A global (volume averaged) model of a chlorine discharge: Dilution with argon and oxygen

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Chlorine is an electronegative diatomic gas that is widely used in plasma etching of both semiconductors and metals, in particular poly-silicon gate and aluminum interconnects.

Chlorine atoms are believed to be the primary reactant in plasma etching.

The chlorine molecule has:
- a low dissociation energy (2.5 eV)
- a near-zero threshold energy for dissociative attachment

All electronic excitations of the molecule appear to be dissociative, and no metastable molecular states are of importance.
Outline

- The global (volume averaged) model
  - Model parameters
- Comparison with measurements
- Particle densities
- Sensitivity analysis
- Argon dilution
- Oxygen dilution
- Summary
The global (volume averaged) model
The global (volume averaged) model

A steady state global (volume averaged) model was developed for the chlorine discharge using a revised reaction set.

The following species are included:

- electrons
- the ground state chlorine molecule Cl$_2$(X$^1\Sigma_g^+$, $v = 0$),
- the vibrationally excited ground state chlorine molecules Cl$_2$(X$^1\Sigma_g^+$, $v = 1 - 3$)
- the ground state chlorine atom Cl(3p$^5\,^2P$)
- the negative chlorine ion Cl$^-$
- the positive chlorine ions Cl$^+$ and Cl$_2^+$

The content of the chamber is assumed to be nearly spatially uniform and the power is deposited uniformly into the plasma bulk.

The global (volume averaged) model

- The particle balance equation for a species $X$ is given

$$\frac{dn^{(X)}}{dt} = 0 = \sum_i R_{\text{Generation},i} - \sum_i R_{\text{Loss},i}$$

where $R_{\text{Generation},i}$ and $R_{\text{Loss},i}$, respectively, are the reaction rates of the various generation and loss processes of the species $X$

- The power balance equation, which equates the absorbed power $P_{\text{abs}}$ to power losses due to elastic and inelastic collisions and losses due to charged particle flow to the walls is given as

$$\frac{1}{V} \left[ P_{\text{abs}} - eVn_e \sum_\alpha n^{(\alpha)} \varepsilon_\alpha \kappa_{iz}^{(\alpha)} - euB_0 n_i A_{\text{eff}} (\varepsilon_i + \varepsilon_e) \right] = 0$$
The global (volume averaged) model

For the edge-to-center positive ion density ratio we use

$$h_L \simeq \left[ \left( \frac{0.86}{(3 + \eta L/2\lambda_i)^{1/2}} \frac{1}{1 + \alpha_0} \right)^2 + h_c^2 \right]^{1/2}$$

$$h_R \simeq \left[ \left( \frac{0.8}{(4 + \eta R/\lambda_i)^{1/2}} \frac{1}{1 + \alpha_0} \right)^2 + h_c^2 \right]^{1/2}$$

where $$\alpha_0 \approx (3/2)\alpha$$ is the central electronegativity, $$\eta = 2T_+/(T_+ + T_-)$$ and

$$h_c \simeq \left[ \gamma_-^{1/2} + \gamma_+^{1/2} \left[ n_*^{1/2} n_+/n_-^{3/2} \right] \right]^{-1} \quad \text{and} \quad n_* = \frac{15}{56} \frac{\eta^2}{k_{\text{rec}}\lambda_i} v_i$$

is based on a one-region flat topped electronegative profile

$$\gamma_- = T_e/T_- \quad \text{and} \quad \gamma_+ = T_e/T_+$$

The global (volume averaged) model

The diffusional losses of the neutral chlorine atoms to the reactor walls are given by

\[ k_{\text{Cl, wall}} = \left[ \frac{\Lambda_{\text{Cl}}^2}{D_{\text{Cl}}} + \frac{2V(2 - \gamma_{\text{rec}})}{Av_{\text{Cl}}\gamma_{\text{rec}}} \right]^{-1} \text{ s}^{-1} \]

