Supplementary Information for

Thermal Atomic Layer Etching of Aluminum Oxide (Al_2O_3) Using Sequential Exposures of Niobium Pentafluoride (NbF_5) and Carbon Tetrachloride (CCl_4): A Combined Experimental and Density Functional Theory Study of Etch Mechanism

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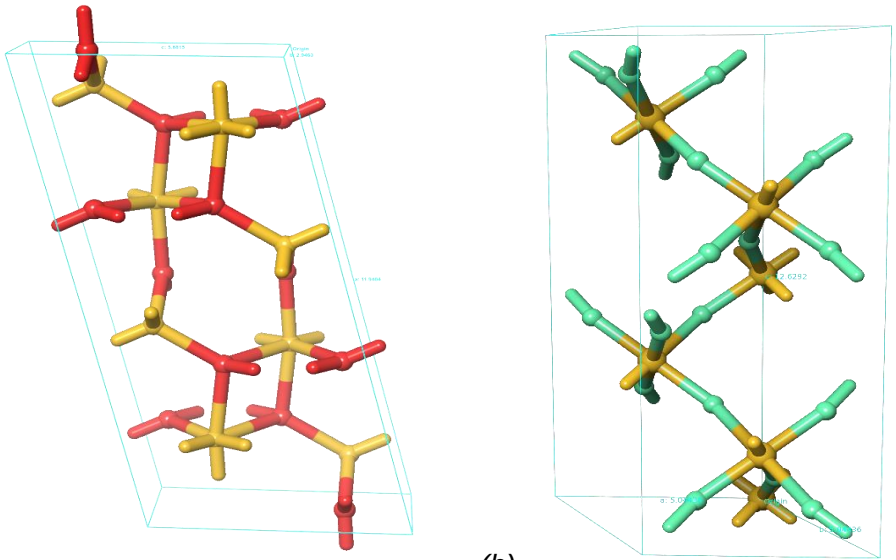
S1. Bulk calculations

The monoclinic θ-Al_2O_3 polymorph[1] was used as a periodic model for ALD-deposited amorphous alumina. Cell and atomic coordinates of the $(Al_2O_3)_4$ unit cell were optimized at PBE level with *Quantum ESPRESSO* using 1×6×2 k-points in the *C*12/*m*1 space group (#12) to yield lattice parameters *a*=11.94 Å, *b*=2.946 Å, *c*=5.682 Å, α=γ=90°, β=104.04°; see Figure S1a. Coordinates are available as a CIF file. The total electronic energy is -110.965 Ry/Al_2O_3.

AlF_3 is rhombohedral under ambient conditions (space group $R\bar{3}c$, #167)[2] and this structure containing 6 formula units per unit cell was optimized at PBE level with *Quantum ESPRESSO* using 4×4×2 k-points to yield *a*=*b*=5.0443 Å, *c*=12.6292 Å, α=β=90°, γ=120°; See Figure S1b.

[1] E. Husson, Y. Repelin, *Eur. J. Solid State Inorg. Chem.* **33** 1223-1231 (1996).

[2] C. R. Morelock, J. C. Hancock, A. P. Wilkinson, *J. Solid State Chem.* **219**, 143-147 (2014).



(a) (b)

Figure S1: Optimized unit cells of bulk structures of (a) θ-Al_2O_3 and (b) AlF_3 (Al=yellow, O=red, F=light green).

S2. Slab calculations

Slab models of the bare surface were obtained by cleaving θ-Al_2O_3 along seven low-index faces with 10 Å of vacuum and relaxing atomic positions at the PBE level using the k-point sets listed in Table S1. In each case, a series of three slab thicknesses (with *N* Al_2O_3 units per slab) were used to check convergence of bulk and surface energy, by interpolating across the electronic energies of the relaxed slabs (E_{total}) according to:

$$E_{surf} = [E_{total} - N.E_{bulk}]/2A$$

where *A* is the cross-sectional area of the slab and the factor of two accounts for the top and bottom surfaces.[3] The resulting structures and energies are listed in Table S1 and Figure S2. Coordinates are available as CIF files.

