A global (volume averaged) model of a chlorine discharge

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Outline

- 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
    - Creation and destruction
- Sensitivity analysis
- Argon 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 $\mathrm{Cl_2}(X\,{}^1\Sigma_{\mathrm{g}}^{+}, v = 0)$,
    - the vibrationally excited ground state chlorine molecules $\mathrm{Cl_2}(X\,{}^1\Sigma_{\mathrm{g}}^{+}, v = 1 - 3)$
    - the ground state chlorine atom $\mathrm{Cl(3p^{5}\,{}^2P)}$
    - the negative chlorine ion $\mathrm{Cl^-}$
    - the positive chlorine ions $\mathrm{Cl^+}$ and $\mathrm{Cl_2^+}$
- The content of the chamber is assumed to be nearly spatially uniform and the power is deposited uniformly into the plasma bulk

Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 015001 (2010)

The global (volume averaged) model

- The particle balance equation for a species X is given

  $$\frac{\mathrm{d}n^{(X)}}{\mathrm{d}t} = 0 = \sum_i R^{(X)}_{\mathrm{Generation},i} - \sum_i R^{(X)}_{\mathrm{Loss},i}$$

  where $R^{(X)}_{\mathrm{Generation},i}$ and $R^{(X)}_{\mathrm{Loss},i}$, 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_{abs} to power losses due to elastic and inelastic collisions and losses due to charged particle flow to the walls is given as

  $$\frac{1}{V}\left[P_{\mathrm{abs}} - eVn_{\mathrm{e}} \sum_{\alpha} n^{(\alpha)} \mathcal{E}_{\mathrm{c}}^{(\alpha)} k_{\mathrm{iz}}^{(\alpha)} - eu_{\mathrm{B0}} n_{\mathrm{i}} A_{\mathrm{eff}} (\mathcal{E}_{\mathrm{i}} + \mathcal{E}_{\mathrm{e}})\right] = 0$$

The global (volume averaged) model

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

$$h_L \simeq \left[\left(\frac{0.86}{(3 + \eta L/2\lambda_\mathrm{i})^{1/2}} \frac{1}{1+\alpha_0} \right)^2 + h_\mathrm{c}^2 \right]^{1/2}$$

$$h_R \simeq \left[\left(\frac{0.8}{(4 + \eta R/\lambda_\mathrm{i})^{1/2}} \frac{1}{1+\alpha_0} \right)^2 + h_\mathrm{c}^2 \right]^{1/2}$$

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

$$h_\mathrm{c} \simeq \left[\gamma_-^{1/2} + \gamma_+^{1/2} [n_*^{1/2} n_+ / n_-^{3/2}] \right]^{-1} \quad \text{and} \quad n_* = \frac{15}{56} \frac{\eta^2}{k_\mathrm{rec}\lambda_\mathrm{i}} v_\mathrm{i}$$

  is based on a one-region flat topped electronegative profile

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

Kim et al., J. Vac. Sci. Technol. A, **24** 2025 (2006)

The global (volume averaged) model

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

$$k_{\mathrm{Cl,wall}} = \left[\frac{\Lambda_{\mathrm{Cl}}^2}{D_{\mathrm{Cl}}} + \frac{2V(2-\gamma_{\mathrm{rec}})}{A v_{\mathrm{Cl}} \gamma_{\mathrm{rec}}} \right]^{-1} \quad \mathrm{s}^{-1}$$

  - D_{Cl} is the diffusion coefficient for neutral chlorine atoms
  - $v_{\mathrm{Cl}} = (8eT_{\mathrm{g}}/\pi m_{\mathrm{Cl}})^{1/2}$ is the mean Cl velocity
  - γ_{rec} is the wall recombination coefficient for neutral chlorine atoms on the wall surface
  - Λ_{Cl} is the effective diffusion length of neutral chlorine atoms

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

- The wall recombination coefficient γ_{rec} is one of the most important parameters in chlorine discharge modelling