- \( D_{\text{Cl}} \) is the diffusion coefficient for neutral chlorine atoms
- \( v_{\text{Cl}} = \left( \frac{8eT_g}{\pi m_{\text{Cl}}} \right)^{1/2} \) is the mean Cl velocity
- \( \gamma_{\text{rec}} \) is the wall recombination coefficient for neutral chlorine atoms on the wall surface
- \( \Lambda_{\text{Cl}} \) is the effective diffusion length of neutral chlorine atoms

\[ \Lambda_{\text{Cl}} = \left[ \left( \frac{\pi}{L} \right)^2 + \left( \frac{2.405}{R} \right)^2 \right]^{-1/2} \]

The wall recombination coefficient \( \gamma_{\text{rec}} \) is one of the most important parameters in chlorine discharge modelling.
Model parameters
Surface recombination

- The wall recombination probability, $\gamma_{\text{rec}}$, is a very important quantity in all low pressure molecular discharges.
- We use the wall recombination coefficient measured by Stafford et al. (2009) for stainless steel.


A fit to the measured data is for anodized aluminum

$$\log_{10}(\gamma_{\text{rec}}) = -0.82 - 1.59 \times \exp(-1.81 \times \frac{[\text{Cl}]}{[\text{Cl}_2]})$$

and for stainless steel

$$\log_{10}(\gamma_{\text{rec}}) = -1.22 - 1.34 \times \exp(-1.48 \times \frac{[\text{Cl}]}{[\text{Cl}_2]})$$
Donnelly and Malyshev (2000) found that the neutral chlorine gas temperature was between 300 and 1250 K, increasing with power and pressure up to 1000 W and 20 mTorr.

A fit through the measured data gives

\[ T_g(P_{\text{abs}}, p) = 300 + s(p) \frac{\log_{10}(P_{\text{abs}}/40)}{\log_{10}(40)} \]

where

\[ s(p) = 1250 \left(1 - e^{-0.091 \times p}\right) + 400 e^{-0.337 \times p} \]
Comparison with experiments
Comparison with experiments

- Densities of neutral Cl atoms and electrons versus power
- The agreement with the measured electron density is excellent
- The calculated density of atomic chlorine is in a very good agreement with the measured data at both 1 and 10 mTorr

Malyshev and Donnelly, J. Appl. Phys. 90 1130 (2001)

- inductively coupled cylindrical stainless steel chamber
- \( L = 20 \text{ cm and } R = 18.5 \text{ cm} \)
Particle densities
Particle densities

- Atomic chlorine Cl is the dominant particle at low pressure, but the chlorine molecule Cl\(_2\) has a larger density above 20 mTorr.
- The density of the atomic ion Cl\(^+\) is always much smaller than the Cl\(_2\)\(^+\) density, decreasing with pressure.
- A cylindrical stainless steel chamber radius \(R = 18.5\) cm, length \(L = 20\) cm.

\[ P_{\text{abs}} = 323\ \text{W} \]
Sensitivity analysis
Sensitivity analysis – EEDF

- The discharge pressure was 10 mTorr and the absorbed power 323 W
- We allow the electron energy distribution function to vary according to the general distribution function

\[ f(\varepsilon) = c_1 \varepsilon^{1/2} \exp(-c_2 \varepsilon^x) \]

where the coefficients \( c_1 \) and \( c_2 \) depend on the energy \( \varepsilon \) and the distribution parameter \( x \)

<table>
<thead>
<tr>
<th>( x ): 1 – 2</th>
<th>([\text{Cl}]/n_g)</th>
<th>([\text{Cl}^+]/n_+)</th>
<th>(\alpha)</th>
<th>(T_e)</th>
<th>(n_e)</th>
</tr>
</thead>
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<tr>
<td>(\downarrow) 1.01</td>
<td>(\downarrow) 1.40</td>
<td>(\uparrow) 1.34</td>
<td>(\uparrow) 1.43</td>
<td>(\downarrow) 1.65</td>
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</tbody>
</table>

