

Supplementary Material for “Origin of Enhanced Thermal Atomic Layer Etching of Amorphous HfO₂”

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S1. Pair distribution function of amorphous HfO₂ bulk model.

Figure S1 shows the pair distribution function (PDF) of amorphous HfO₂ bulk model structure quenched at 10 K/ps rate. We are using a unit cell of 216 atoms (72 Hf and 144 O) and the plot uses 300 data points. The different pairs are colour-coded in Figure S1, with Hf-O pairs represented with a red line, Hf-Hf in black and O-O in green. The absence of long-range order in our as-quenched hafnia model reflects the amorphous distribution of this solid.

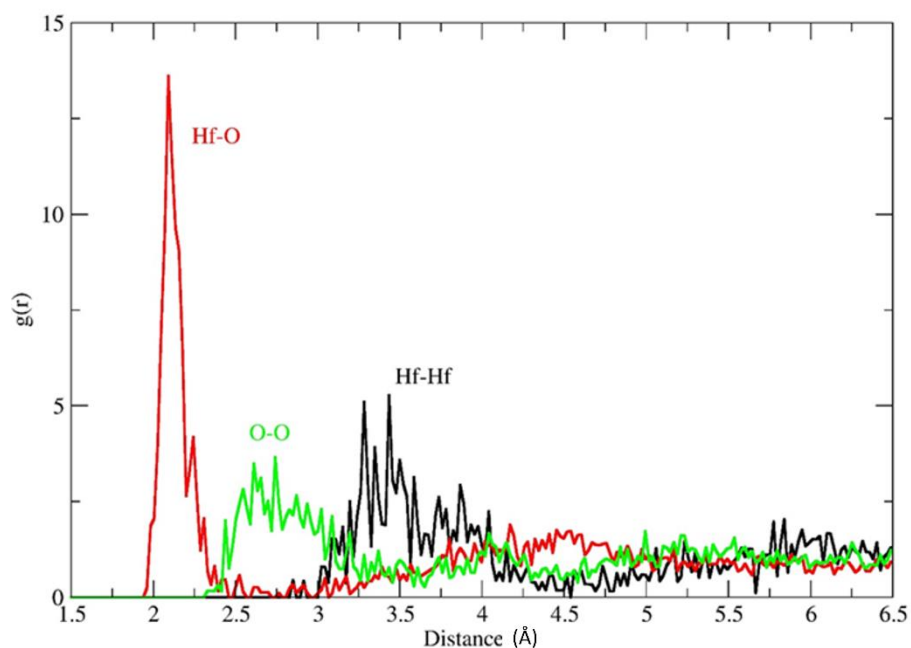
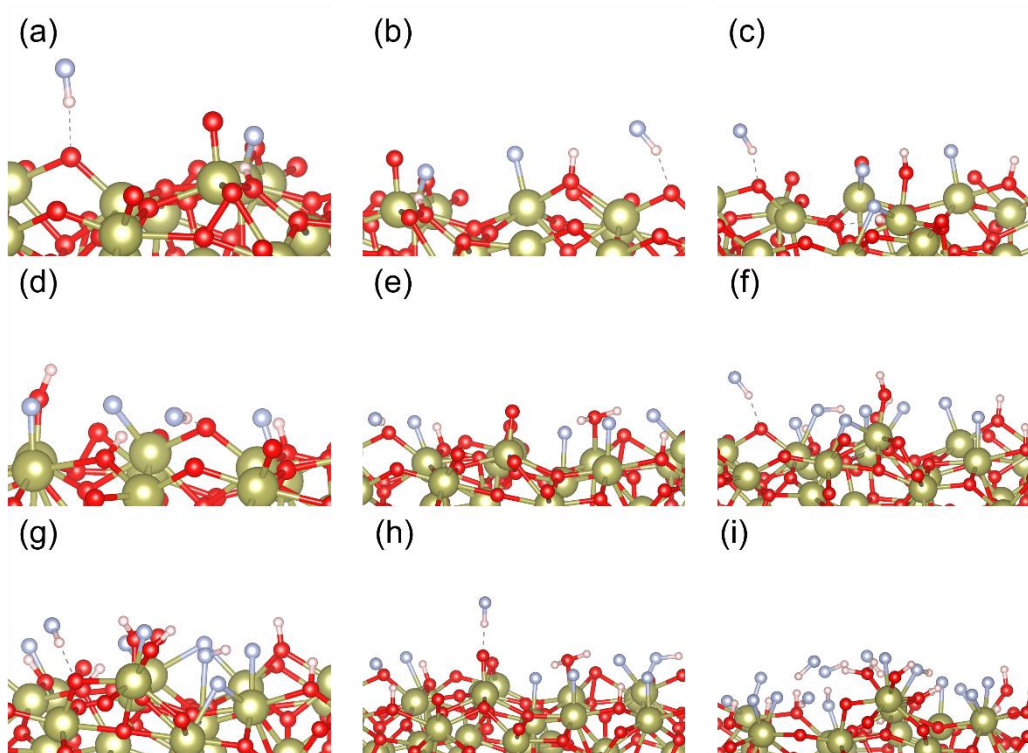