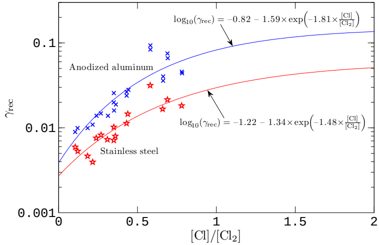
Model parameters

Surface recombination

- The wall recombination probability, $\gamma_{\rm rec}$, 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

Guha et al. J. Appl. Phys., **103** 013306 (2008)

Stafford et al. J. Phys. D: Appl. Phys. **42** 055206 (2009)



A fit to the measured data is for anodized aluminum

$$\log_{10}(\gamma_{\rm rec}) = -0.82 - 1.59 \exp\left(-1.81 \times \frac{[\rm Cl]}{[\rm Cl_2]}\right)$$

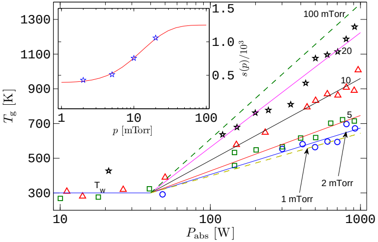
and for stainless steel

$$\log_{10}(\gamma_{\rm rec}) = -1.22 - 1.34 \exp\left(-1.48 \times \frac{[\rm Cl]}{[\rm Cl_2]}\right)$$

Gas temperature

- 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

Donnelly and Malyshev, Appl. Phys. Lett. **77** 2467 (2000)



A fit through the measured data gives

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

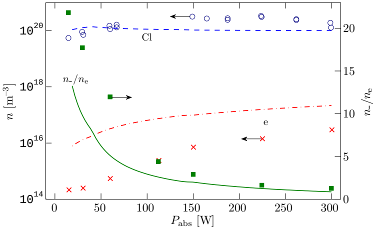
where

$$s(p) = 1250\,(1 - e^{-0.091\times p}) + 400\,e^{-0.337\times p}$$

Comparison with experiments

Comparison with experiments

- The calculated Cl atom density shows a very good agreement with the measured data
- The electronegativity n_{-}/n_{e} shows a good agreement at high power but fair agreement at lower power
- The model calculations show much higher electron density than the measured values

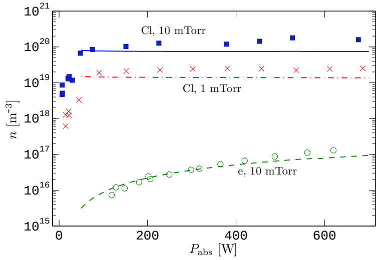


- inductively coupled cylindrical stainless steel chamber
- $L = 8.5$ cm and $R = 10$ cm
- $p = 10$ mTorr and $q = 10$ sccm

Corr et al., J. Phys. D: Appl. Phys. **41** 185202 (2008)

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



- inductively coupled cylindrical stainless steel chamber
- $L = 20$ cm and $R = 18.5$ cm

Malyshev and Donnelly, J. Appl. Phys. **88** 6207 (2000)

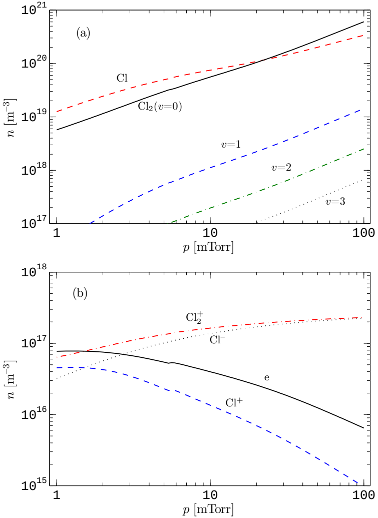
Malyshev and Donnelly, J. Appl. Phys. **90** 1130 (2001)

