Electronic Supplementary information for "Prediction and Validation of the Process Window for Atomic Layer Etching: HF Exposure on TiO$_2$"

Suresh Kondati Natarajan,[†,‡] Austin M. Cano,[¶] Jonathan L. Partridge,[¶] Steven M. George,[¶] and Simon D. Elliott[§]

†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

¶Department of Chemistry, University of Colorado at Boulder, Colorado 80309, USA

§Schrödinger Inc., 120 West 45 [th] Street, 17 [th] Floor, New York, NY 10036-4041, USA.

E-mail:

S0: Surface Convergence Tests On Un-Relaxed Models

Table 1: Convergence test of the surface thickness from un-relaxed surface models

Material	Surface	Layers	Thickness [Å]	Surface Energy [J/m^2]
TiO$_2$	(1 1 0)	7	22.4	1.306
		5	**15.7**	**1.310**
		3	9.1	1.329

Table 2: Convergence test of the energy cutoff from un-relaxed surface models

Material	Surface	Layers	Energy Cutoff	Surface Energy [J/m^2]
TiO$_2$	(1 1 0)	5	350	1.323
		5	**400**	**1.310**
		5	450	1.305

S1: Free energy tables

Table 3: Contributions to the reaction free energy of CVE1 reaction of TiO$_2$.

Temp. [K]	ΔE	$\Delta E + \Delta$ZPE	$\Delta W(T)$	ΔH [eV]	$T\Delta S$	$RT\ln(Q)$	ΔG
0.000	-1.393	-1.202	0.000	-1.202	0.000	0.000	-1.202
50.000	-1.393	-1.202	-0.009	-1.212	-0.011	-0.003	-1.204
100.000	-1.393	-1.202	-0.018	-1.220	-0.034	-0.007	-1.193
150.000	-1.393	-1.202	-0.026	-1.229	-0.061	-0.010	-1.178

Table 3 – *Continued from previous page*

Temp.	ΔE	$\Delta E + \Delta ZPE$	$\Delta W(T)$	ΔH	$T\Delta S$	$RT\ln(Q)$	ΔG
[K]				[eV]			
200.000	-1.393	-1.202	-0.037	-1.239	-0.093	-0.013	-1.160
250.000	-1.393	-1.202	-0.048	-1.250	-0.128	-0.016	-1.138
300.000	-1.393	-1.202	-0.059	-1.261	-0.166	-0.020	-1.114
350.000	-1.393	-1.202	-0.070	-1.273	-0.206	-0.023	-1.090
400.000	-1.393	-1.202	-0.081	-1.283	-0.247	-0.026	-1.063
450.000	-1.393	-1.202	-0.090	-1.292	-0.288	-0.029	-1.034
500.000	-1.393	-1.202	-0.099	-1.302	-0.329	-0.033	-1.005
550.000	-1.393	-1.202	-0.107	-1.310	-0.370	-0.036	-0.976
600.000	-1.393	-1.202	-0.115	-1.317	-0.412	-0.039	-0.945
650.000	-1.393	-1.202	-0.121	-1.324	-0.453	-0.042	-0.913
700.000	-1.393	-1.202	-0.127	-1.329	-0.494	-0.046	-0.881
750.000	-1.393	-1.202	-0.133	-1.335	-0.535	-0.049	-0.850
800.000	-1.393	-1.202	-0.137	-1.340	-0.575	-0.052	-0.817
850.000	-1.393	-1.202	-0.141	-1.344	-0.615	-0.055	-0.784
900.000	-1.393	-1.202	-0.146	-1.348	-0.656	-0.059	-0.751
950.000	-1.393	-1.202	-0.149	-1.351	-0.696	-0.062	-0.718
1000.000	-1.393	-1.202	-0.152	-1.354	-0.736	-0.065	-0.684

Table 4: Contributions to the reaction free energy of SL1 reaction of TiO_2.

