cycle)	Temperature (°C)	Ref.	No. of metal atoms removed per nm^2
HfO_2	HF and $Sn(acac)_2$	0.070	150	[2]	0.20
HfO_2	HF and $Sn(acac)_2$	0.087	175	[2]	0.25
HfO_2	HF and $Sn(acac)_2$	0.116	200	[2]	0.33
HfO_2	HF and $Sn(acac)_2$	0.124	225	[2]	0.36
HfO_2	HF and $Sn(acac)_2$	0.117	250	[2]	0.34
HfO_2	HF and $Sn(acac)_2$	0.06	200	[3]	0.17
HfO_2	HF and DMAC	0.77	250	[3]	2.21
HfO_2	HF and TMA	0.10	300	[3]	0.29
HfO_2	HF and $SiCl_4$	0.05	350	[3]	0.14
HfO_2	HF and $TiCl_4$	0.11	200	[4]	0.32
HfO_2	HF and $TiCl_4$	0.18	225	[4]	0.52
HfO_2	HF and $TiCl_4$	0.29	250	[4]	0.83
HfO_2	HF and $TiCl_4$	0.46	275	[4]	1.32
HfO_2	HF and $TiCl_4$	0.59	300	[4]	1.69
HfO_2	HF and DMAC	0.36	200	[5]	1.03
HfO_2	HF and DMAC	0.79	225	[5]	2.26
HfO_2	HF and DMAC	0.98	250	[5]	2.81
HfO_2	HF and DMAC	1.10	275	[5]	3.15
HfO_2	HF and DMAC	1.24	300	[5]	3.55

Table 2: Summary of experimental etch rates for thermal ALE of HfO_2.

Material	Precursors	Etch Rate (Å/ cycle)	Temperature (°C)	Ref.	No. of metal atoms removed per nm^2
ZrO_2	HF and $Sn(acac)_2$	0.14	200	[3]	0.40
ZrO_2	HF and DMAC	0.96	250	[3]	2.75
ZrO_2	HF and TMA	negligible	300	[3]	negligible
ZrO_2	HF and $SiCl_4$	0.14	350	[3]	0.40
ZrO_2	HF and $TiCl_4$	0.38	250	[4]	1.10
ZrO_2	HF and DMAC	0.91	200	[5]	2.61
ZrO_2	HF and DMAC	1.18	225	[5]	3.38
ZrO_2	HF and DMAC	1.33	250	[5]	3.81
ZrO_2	HF and DMAC	1.51	275	[5]	4.33
ZrO_2	HF and DMAC	1.59	300	[5]	4.55

Table 3: Summary of experimental etch rates for thermal ALE of ZrO_2.

S6. HF addition energy

An exponential function ($f(x) = Ae^{-Bx} + C$) was fitted to the binding energy vs HF coverage plots (b) in Figures 11 and 12. The derivative of that fit ($\frac{d}{dx} f(x) = ABe^{-Bx}$) gives the rate of change of the binding energy with respect to increasing HF coverage which is the HF addition energy. The surface is saturated when the derivative becomes zero. As the number of HF added increases the HF addition energy decreases.

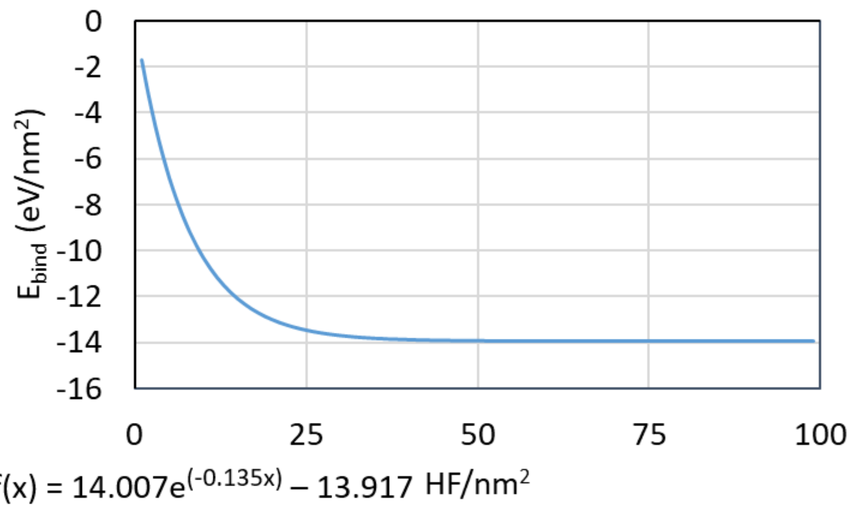


Figure 9: Binding energy for increasing HF coverage for HfO_2.