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

  $P_{abs} = 323$ W



Creation and destruction of Cl atoms

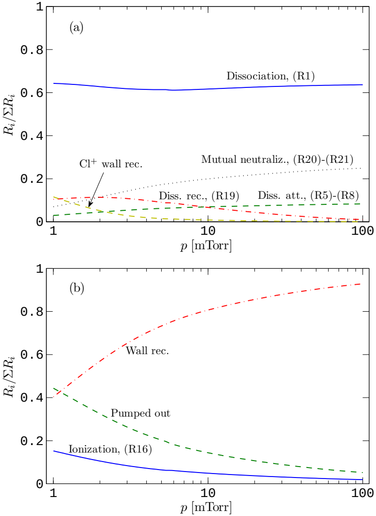
- Electron impact dissociation

  $$e + Cl_2 \longrightarrow Cl + Cl + e$$

  is the most important channel for creation of Cl atoms
- Recombination at the wall

  $$Cl \longrightarrow \frac{1}{2}Cl_2$$

  accounts for 40 – 93 % and is the most important channel for Cl atom loss



Creation and destruction of Cl^- ions

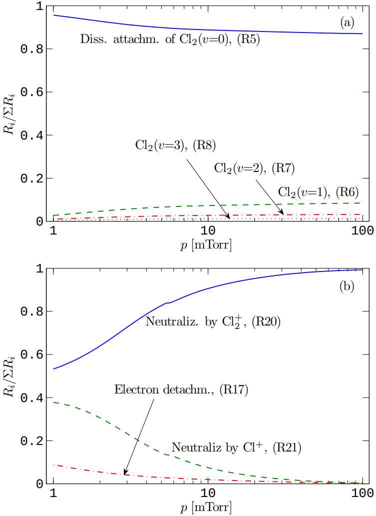
- The production of Cl^--ions is only due to dissociative electron attachment

$$e + Cl_2 \longrightarrow Cl + Cl^-$$

- Vibrational levels contribute at most 14 % at 100 mTorr
- Cl^- ions are primarily lost by mutual neutralization

$$Cl^- + Cl_2^+ \longrightarrow Cl + Cl + Cl$$

$$Cl^- + Cl^+ \longrightarrow Cl + Cl$$



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

  $$f(\mathcal{E}) = c_1 \mathcal{E}^{1/2} \exp(-c_2 \mathcal{E}^x)$$

  where the coefficients c_1 and c_2 depend on the energy $\mathcal{E}$ and the distribution parameter x

	$[\mathrm{Cl}]/n_\mathrm{g}$	$[\mathrm{Cl}^+]/n_+$	α	$\mathrm{T_e}$	n_e
x: 1 – 2	↓ 1.01	↓ 1.40	↑ 1.34	↑ 1.43	↓ 1.65

Gudmundsson, Plasma Sources Sci. Technol., **10** 76 (2001)

Sensitivity analysis – γ_{rec}

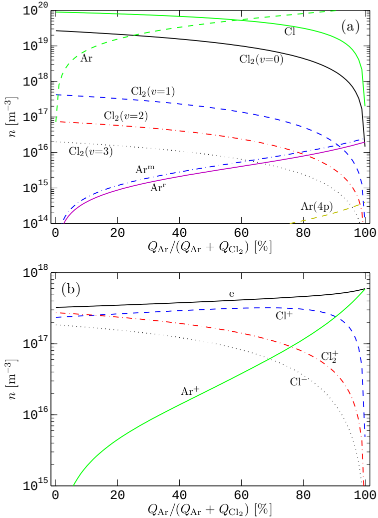
	$[\mathrm{Cl}]/n_{\mathrm{g}}$	$[\mathrm{Cl}^{+}]/n_{+}$	α	$\mathrm{T_e}$	n_{e}
γ_{rec}: 10^{-4} – 1	↓ 5.75	↓ 34.6	↑ 4.25	↑ 1.13	↓ 1.59

- The wall recombination coefficient γ_{rec} determines the rate coefficient for recombination of neutrals on the wall
- However, varying γ_{rec} has a much larger effect on the atomic ion fraction than on the dissociation fraction

