

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 $\text{Cl}_2(X^1\Sigma_g^+, v = 0)$,
 - the vibrationally excited ground state chlorine molecules $\text{Cl}_2(X^1\Sigma_g^+, v = 1 - 3)$
 - the ground state chlorine atom $\text{Cl}(3p^5^2P)$
 - 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

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

where $R_{\text{Generation},i}^{(X)}$ and $R_{\text{Loss},i}^{(X)}$, 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

$$\frac{1}{V} \left[P_{\text{abs}} - eVn_e \sum_{\alpha} n^{(\alpha)} \mathcal{E}_c^{(\alpha)} k_{iz}^{(\alpha)} - eu_{B0} n_i A_{\text{eff}} (\mathcal{E}_i + \mathcal{E}_e) \right] = 0$$

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

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

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_{Cl} is the diffusion coefficient for neutral chlorine atoms
- $v_{\text{Cl}} = (8eT_g/\pi m_{\text{Cl}})^{1/2}$ 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

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

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

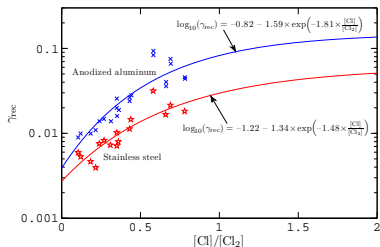
Model parameters

Surface recombination

- The wall recombination probability, γ_{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

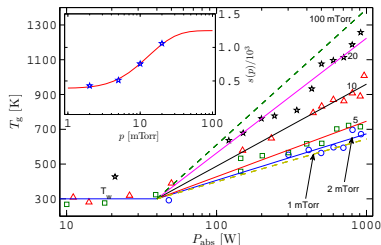
$$\log_{10}(\gamma_{\text{rec}}) = -0.82 - 1.59 \exp\left(-1.81 \times \frac{[\text{Cl}]}{[\text{Cl}_2]}\right)$$

and for stainless steel

$$\log_{10}(\gamma_{\text{rec}}) = -1.22 - 1.34 \exp\left(-1.48 \times \frac{[\text{Cl}]}{[\text{Cl}_2]}\right)$$

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



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

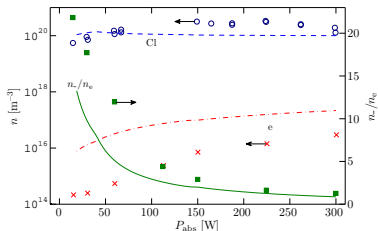
$$s(p) = 1250 (1 - e^{-0.091 \times p}) + 400 e^{-0.337 \times p}$$

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

Comparison with experiments

Comparison with experiments

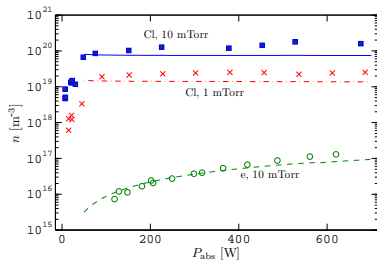
- The calculated Cl atom density shows a very good agreement with the measured data
- The electronegativity n_-/n_e shows a good agreement at high power but fair agreement at lower power
- The model calculations show much higher electron density than the measured values



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

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)

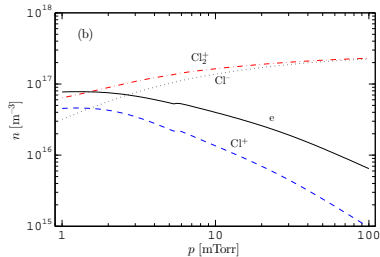
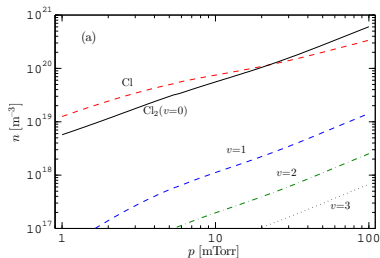
Malyshev and Donnelly, J. Appl. Phys. **90** 1130 (2001)