Temp.	ΔE	$\Delta E + \Delta ZPE$	$\Delta W(T)$	ΔH	$T\Delta S$	$RT\ln(Q)$	ΔG
[K]				[eV]			
0.000	-2.503	-2.222	-0.000	-2.222	0.000	0.000	-2.222
50.000	-2.503	-2.222	-0.021	-2.243	-0.111	0.045	-2.090

Table 4 – *Continued from previous page*

Temp.	ΔE	$\Delta E + \Delta$ZPE	$\Delta W(T)$	ΔH	$T\Delta S$	$RT\ln(Q)$	ΔG
[K]				[eV]			
100.000	-2.503	-2.222	-0.033	-2.255	-0.238	0.090	-1.928
150.000	-2.503	-2.222	-0.037	-2.259	-0.363	0.135	-1.762
200.000	-2.503	-2.222	-0.036	-2.258	-0.482	0.180	-1.596
250.000	-2.503	-2.222	-0.031	-2.253	-0.598	0.225	-1.431
300.000	-2.503	-2.222	-0.024	-2.246	-0.710	0.270	-1.266
350.000	-2.503	-2.222	-0.016	-2.238	-0.819	0.316	-1.105
400.000	-2.503	-2.222	-0.006	-2.228	-0.926	0.361	-0.944
450.000	-2.503	-2.222	0.005	-2.217	-1.030	0.406	-0.781
500.000	-2.503	-2.222	0.017	-2.205	-1.132	0.451	-0.622
550.000	-2.503	-2.222	0.030	-2.192	-1.231	0.496	-0.466
600.000	-2.503	-2.222	0.043	-2.179	-1.329	0.541	-0.310
650.000	-2.503	-2.222	0.058	-2.164	-1.425	0.586	-0.153
700.000	-2.503	-2.222	0.073	-2.149	-1.519	0.631	-0.001
750.000	-2.503	-2.222	0.088	-2.134	-1.611	0.676	0.152
800.000	-2.503	-2.222	0.105	-2.117	-1.701	0.721	0.305
850.000	-2.503	-2.222	0.122	-2.100	-1.790	0.766	0.456
900.000	-2.503	-2.222	0.139	-2.083	-1.878	0.811	0.606
950.000	-2.503	-2.222	0.157	-2.065	-1.964	0.857	0.755
1000.000	-2.503	-2.222	0.174	-2.048	-2.049	0.902	0.902

Table 5: Contributions to the reaction free energy of CVE2 reaction of TiO₂.

Temp. [K]	ΔE	$\Delta E + \Delta \mathrm{ZPE}$	$\Delta W(T)$	ΔH	$T\Delta S$	$RT\ln(Q)$	ΔG
				[eV]			
0.000	2.005	2.055	0.000	2.055	0.000	0.000	2.055
50.000	2.005	2.055	0.003	2.058	0.050	-0.026	1.982
100.000	2.005	2.055	0.003	2.058	0.100	-0.052	1.907
150.000	2.005	2.055	-0.002	2.053	0.144	-0.077	1.832
200.000	2.005	2.055	-0.010	2.045	0.182	-0.103	1.759
250.000	2.005	2.055	-0.021	2.034	0.215	-0.129	1.689
300.000	2.005	2.055	-0.034	2.022	0.245	-0.155	1.622
350.000	2.005	2.055	-0.047	2.008	0.272	-0.181	1.556
400.000	2.005	2.055	-0.060	1.995	0.297	-0.206	1.492
450.000	2.005	2.055	-0.073	1.982	0.320	-0.232	1.430
500.000	2.005	2.055	-0.086	1.969	0.342	-0.258	1.369
550.000	2.005	2.055	-0.098	1.957	0.363	-0.284	1.310
600.000	2.005	2.055	-0.110	1.945	0.384	-0.310	1.252
650.000	2.005	2.055	-0.122	1.933	0.403	-0.335	1.194
700.000	2.005	2.055	-0.134	1.922	0.422	-0.361	1.138
750.000	2.005	2.055	-0.145	1.910	0.441	-0.387	1.082
800.000	2.005	2.055	-0.156	1.899	0.459	-0.413	1.028
850.000	2.005	2.055	-0.166	1.889	0.477	-0.439	0.974
900.000	2.005	2.055	-0.177	1.878	0.494	-0.464	0.920
950.000	2.005	2.055	-0.187	1.868	0.511	-0.490	0.867
1000.000	2.005	2.055	-0.197	1.858	0.527	-0.516	0.814

Table 6: Contributions to the reaction free energy of SL2 reaction of TiO$_2$.