The computed surface energies show that the (1 0 0) termination is the most stable when bare. However, because it is extremely flat, this termination undergoes substantial distortion when fluorinated, indicating that it is not representative of surfaces that occur during the ALEt process. The other surfaces show some degree of corrugation both when bare and when fluorinated, making them more suitable as surface models for ALEt. The most stable corrugated termination, ($\bar{2}$ 0 1) at E_{surf}=1.1 $J.m^{-2}$, was therefore selected to investigate the ALEt chemistry. Convergence was achieved for the 3-layer ($\bar{2}$ 0 1) slab with 10 Å vacuum. A 2×1 supercell with total formula $(Al_2O_3)_{24}$ was used for the calculations detailed in the main paper.

S3. Entropy estimation

To obtain total energies of the gas-phase precursors NbF_5 and CCl_4 and potential gas-phase products $NbClF_4$, $NbCl_5$, $NbOF_3$, $CFCl_3$, CF_4, $COCl_2$, CO_2, AlF_3 and $AlCl_3$, each

[3] V. Fiorentini, M. Methfessel, *J. Phys. Condens. Matter* **8**, 6525-6529 (1996).

isolated molecule was optimized at PBE level using *Quantum ESPRESSO* within a cubic 15×15×15 Å cell using one k-point at Γ.

We propose that the contribution from gas-phase species dominates the entropy change for these gas-surface reactions. We therefore assume that the vibrational entropy of the solids and surfaces may be considered constant relative to the gas-phase contributions, which along with the zero rotational and translational entropy of the solids, gives $\Delta S(\text{surf})=0$. This approximation means that $\Delta S=\Delta S(\text{gas})$, which can be computed efficiently with molecular quantum chemistry.

Structural optimization and vibrational analysis was therefore carried out for the gas-phase reactant and product molecules listed above at the PBE/LAV3D** level with the *Jaguar* code to give entropies at the pressures and temperatures of interest ($100°C<T<600°C$).

Table S1: Computed structural and energetic data of the surface slabs depicted in Figure S2.

(*h k l*)	cell parameters, α = β = 90°				k-points	slab thickness	atoms per slab	PBE total energies (Ry)	bulk energy (Ry/Al_2O_3)	surface energy (Ry/cell)	surface energy ($J.m^{-2}$)	coordination at surface
	a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	**γ (°)**								
(1 0 0)	5.68	2.95	23.17 28.96 34.75	90.00	1×2×1	4 layers 6 layers 8 layers	20 30 40	-444.012 -666.054 -888.096	-111.021	0.071	0.5	Al = 4, 5 O = 3
($\bar{2}$ 0 1)	2.95	14.35	18.50 22.71 27.08	90.00	2×1×1	2 layers 3 layers 4 layers	40 60 80	-887.463 -1331.436 -1775.394	-110.991	0.464	1.2	Al = 4, 6 O = 3
(1 0 1)	2.95	14.42	18.75 23.13 27.51	90.00	2×1×1	2 layers 3 layers 4 layers	40 60 80	-887.242 -1331.108 -1775.014	-110.972	0.537	1.4	Al = 4, 6 O = 2, 3, 4
(1 1 1)	12.30	14.41	19.30 23.95 28.60	26.22	1×1×1	4 layers 6 layers 8 layers	80 120 160	-1774.266 -2661.933 -3549.642	-110.961	1.116	1.6	Al = 3, 4, 5 O = 2, 3
(0 1 1)	11.94	6.40	18.87 21.77 24.67	102.44	1×1×1	6 layers 8 layers 10 layers	60 80 100	-1330.418 -1774.267 -2218.121	-110.963	1.139	1.7	Al = 3, 4, 5 O = 2, 3
(0 1 0)	11.94	5.68	18.88 21.79 24.73	75.96	1×1×1	6 layers 8 layers 10 layers	60 80 100	-1330.083 -1773.867 -2217.534	-110.931	1.072	1.8	Al = 3, 4 O = 2
(0 0 1)	11.94	2.95	20.25 25.38 30.51	90.00	1×2×1	2 layers 3 layers 4 layers	40 60 80	-887.224 -1331.177 -1775.136	-110.989	0.689	2.1	Al = 3, 5 O = 2, 3

