Supporting Material A Molecular Dynamics Study of Silicon Atomic Layer Etching by Chorine Gas and Argon Ions

Joseph R. Vella,[†] David Humbird,[‡] and David B. Graves[*,¶]

†Princeton Plasma Physics Laboratory, Princeton, NJ 08540 USA

‡DWH Consulting, Centennial, CO 80112 USA

¶Princeton Plasma Physics Laboratory, Princeton, NJ 08540 USA and Department of Chemical and Biological Engineering,Princeton University, Princeton, NJ 08540 USA

E-mail: dgraves@pppl.gov

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SI. REBO Force Field

Si-Si, Si-Cl, and Cl-Cl interactions are described using the REBO potential. The REBO potential describes the total potential energy of a collection of atoms by a sum over bond energies,

$$U = \sum_i \sum_{j>i} \phi_{ij}. \tag{S1}$$

In this equation, U is the total potential energy and ϕ_{ij} is the bond energy between atoms i and j. The bond energy is described as a sum of a repulsive component (V_R^{ij}) and attractive component, (V_A^{ij}):

$$\phi_{ij} = V_R^{ij} - \overline{b_{ij}} V_A^{ij}. \tag{S2}$$

$\overline{b_{ij}}$ is the bond order term used to scale the attractive component. The repulsive contribution is described by the functional form:

$$V_R^{ij}(r_{ij}) = \begin{cases} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r_{ij}} \left(\sum_{i=1}^{3} c_i \exp\left(- \frac{d_i r_{ij}}{a} \right) \right) + s & r_{ij} \leq r_a \\ c_R + \exp\left(a_R r_{ij} + b_R \right) & r_a < r_{ij} \leq r_b \\ f_{ij}(r_{ij}) A_{ij} \exp(-\lambda_{ij} r_{ij}) & r > r_b, \end{cases} \tag{S3}$$

where r_{ij} is the distance between atoms i and j , f_{ij} is a switching function that smoothly turns interactions off near the cut-off, s, a_R, b_R, and x_R, λ_{ij}, A_{ij}, r_a, and r_b are two-body fitting parameters. Z_i is the nuclear charge of atom i, e is the elementary charge, ε_0 is the permittivity of free space. a is the screening length (in Å) given by:

$$a = 0.83 \left(\frac{9\pi^2}{128} \right)^{1/3} (0.5292) \left(Z_i^{0.5} + Z_j^{0.5} \right)^{-2/3}. \tag{S4}$$

c_i values are (0.35,0.55,0.1) and d_i values are (0.3,1.2,6.0). The two-body fitting parameters for the repulsive portion of the potential are given in Table S0.

Table S1: Two-body Parameters for the Repulsive Potential.

Interaction	Si–Si	Si–Cl	Cl–Cl
r_a, Å	0.286968	0.300000	0.300000
r_b, Å	0.652200	0.800000	0.800000
a_R, Å^{-1}	-7.155376	-7.108443546	-5.093518
b_R	9.502208	9.622960686	9.516830
c_R, eV	237.361562	77.76670812	62.482094
s, eV	296.792932	106.164425	948.058599
A_{ij}, eV	1830.800000	1234.010000	7248.247000
λ_{ij}, Å^{-1}	2.479900	2.822900	4.008800

The attractive contribution is given by:

$$V_A^{ij}(r_{ij}) = f_{ij}(r_{ij}) B_{ij} \exp(-\mu_{ij} r_{ij}), \tag{S5}$$

where B_{ij} and μ_{ij} are two-body fitting parameters. The two-body fitting parameters for the attractive portion of the potential are given in Table S2.

Table S2: Two-body Parameters for the Attractive Potential.

Interaction	Si–Si	Si–Cl	Cl–Cl
B_{ij}, eV	471.1800	142.6061	269.7098
μ_{ij}, Å^{-1}	1.7322	1.4114	2.0044

The switching function is given by:

$$f_{ij}(r_{ij}) = S\left(\frac{r_{ij} - r_{ij}^{min}}{r_{ij}^{max} - r_{ij}^{min}}\right) = S(t) = \begin{cases} 1 & t \le 0 \\ 1 - t^3(6t^2 - 15t + 10) & 0 < t < 1 \\ 0 & t \ge 1, \end{cases} \tag{S6}$$

where r_{ij}^{min} and r_{ij}^{max} are pair-wise specific cut-off parameters. The cut-off parameters for the switching function are given in Table S3.

Table S3: Cut-Off Parameters for the Switching Function.

Interaction	Si–Si	Si–Cl	Cl–Cl
r_{ij}^{min}, Å	2.700	2.320	2.284
r_{ij}^{max}, Å	3.000	2.620	2.584

We now focus on the bond order, $\overline{b_{ij}}$, term introduced in Equation S2. This term is calculated as the average of the i-j and j-i bond orders:

$$\overline{b_{ij}} = \frac{1}{2}\big[b_{ij} + b_{ji}\big], \tag{S7}$$

where b_{ij} is calculated by considering the contributions of atoms that neighbor atom i with:

$$b_{ij} = \left[1 + \Big[\zeta_{ij} + H_{ij}\big(N_{ij}^{(Cl)}, N_{ij}^{(Si)}\big)\Big]^{\eta_{ij}}\right]^{-\delta_{ij}}. \tag{S8}$$

η_{ij} and δ_{ij} are fitting parameters. ζ_{ij} is calculated using the equation:

$$\zeta_{ij} = \sum_{k\neq j} f_{ik}(r_{ij})\big[c_{ij}^b + d_{ij}^b[h_{ij}^b + \cos(\theta_{ijk})]\big] \exp\left[\alpha_{ij}\big[(r_{ij} - R_{ij}^{(e)}) - (r_{ik} - R_{ik}^{(e)})\big]^{\beta_{ij}}\right]. \tag{S9}$$

θ_{ijk} is the angle between atoms i, j, and k. $R_{ij}^{(e)}$ is the equilibrium dimer bond length between the atom types of atom i and j. c_{ij}^b, d_{ij}^b, h_{ij}^b, α_{ij}, and β_{ij} are all fitting parameters. The fitting parameters for the bond order term are given in Table S4.

Table S4: Fitting Parameters for the Bond Order Term.

Interaction	Si–Si	Si–Cl	Cl–any
η_{ij}	0.78734	1.0	1.0
δ_{ij}	0.635050	0.80469	0.5
c_{ij}^b	0.0	0.0216	4.0
d_{ij}^b	0.160	0.270	0.0
h_{ij}^b	-0.59826	-0.0470	0.0
α_{ij}, Å^{-3}	5.197495	4.0	6.0
β_{ij}	3.0	3.0	1.0
$R_{ij}^{(e)}$, Å	2.35	2.019	1.9878

Finally, H_{ij} is the Brenner correction function. Values of the function at specified nodes are given in Table S5.

Table S5: Values of Brenner correction function at integer points. All values not given are 0. Derivatives (not shown but required for bicubic interpolation) are found by 2nd order finite differences.

x	y	$H_{\mathrm{SiCl}}(x,y)$
0	2	-0.05
0	3	-0.11
1	0	-0.088
1	2	-0.06
2	0	1.09
2	1	0.015
3	0	-0.068