Supplementary information

Selective Etching Mechanism of Silicon Oxide Against Silicon by Hydrogen Fluoride: A Density Functional Theory Study

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Bond dissociation energy (BDE) in gas-phase molecules

The method described in the literature[1–3] was used to compute the bond dissociation energies (BDEs).

Bonds	Molecular sample	Chemical structure Schematic	Atomistic structure Schematic	BDE (eV)
Si–F	$F_3Si–F$	F–Si–F (with F above and F below)		7.07
O–H	HO–H	H–O–H		5.20
H–F	H–F	H–F		6.02
H–H	H–H	H–H		4.25

Fig. S1. The bond dissociation energy (BDE) values in gas-phase molecules.

BDE in the species on the SiO$_2$ surface models

Bonds	Species sample	Chemical structure Schematic	Atomistic structure Schematic	BDE (eV)
Si–O	–Si–OH*			6.15
Si–O	–Si–OH*			6.20
Si–O	–Si–O–			7.17
Si–O	–Si–O–			6.16
Si–F	–Si–F*			7.21
Si–F	–(F)Si–F*			7.08
Si–F	–(F)$_2$Si–F*			7.07
O–H	–SiO–H*			5.04
O–H	–SiO–H*			5.14

Fig. S2. The bond dissociation energy (BDE) values in surface species on hydroxylated and fluorinated SiO$_2$ surfaces.

Desorption of H₂O after the first fluorination step of SiO₂ by HF

The method described in the literature[1] was used to compute the temperature-dependent desorption free energy of a byproduct after the reaction of HF with the SiO_2 surface model.

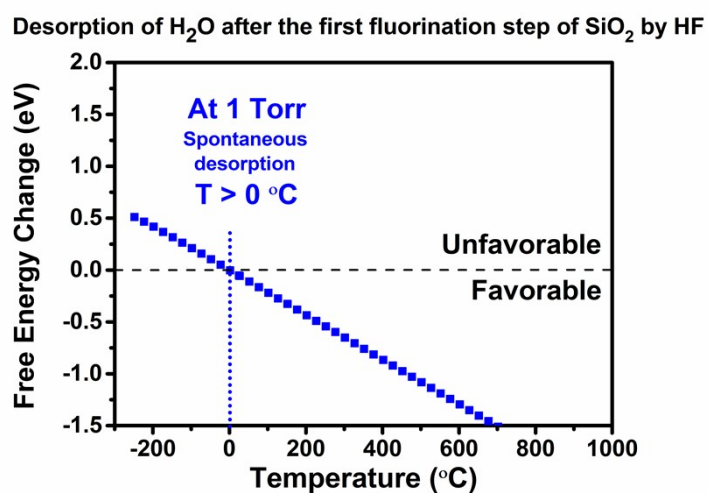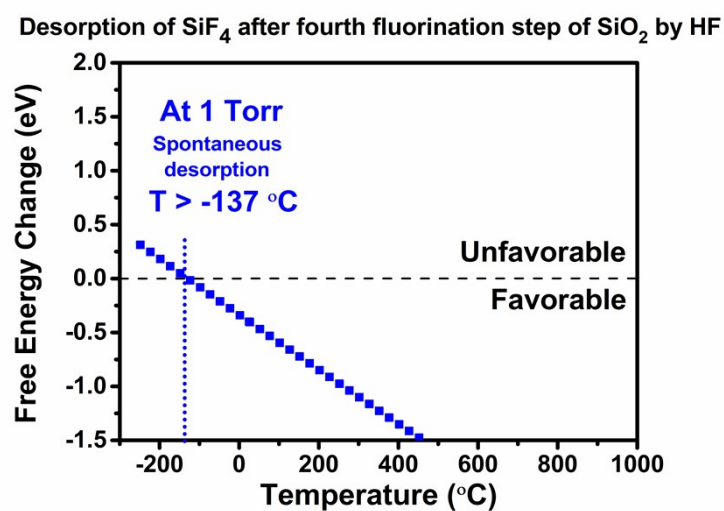**Desorption of H₂O after the first fluorination step of SiO₂ by HF**

Fig. S3. The temperature-dependent free energy change for the desorption of H_2O after the first fluorination step of silicon oxide by hydrogen fluoride.