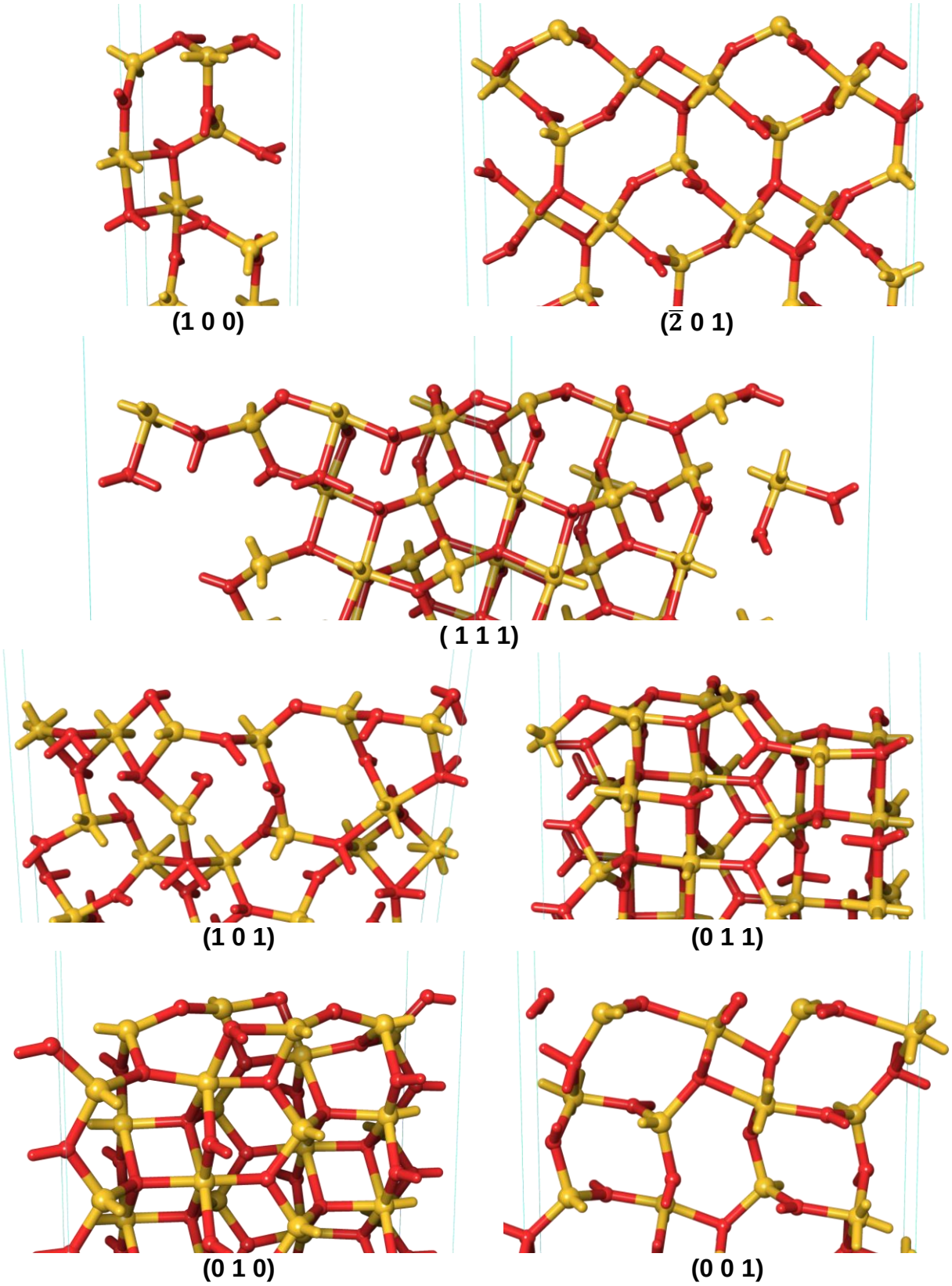


Figure S2: Optimized surface slabs, showing the top face of one cell of the periodically-repeating structure (Al=yellow, O=red). Structural and energetic data are in Table S1.

S4. GIXRD analysis of aluminum fluoride

The figure below, shows the crystalline phase of the formed aluminum fluoride after prolonged fluorination step. The fluorination was performed at 460ºC with 3 s long NbF_5 pulses for 150 cycles.