Argon dilution

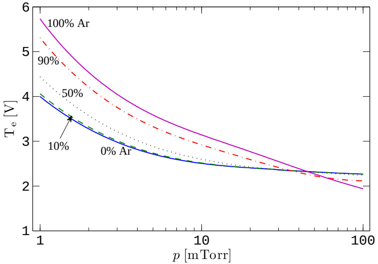
Argon dilution – particle densities

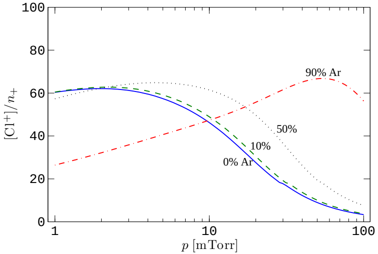
- The discharge is highly dissociated with Cl atoms being the dominant neutral until the argon content is 60%
- The Cl^+ density increases until the argon dilution is 68%
- This is likely a result of the increased electron temperature



Particle densities

- The electron temperature increases with argon content at low and intermediate pressures
- The pressure dependence of the fraction of Cl^+ 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





Summary

Summary

- A global model of Cl_2 and Cl_2/Ar discharges has been developed
- The chlorine discharge remains highly dissociated in all conditions, being over 20 % at the lowest power and highest pressure explored
- Electron impact dissociation is responsible for most of the Cl production, or roughly 55 – 65 %
- Cl atoms are lost mainly at the wall and to pumping
- Cl^- ions are essentially entirely produced in dissociative attachment of electrons to Cl_2 and lost to mutual neutralization with Cl^+ and Cl_2^+
- The effect of vibrationally excited chlorine molecules $Cl_2(v > 0)$ is not great, at most increasing the Cl^- production by about 14 %

References

Corr, C. S., E. Despiau-Pujo, P. Chabert, W. G. Graham, F. G. Marro, and D. B. Graves (2008). Comparison between fluid simulations and experiments in inductively coupled argon/chlorine plasmas. *Journal of Physics D: Applied Physics 41*(18), 185202.

Donnelly, V. M. and M. V. Malyshev (2000). Diagnostics of inductively coupled chlorine plasmas: Measurements of neutral gas temperature. *Applied Physics Letters 77*, 2467 – 2469.

Fuller, N. C. M., I. P. Herman, and V. M. Donnelly (2001). Optical actinometry of Cl_2, Cl, Cl^+, and Ar^+ densities in inductively coupled Cl_2–Ar plasmas. *Journal of Applied Physics 90*(7), 3182–3191.

Gudmundsson, J. T. (2001). On the effect of the electron energy distribution on the plasma parameters of argon discharge: A global (volume averaged) model study. *Plasma Sources Science and Technology 10*(1), 76–81.

Guha, J., V. M. Donnelly, and Y.-K. Pu (2008). Mass and Auger electron spectroscopy studies of the interactions of atomic and molecular chlorine on a plasma reactor wall. *Journal of Applied Physics 103*(1), 013306.

Kim, S., M. A. Lieberman, A. J. Lichtenberg, and J. T. Gudmundsson (2006). Improved volume-averaged model for steady and pulsed-power electronegative discharges. *Journal of Vacuum Science and Technology A 24*(6), 2025–2040.

Malyshev, M. V. and V. M. Donnelly (2000). Diagnostics of inductively coupled chlorine plasmas: Measurement of Cl_2 and Cl number densities. *Journal of Applied Physics 88*(11), 6207 – 6215.

Malyshev, M. V. and V. M. Donnelly (2001). Diagnostics of inductively coupled chlorine plasmas: Measurement of electron and total positive ion densities. *Journal of Applied Physics 90*(3), 1130–1137.

Stafford, L., R. Khare, J. Guha, V. M. Donnelly, J.-S. Poirier, and J. Margot (2009). Recombination of chlorine atoms on plasma-conditioned stainless steel surfaces in the presence of adsorbed Cl_2. *Journal of Physics D: Applied Physics 42*(5), 055206.

Thorsteinsson, E. G. and J. T. Gudmundsson (2010). A global (volume averaged) model of the chlorine discharge. *Plasma Sources Science and Technology 19*(1), 015001.