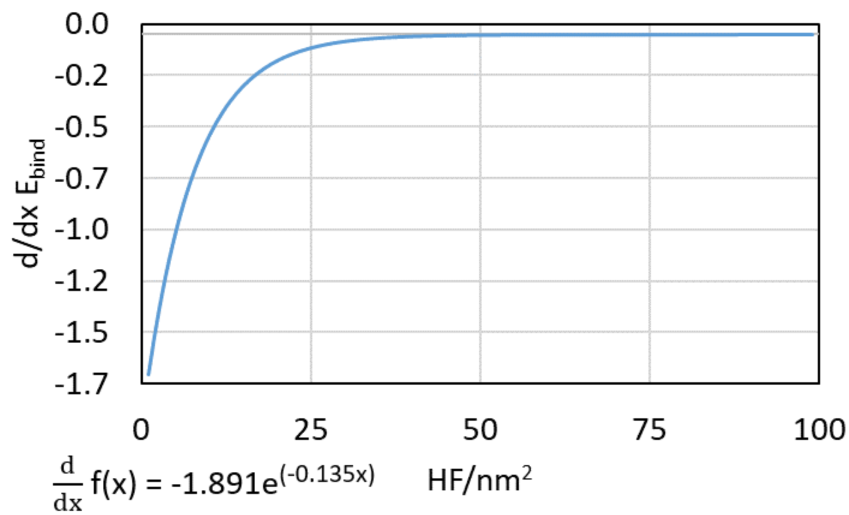


Figure 10: HF addition energy for binding energy with increasing HF coverage for HfO_2.

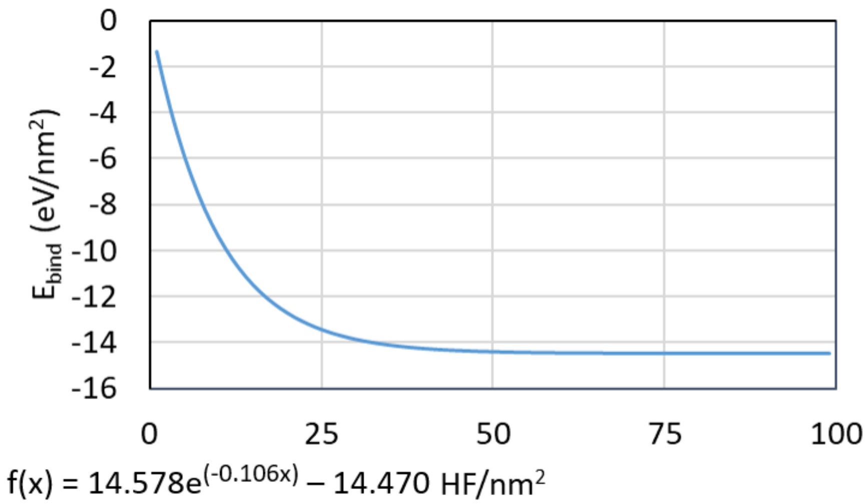


Figure 11: Binding energy for increasing HF coverage for ZrO_2.

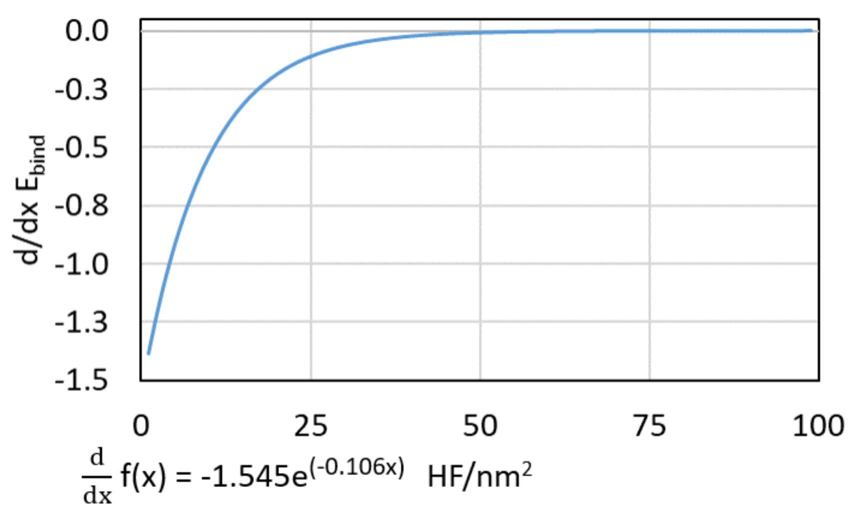


Figure 12: HF addition energy for binding energy with increasing HF coverage for ZrO_2.

References

(1) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(2) Lee, Y.; DuMont, J. W.; George, S. M. Atomic Layer Etching of HfO_2 Using Sequential,

Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF. *ECS J. Sol. State Sci. Technol.* **2015**, *4*, N5013.

(3) Lee, Y.; Huffman, C.; George, S. M. Selectivity in Thermal Atomic Layer Etching Using Sequential, Self Limiting Fluorination and Ligand-Exchange Reactions. *Chem. Mater.* **2016**, *28*, 7657–7665.

(4) Lee, Y.; George, S. M. Thermal atomic layer etching of HfO_2 using HF for fluorination and $TiCl_4$ for ligand-exchange. *J. Vac. Sci. Technol. A* **2018**, *36*, 061504.

(5) Lee, Y.; George, S. M. Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures. *J. Phys. Chem. C* **2019**, *123*, 18455–18466.