Gudmundsson, Plasma Sources Sci. Technol., 10 76 (2001)
Sensitivity analysis – $\gamma_{\text{rec}}$

<table>
<thead>
<tr>
<th>$\gamma_{\text{rec}}$</th>
<th>$[\text{Cl}]/n_g$</th>
<th>$[\text{Cl}^+]/n_+$</th>
<th>$\alpha$</th>
<th>$T_e$</th>
<th>$n_e$</th>
</tr>
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<tr>
<td>$10^{-4} - 1$</td>
<td>↓ 5.75</td>
<td>↓ 34.6</td>
<td>↑ 4.25</td>
<td>↑ 1.13</td>
<td>↓ 1.59</td>
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- The wall recombination coefficient $\gamma_{\text{rec}}$ determines the rate coefficient for recombination of neutrals on the wall.
- However, varying $\gamma_{\text{rec}}$ has a much larger effect on the atomic ion fraction than on the dissociation fraction.
Argon dilution
Argon dilution – particle densities

- The discharge is highly dissociated with Cl atoms being the dominant neutral until the argon content is 60%.
- The $\text{Cl}^+$ density increases until the argon dilution is 68%.
- This is likely a result of the increased electron temperature.
- A cylindrical stainless steel chamber $L = 10$ cm and $R = 10$ cm
  Pressure is $p = 10$ mTorr
  Power $P_{\text{abs}} = 500$ W

$Q_{\text{Cl}_2} + Q_{\text{Ar}} = 100$ sccm
Particle densities

- The electron temperature increases with argon content at low and intermediate pressures.
- The chlorine dissociation increases with argon content.
- The chlorine dissociation fraction decreases with increased pressure above 10 mTorr at low and moderate argon contents.
Particle densities

- The pressure dependence of the fraction of Cl\textsuperscript{+} positive ions can be modified by argon dilution.

- It peaks at low pressure when the argon content is low or moderate, but at high pressure in an argon dominated discharge.

- The peak value increases slightly with increased argon content, even when the argon content has reached 90%.

Oxygen dilution
Particle densities

- The $\text{Cl}^+$ density decreases with increased oxygen dilution.
- The chlorine-oxide molecule $\text{ClO}$ and its ion $\text{ClO}^+$ peak when $\text{Cl}_2$ and $\text{O}_2$ flowrates are roughly equal.
- The $\text{O}_2(\alpha^1\Delta_g)$ density is about 9 – 10 % of the total $\text{O}_2$ density.
- The electron density increases about 30 % between pure chlorine and pure oxygen discharge.

![Graph showing particle densities as a function of $Q_{\text{O}_2}/(Q_{\text{O}_2} + Q_{\text{Cl}_2})$ [\%]].

A cylindrical stainless steel chamber
$L = 10 \text{ cm}$ and $R = 10 \text{ cm}$
$p = 10 \text{ mTorr}$ and $P_{\text{abs}} = 500 \text{ W}$
- The total rate for creation and loss of ClO molecules is at maximum when the oxygen content is 65%.
- Wall recombination of Cl molecules, is the dominating pathway for creation of ClO molecules.
- The bulk processes and recombination of ClO$^+$ ions at the wall account for roughly 33–43% of the total rate for ClO creation, combined.
Summary

- A global model of Cl₂, Cl₂/Ar and Cl₂/O₂ discharges has been developed.
- The chlorine discharge remains highly dissociated in all conditions, being over 20% at the lowest power and highest pressure explored.
- Cl⁻ ions are essentially entirely produced in dissociative attachment of electrons to Cl₂ and lost to mutual neutralization with Cl⁺ and Cl₂⁺.
- The effect of vibrationally excited chlorine molecules Cl₂(ν > 0) is not great, at most increasing the Cl⁻ production by about 14%.
- The Cl⁺ density increases with increased argon dilution but decreases with increased oxygen dilution.
- The ClO molecule is mainly created by recombination at the discharge wall.