Temp.	ΔE	$\Delta E + \Delta$ZPE	$\Delta W(T)$	ΔH	$T\Delta S$	$RT\ln(Q)$	ΔG
[K]				[eV]			
0.000	-1.252	-1.111	-0.000	-1.111	0.000	0.000	-1.111
50.000	-1.252	-1.111	-0.011	-1.122	-0.055	0.023	-1.045
100.000	-1.252	-1.111	-0.016	-1.127	-0.119	0.045	-0.964
150.000	-1.252	-1.111	-0.019	-1.130	-0.181	0.068	-0.881
200.000	-1.252	-1.111	-0.018	-1.129	-0.241	0.090	-0.798
250.000	-1.252	-1.111	-0.016	-1.127	-0.299	0.113	-0.716
300.000	-1.252	-1.111	-0.012	-1.123	-0.355	0.135	-0.633
350.000	-1.252	-1.111	-0.008	-1.119	-0.410	0.158	-0.552
400.000	-1.252	-1.111	-0.003	-1.114	-0.463	0.180	-0.472
450.000	-1.252	-1.111	0.002	-1.109	-0.515	0.203	-0.391
500.000	-1.252	-1.111	0.008	-1.103	-0.566	0.225	-0.311
550.000	-1.252	-1.111	0.015	-1.096	-0.616	0.248	-0.233
600.000	-1.252	-1.111	0.022	-1.089	-0.664	0.270	-0.155
650.000	-1.252	-1.111	0.029	-1.082	-0.712	0.293	-0.076
700.000	-1.252	-1.111	0.037	-1.074	-0.759	0.316	-0.000
750.000	-1.252	-1.111	0.044	-1.067	-0.805	0.338	0.076
800.000	-1.252	-1.111	0.052	-1.059	-0.851	0.361	0.153
850.000	-1.252	-1.111	0.061	-1.050	-0.895	0.383	0.228
900.000	-1.252	-1.111	0.070	-1.041	-0.939	0.406	0.303
950.000	-1.252	-1.111	0.078	-1.033	-0.982	0.428	0.377
1000.000	-1.252	-1.111	0.087	-1.024	-1.025	0.451	0.451

Table 7: Contributions to the reaction free energy of CVE3 reaction of TiO_2.

Temp. [K]	ΔE	$\Delta E + \Delta ZPE$	$\Delta W(T)$	ΔH [eV]	$T\Delta S$	$RT\ln(Q)$	ΔG
0.000	2.130	2.199	-0.000	2.199	0.000	0.000	2.199
50.000	2.130	2.199	0.002	2.201	0.058	-0.027	2.116
100.000	2.130	2.199	0.002	2.201	0.118	-0.053	2.030
150.000	2.130	2.199	-0.001	2.198	0.172	-0.080	1.946
200.000	2.130	2.199	-0.010	2.189	0.220	-0.106	1.863
250.000	2.130	2.199	-0.021	2.178	0.263	-0.133	1.782
300.000	2.130	2.199	-0.033	2.166	0.302	-0.160	1.704
350.000	2.130	2.199	-0.046	2.153	0.338	-0.186	1.628
400.000	2.130	2.199	-0.060	2.140	0.373	-0.213	1.554
450.000	2.130	2.199	-0.073	2.126	0.405	-0.240	1.481
500.000	2.130	2.199	-0.086	2.114	0.437	-0.266	1.411
550.000	2.130	2.199	-0.098	2.101	0.467	-0.293	1.341
600.000	2.130	2.199	-0.110	2.089	0.497	-0.319	1.273
650.000	2.130	2.199	-0.122	2.077	0.526	-0.346	1.205
700.000	2.130	2.199	-0.133	2.066	0.555	-0.373	1.138
750.000	2.130	2.199	-0.145	2.054	0.583	-0.399	1.072
800.000	2.130	2.199	-0.155	2.044	0.611	-0.426	1.007
850.000	2.130	2.199	-0.166	2.033	0.638	-0.453	0.943
900.000	2.130	2.199	-0.176	2.023	0.665	-0.479	0.879
950.000	2.130	2.199	-0.186	2.013	0.692	-0.506	0.815
1000.000	2.130	2.199	-0.195	2.004	0.719	-0.532	0.753

Table 8: Contributions to the reaction free energy of SL3 reaction of TiO$_2$.