Particle densities

Particle densities

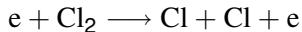
- Atomic chlorine Cl is the dominant particle at low pressure, but the chlorine molecule Cl_2 has a larger density above 20 mTorr
- The density of the atomic ion Cl^+ is always much smaller than the Cl_2^+ density, decreasing with pressure
- a cylindrical stainless steel chamber
radius $R = 18.5$ cm
length $L = 20$ cm

$$P_{\text{abs}} = 323 \text{ W}$$



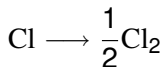
Creation and destruction of Cl atoms

- Electron impact dissociation

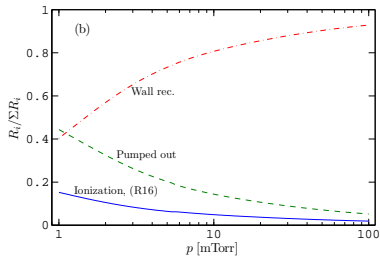
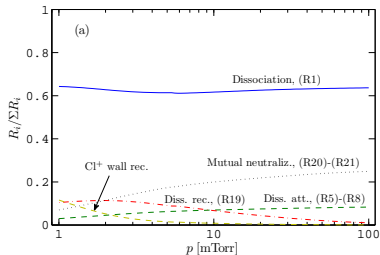


is the most important channel for creation of Cl atoms

- Recombination at the wall

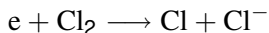


accounts for 40 – 93 % and is the most important channel for Cl atom loss



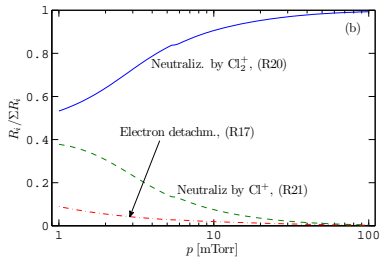
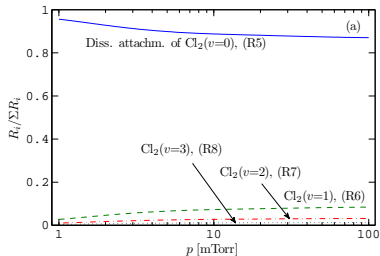
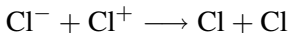
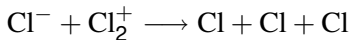
Creation and destruction of Cl^- ions

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



- Vibrational levels contribute at most 14 % at 100 mTorr

- Cl^- ions are primarily lost by mutual neutralization



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

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

Sensitivity analysis – γ_{rec}

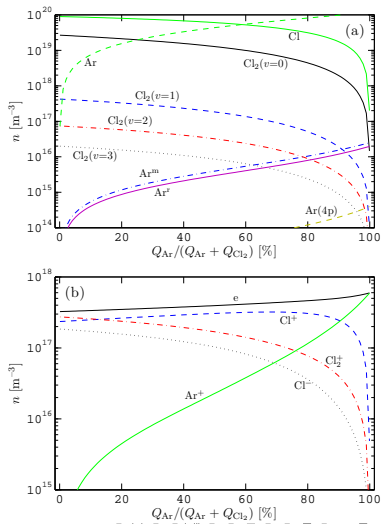
	$[\text{Cl}]/n_{\text{g}}$	$[\text{Cl}^+]/n_{+}$	α	T_{e}	n_{e}
$\gamma_{\text{rec}}: 10^{-4} - 1$	↓ 5.75	↓ 34.6	↑ 4.25	↑ 1.13	↓ 1.59

- 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

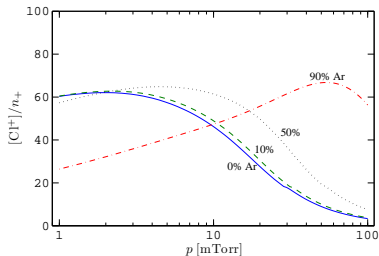
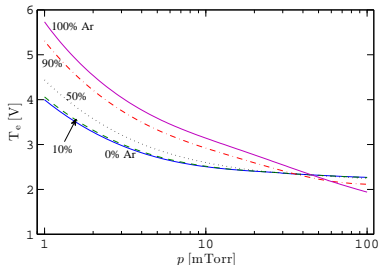
Argon dilution – particle densities

- 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 $\text{Cl}_2(\nu > 0)$ is not great, at most increasing the Cl^- production by about 14 %

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