Computational Modeling of Processing Plasmas: Instabilities and Fluorocarbon Chemistry

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Abstract: Fluorocarbon gases are frequently used in radiofrequency processing plasmas in the semiconductor industry. Recently they have also been used in biomedical applications of plasmas to deactivate toxins using atmospheric pressure plasmas. In this work, we use computational models to examine the stability criteria and the chemistry of these plasmas at low pressure and atmospheric pressure.

Keywords: radiofrequency plasmas, electronegative plasma chemistry, instabilities

1. Plasma Processing of Materials

Low-temperature plasmas have been used to deliver fluxes of reactive and energetic species for many industries. In semiconductor processing, low temperature plasmas are essential for selective and anisotropic etching of materials and to deposit thin films. In biomedical applications, plasmas have been used to generate reactive oxygen and nitrogen species for triggering immune responses. Sterilization of water, deactivation of pathogens, and destruction of environmentally harmful molecules have all been explored.

In many of these systems, diagnostics, especially regarding the plasma chemistry are extremely challenging in general and impractical in realistic configurations. Computational modeling can provide beneficial insights on reaction pathways. In this paper, we will describe the behaviour of plasmas containing electronegative gases in two very different regimes.

Chitosan is a polymer used in medicine for wound treatment, drug delivery and other applications. Processing chitosan to remove pyrogens, or fever-causing components, is a critical and expensive part of producing medical-grade chitosan. Dielectric barrier discharge treatment of chitosan at atmospheric pressure has been demonstrated as effective for depyrogenation [1]. Plasma discharges in fluorine containing gases, such as CF_4, may provide more rapid destruction of these pyrogens. Motivated by this application, we use computational modeling to investigate the pathways and reactive species produced at atmospheric pressure.

For low pressure radiofrequency (RF) plasmas, uniformity is often a critical goal. Instabilities in the plasma dynamics can cause destructive arcing, or self-organization which leads to nonuniformity. Stability criterion are derived for low pressure RF plasmas in 1D, and these are evaluated to explore the process window where the uniform plasma is stable.

2. Global Model of Atmospheric Pressure Plasma with CF_4

A 0-dimensional well-stirred reactor model is used to investigate the production of reactive species in an Ar/CF_4 plasma. Multibolt, a multi-term Boltzmann solver, is used to calculate electron energy distribution functions and reaction rates [2,3].

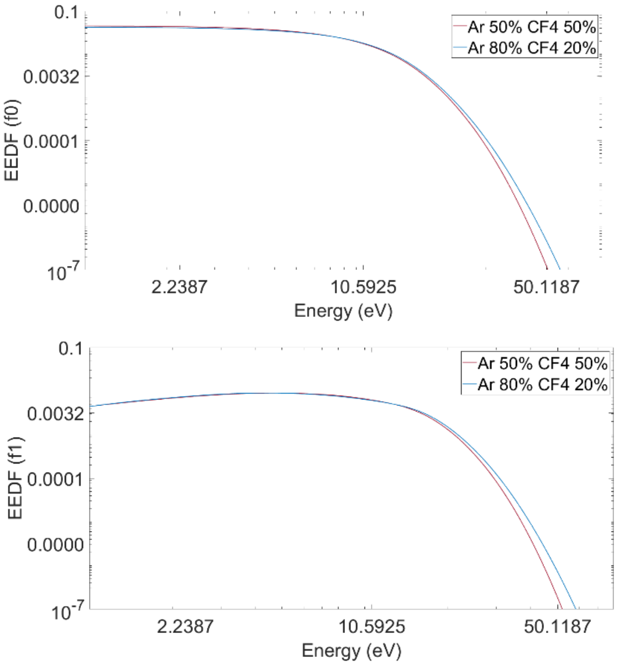

Fig. 1. Electron energy distribution functions calculated in Ar/CF_4 mixtures with 20% and 50% CF_4 at 301 Td. The EEDF is divided into (upper) the isotropic component and (lower) the anisotropic component.

As expected, the ionization rate increases monotonically with E/N. The 2-body attachment rate has a maximum at approximately 100 Td for 20% CF_4 and 200 Td for 50% CF_4.

