Supporting Material: Dynamics of Plasma Atomic Layer Etching: Molecular Dynamics Simulations and Optical Emission Spectroscopy

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SI. Surface Fluxes and Impact Fluences Calculations

1. Cl_2 molecules at 300K. Wall collision flux (gas kinetic theory) = ¼ n_{Cl2} v_{mean}

n_i=P_i/kT ideal gas law; P_i = partial pressure species i

v_{mean} (m/s; gas kinetic theory) = $(8\ kT/p\ m_i)^{0.5}$; m_i = molecular mass (kg); kT (J)

m_{Cl2} = (70.1 g/mole)(1 mole/6.02 x 10^{23} molecules) = 11.6 x 10^{-23} g = 11.6 x 10^{-26} Kg

k = 1.38 x 10^{-23} J/K

kT = 4.14 x 10^{-21} J

v_{mean} = [(8 x 4.14 x 10^{-21} J)/(3.14159 x 11.6 x 10^{-26} Kg)]$^{0.5}$ = **301 m/s = 3 x 10^4 cm/s**

At T = 300K, 20 mTorr pressure total; if Cl_2 is 20/100 or 1/5 of total pressure
(1 Pa/7.5mT) x 20 mT x 1/9 = 0.53 Pa

Ideal gas law: n_{Cl2} = P_{Cl2}/kT = 0.53 Pa/(4.14 x 10^{-21} J) = 1.3 x 10^{20} m^{-3} = **1.3 x 10^{14} cm^{-3}**

Cl_2 flux = ¼ n_{Cl2} v_{mean} = ¼ (1.3 x 10^{14} cm^{-3}) (3 x 10^4 cm/s) = ***9.8 x 10^{17} cm^{-2} s^{-1}***

2. Ar^+ flux = 3.7 x 10^{16} cm^{-2} s^{-1}

Average surface impact times for surface area of 10^3 A^2 = 10^{-13} cm^2

Cl_2 molecules:
t_{Cl2} ~ 1/(area x flux) = 1/[10^{-13} cm^2 x 5.3 x 10^{17} cm^{-2} s^{-1}] = ***0.02 ms = 20 ms***

Ar^+:
t_{Ar+} ~ 1/(area x flux) = 1/[10^{-13} cm^2 x 3.7 x 10^{16} cm^{-2} s^{-1}] ***= 0.27 ms = 270 ms***

SII. Cl Surface Coverage of MD Simulations Using Additional Exposure

Figure S1 gives the Cl uptake as a function of cycle number for a simulation using a longer Cl_2 exposure period relative than those mentioned in the main text. Note that the Cl uptake saturates around a value of 1 $\times 10^{15}$ Cl/cm^2, similar to what was seen in the main text. Therefore, a larger Cl_2 fluence would not change the results of the MD simulations.

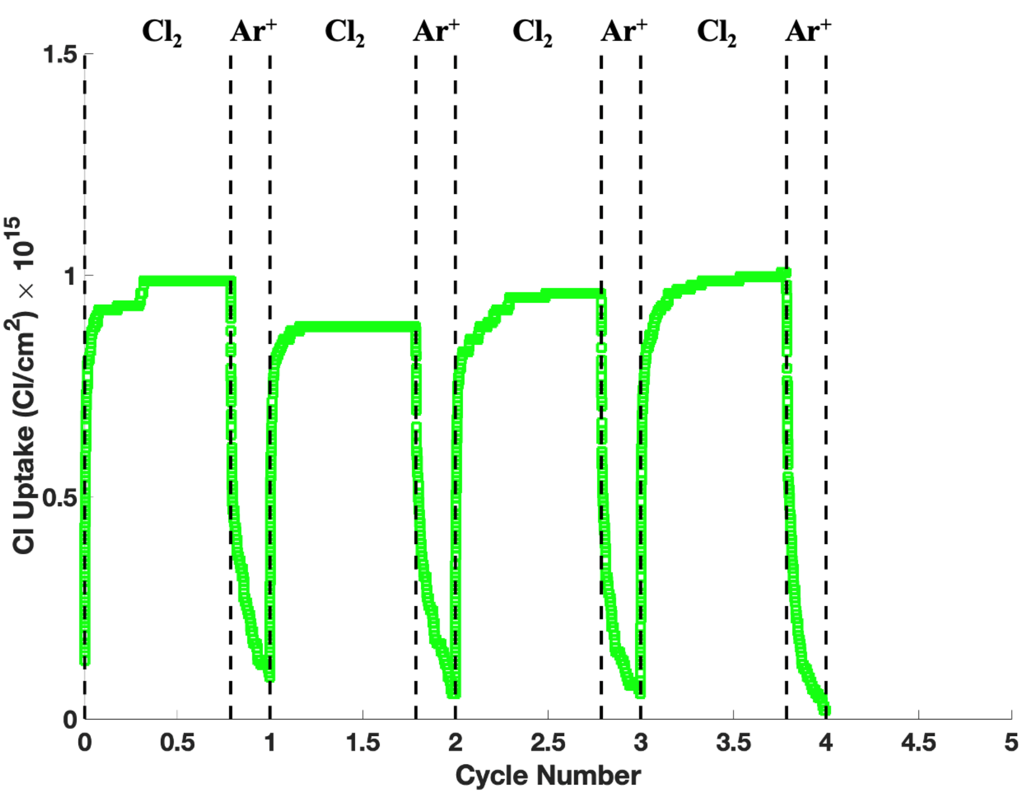

Figure S1: Cl uptake as a function of cycle number for a MD simulation using a longer Cl_2 exposure period when compared to those mentioned in the main text. The Cl_2 fluence for this simulation is 1.88×10^{17} Cl_2 molecules/cm^2 or roughly 188 ML of Cl_2 molecules. The Ar^+ ion energy is 80 eV. Note we only show Cl uptake after the simulation has reached cyclic steady state.