Temp. [K]	ΔE	$\Delta E + \Delta$ZPE	$\Delta W(T)$	ΔH [eV]	$T\Delta S$	$RT\ln(Q)$	ΔG
0.000	-0.360	-0.102	0.000	-0.102	0.000	0.000	-0.102
50.000	-0.360	-0.102	-0.013	-0.115	-0.045	0.022	-0.049
100.000	-0.360	-0.102	-0.021	-0.123	-0.101	0.043	0.021
150.000	-0.360	-0.102	-0.024	-0.126	-0.156	0.065	0.094
200.000	-0.360	-0.102	-0.023	-0.125	-0.207	0.087	0.167
250.000	-0.360	-0.102	-0.019	-0.122	-0.255	0.109	0.241
300.000	-0.360	-0.102	-0.014	-0.117	-0.300	0.130	0.313
350.000	-0.360	-0.102	-0.007	-0.110	-0.343	0.152	0.383
400.000	-0.360	-0.102	0.000	-0.102	-0.383	0.174	0.452
450.000	-0.360	-0.102	0.009	-0.093	-0.421	0.196	0.523
500.000	-0.360	-0.102	0.020	-0.083	-0.457	0.217	0.591
550.000	-0.360	-0.102	0.031	-0.072	-0.492	0.239	0.657
600.000	-0.360	-0.102	0.043	-0.060	-0.524	0.261	0.725
650.000	-0.360	-0.102	0.055	-0.047	-0.555	0.282	0.789
700.000	-0.360	-0.102	0.068	-0.034	-0.584	0.304	0.851
750.000	-0.360	-0.102	0.082	-0.021	-0.611	0.326	0.917
800.000	-0.360	-0.102	0.096	-0.007	-0.638	0.348	0.978
850.000	-0.360	-0.102	0.110	0.008	-0.662	0.369	1.040
900.000	-0.360	-0.102	0.126	0.023	-0.686	0.391	1.100
950.000	-0.360	-0.102	0.141	0.038	-0.708	0.413	1.158
1000.000	-0.360	-0.102	0.157	0.054	-0.729	0.434	1.217

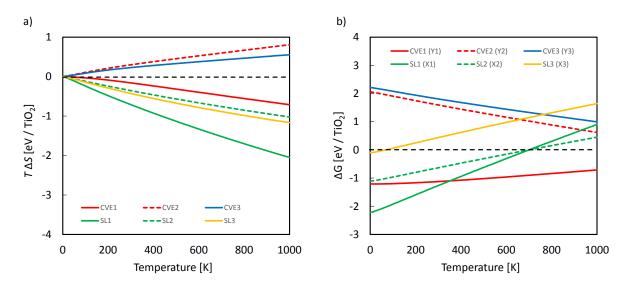# S2: Entropy and Free Energy Comparison

Figure 1: Comparison of the $T\Delta S$ (a) and ΔG (b) contributions of all postulated reactions of TiO_2 and HF interaction.

S3: Changes in Product Pressure

Product pressures can not be controlled in a thermal etch reactor, however it is interesting
to study the effect of changes in the product pressure. Since the number of product gas
molecules are lesser in the SL reaction as compared to the CVE reaction, the cross-over
temperature will increase with increase in the product pressure. In other words, the increase
in the slope of the SL FEP is smaller than the increase in the slope of the CVE FEP,
with increase in product pressure. The heat maps of CVE1 and SL1 reactions of TiO_2
at varying product pressures are shown in Figures 2. The heat maps in the first row of
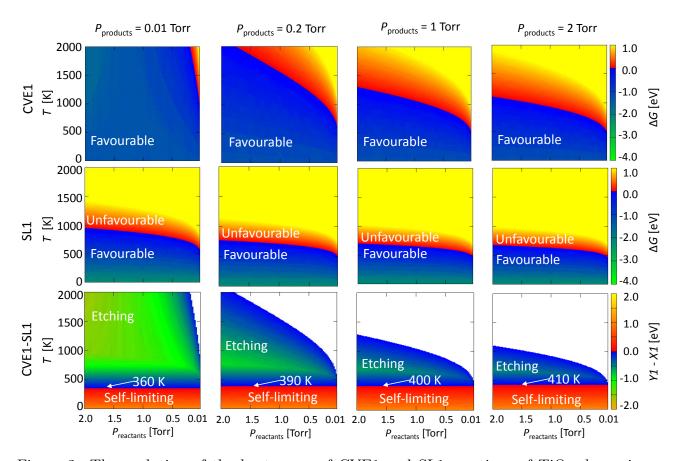
Figure 2: The evolution of the heat maps of CVE1 and SL1 reactions of TiO_2 shown in
Figure 13 of main text with respect to changes in product pressure.