Desorption of SiF$_4$ after the fourth fluorination step of SiO$_2$ by HF

Fig. S4. The temperature-dependent free energy change for the desorption of SiF$_4$ after the fourth fluorination step of silicon oxide by hydrogen fluoride.
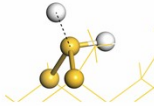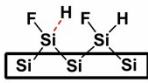
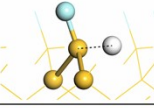# BDE in the species on the silicon surface models
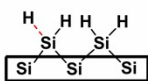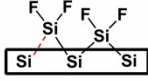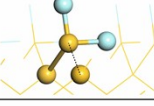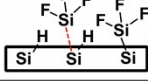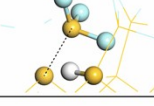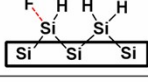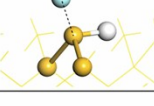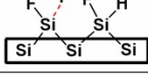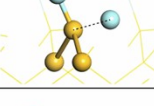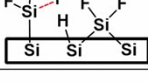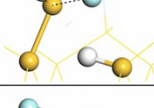
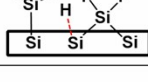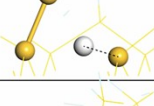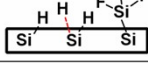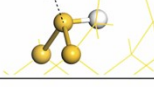| Bonds	Species sample	Chemical structure Schematic	Atomistic structure Schematic	BDE (eV)
Si–H	–Si–H*			3.23
Si–H	–Si–H*			3.20
Si–Si	–Si–Si–			2.47
Si–Si	–Si–Si–			2.02
Si–F	–Si–F*			5.97
Si–F	–Si–F*			6.12
Si–F	–Si–F*			6.53
Si–H	–Si–H*			3.01
Si–H	–Si–H*			3.18

Fig. S5. The bond dissociation energy (BDE) values in surface species on hydrogenated and fluorinated Si surfaces.

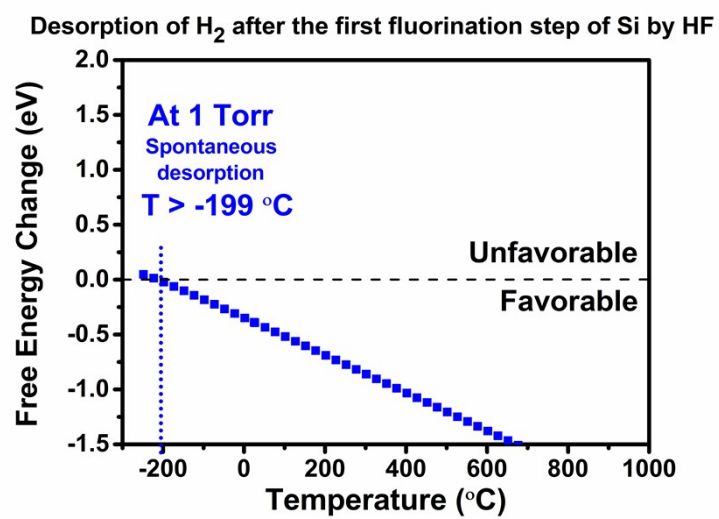# Desorption of H₂ after the first fluorination step of silicon by HF

Fig. S6. The temperature-dependent free energy change for the desorption of H_2 after the first fluorination step of silicon by hydrogen fluoride.

Desorption of SiF₄ after the fourth fluorination step of silicon by HF
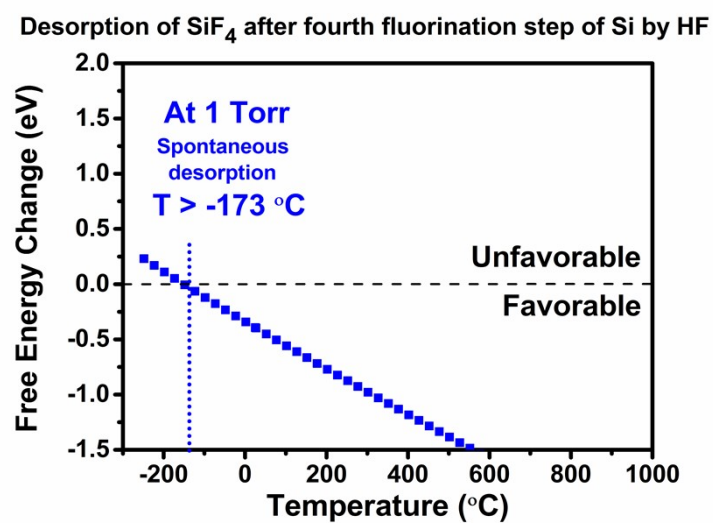

Fig. S7. The temperature-dependent free energy change for the desorption of SiF₄ after the fourth fluorination step of silicon by hydrogen fluoride.

References

[1] S. Kim, R. Hidayat, H. Roh, J. Kim, H.-L. Kim, K. Khumaini, M. Park, J.-H. Seok, J.W. Park, and W.-J. Lee, J. Mater. Chem. C **10**, 6696 (2022).

[2] A.K. Chandra and T. Uchimaru, J. Phys. Chem. A **104**, 9244 (2000).

[3] S.J. Blanksby and G.B. Ellison, Acc. Chem. Res. **36**, 255 (2003).