Figure S1. Pair distribution function (PDF) of amorphous HfO_2 bulk model structure quenched at 10 K/ps rate.

S2. Mixed molecular and dissociative adsorption of the HF molecules.

Figure S2 shows for amorphous HfO_2 the geometries that did not result in complete dissociation of the HF molecules.



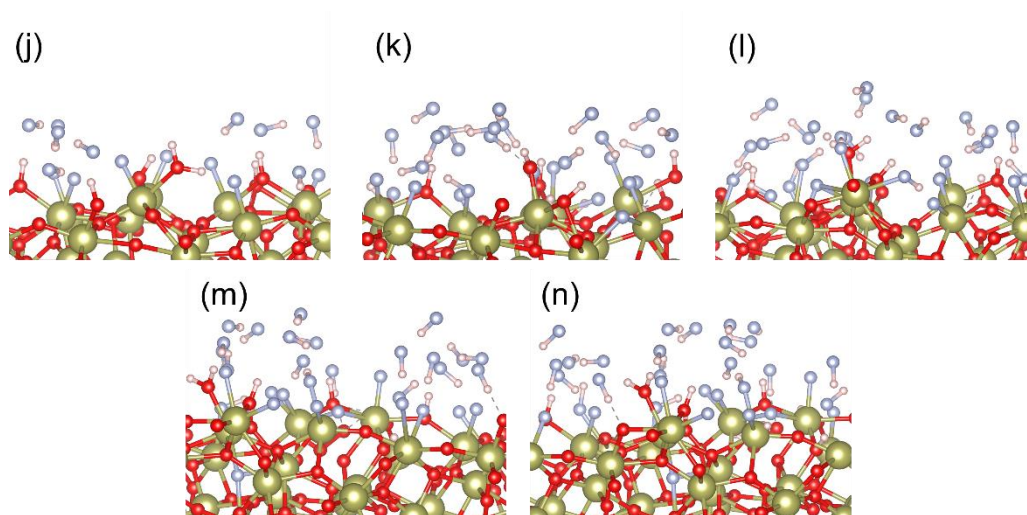


Figure S2. Relaxed geometries for different HF coverages of amorphous HfO_2 where a mixture of molecular and dissociative adsorption of HF is observed. (a) 2HF A, (b) 3HF A, (c) 4HF A (d) 4HF C, (e) 5HF C, (f) 8HF A, (g) 8HF B, (h) 8HF C, (i) 16HF A, (j) 16HF B, (k) 28HF, (l) 30HF, (m) 32 HF and (n) 34 HF. The colour coding is brown = Hf, red = O, white = H and blue = F.

S3. Explanation of error bar.

The ± 0.3 error is defined by the following, 4 F atoms leads to the etching of 1 Hf atom so the coverage of Hf that can be etched is 0.25 of the F coverage (round to 0.3). This was based on a similar analysis from where 3 F atoms leads to the etching of 1 Al atom so the coverage of Al that can be etched is 0.33 of the Al coverage (round to 0.3).^{1,2}

References

¹ S. Kondati Natarajan and S.D. Elliott, Chem. Mater. **30**, 5912 (2018).

² R. Mullins, S. Kondati Natarajan, S.D. Elliott, and M. Nolan, Chem. Mater. **32**, 3414 (2020).