Figure 2 correspond to the CVE1 reaction at different product pressures of 0.01 Torr, 0.2
Torr, 1 Torr and 2 Torr. Similarly, the heat maps in the second and third rows correspond
to the SL1 reaction and the corresponding minimum barrier, respectively. The white region

10

in the minimum barrier maps indicates the situation where both CVE1 and SL1 reactions are unfavourable. It is possible that in this region other etch reactions with different etch by-products are favourable or the reverse reaction, *i.e.* deposition, takes place. From the CVE1 and SL1 reaction maps, we find that the slope of the FEPs increase with the product pressure, in other words, the reactions become less favourable as the product pressure is increased. Also with the increase in product pressure the threshold temperature at which CVE1 becomes favourable increases from 360 K (87°C) at 0.01 Torr to 410 K (137°C) at 2 Torr. This is because the number of gas phase product molecules in the CVE1 reaction is larger than in the SL1 reaction, therefore the increase in the slope of the SL reaction is smaller than that of the CVE reaction. Similarly, the heat maps of the CVE2-SL2 and CVE3-SL3 reactions are given in Figures 3 and 4, respectively.
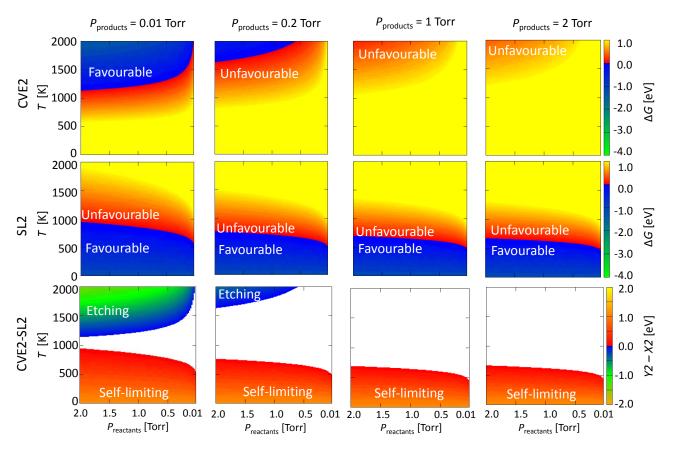

Figure 3: The evolution of the heat maps of CVE2 and SL2 reactions of TiO_2 with respect to changes in product pressure.
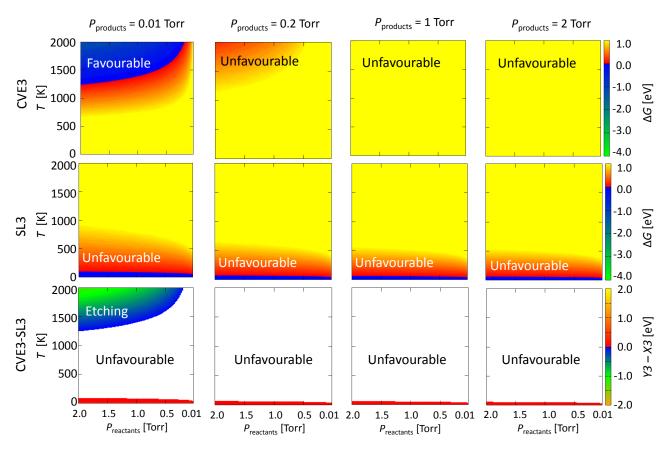
Figure 4: The evolution of the heat maps of CVE3 and SL3 reactions of TiO_2 with respect to changes in product pressure.