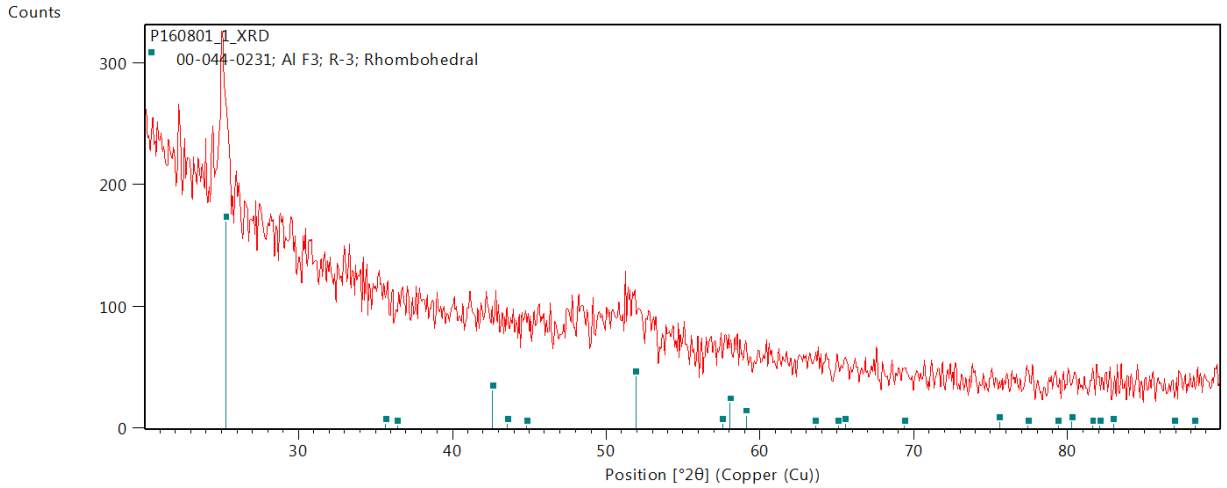


Figure S4.1: GIXRD analysis of the formed aluminum fluoride layer after prolonged fluorination at 460ºC.

S5. Surface Morphology by AFM

Figure S5.1 shows the surface morphology by AFM of about 56 nm unetched aluminum oxide, the same after exposing it to total of 150 cycles of 3s long CCl_4 pulses (no change in the thickness observed), and after etching about 22 nm of Al_2O_3 by NbF_5 + CCl_4 etch process. For the etching, 0.5 s long NbF_5 pulse and 3.0 s CCl_4 pulse times with intermittent 6.0 s long N2 purge steps. The total of 200 etch cycles were performed at 460ºC. AFM showed no significant increase in the roughness (r.m.s) after CCl_4 exposure. However, a slight increase in the roughness to 0.27 nm was observed after etching, similarly to the conclusion made from TEM.

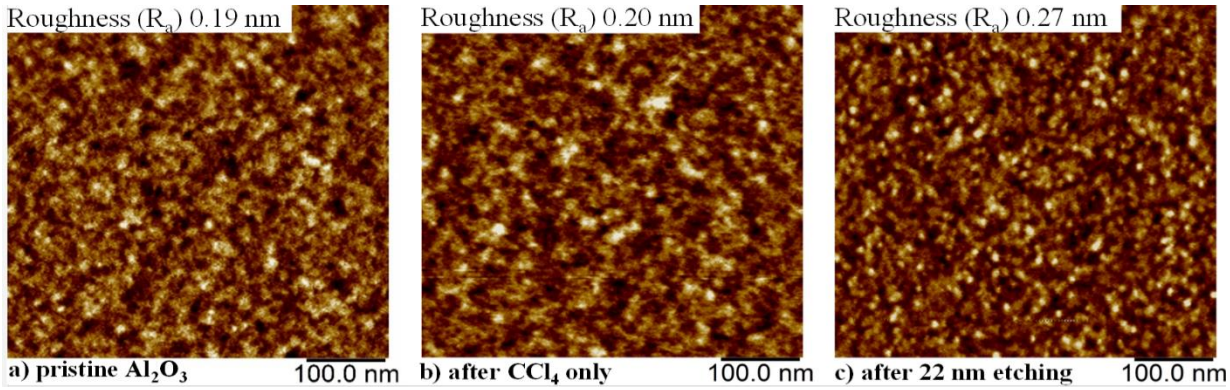


Figure S5.1: Surface morphology by AFM of: a) about 56 nm unetched Al_2O_3, b) after 150 cycles of 3 s long CCl_4 pulses, c) about 22 nm etched Al_2O_3 by NbF_5 + CCl_4 etch process at 460ºC.