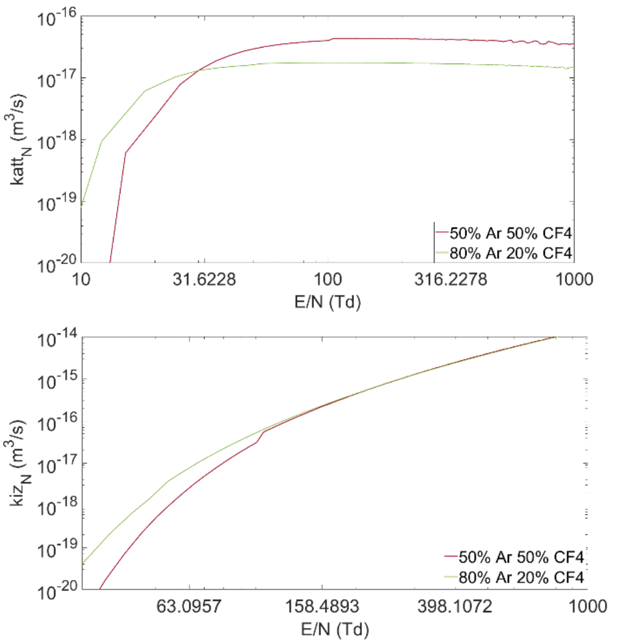

Fig. 2. Total reaction rates of electron impact processes at various reduced electric field (E/N) values. (upper) k_{att} refers to the total attachment rate and (lower) k_{iz} refers to the total ionization rate. Results are shown for 20% and 50% CF_4.

A 6-term spherical harmonic expansion was used in Multibolt to calculate the electron energy distributions (EEDFs) for multiple mixtures of CF_4 and Ar, shown in Fig. 1 [4,5]. As the CF_4 fraction increases, more energy is lost from inelastic processes such as vibrational excitation, and the average electron energy decreases.

The reaction rates calculated by Multibolt are used in a global model of a plasma with CF_4 admixtures. The volumetric power deposition will be specified for the electron energy equation based on an atmospheric pressure dielectric barrier discharges. The reactive species production will be studied as the CF_4 concentration and power deposition is varied.

3. Stability in Radiofrequency Plasmas

Low pressure, radiofrequency plasma discharges are used for the processing of semiconductors. To provide ideal control, they would operate stably and uniformly over a maximum range of pressures, powers, and gas composition. Instabilities can lead to destructive modes like arcing, which are detrimental to individual wafers and entire processing tools. Instabilities may also evolve into less destructive, but still problematic modes like striations and plasmoids which prevent process uniformity. Both of these possibilities may appear as unstable conditions in a linear stability analysis.

Désangeles *et al*. recently derived a stability criterion for a co-axial inductively coupled plasma geometry which matched experiment, but the geometry of this setup is quite different than that of most semiconductor processing reactors [6]. Recently, a modeling study by Bera *et al*. demonstrated that the electron energy transport term χ_e, the thermoelectric transport coefficient was critical in the evolution of plasmoids in a planar CCP [7].

In this work, we derive a stability criterion for planar inductive and capacitively coupled plasmas. The ionization rates and transport coefficients are calculated using MultiBolt [4].

First, we look at a planar inductively coupled plasma, where the steady state conditions are derived by balancing the ionization in the bulk with the diffusion losses to the walls:

$$\frac{\partial n_e}{\partial t} - D_a \frac{\partial^2 n_e}{\partial x^2} = \nu_{iz} n_e, \qquad (1)$$

where n_e is the electron density, D_a is the ambipolar diffusion coefficient, and υ_{iz} is the ionization frequency. In the steady state,

$$\frac{\partial^2 n_e}{\partial x^2} - \frac{\nu_{iz} n_e}{D_a} = 0 \qquad (2)$$

The steady state temperature calculated using the balance is shown in Fig. 3. This analysis will be extended to Ar with CF_4 gas admixtures.

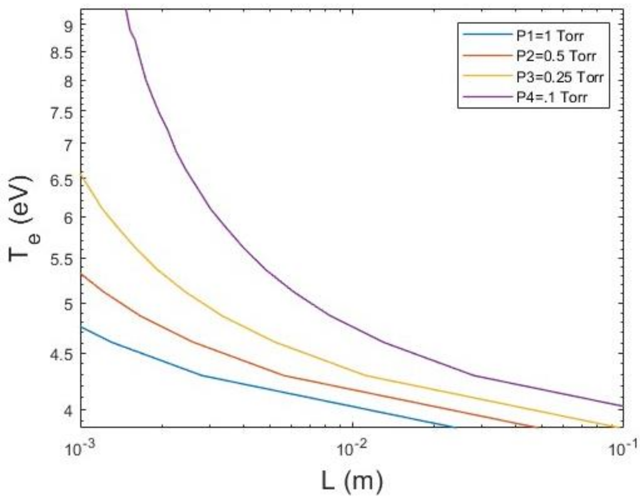

Fig. 3. The steady state electron temperature in a 1D Ar discharge from balancing bulk ionization with diffusion to the walls for various gap sizes.

This simple balance allows the use of a linear stability analysis to investigate the regions in parameter space where the discharge maybe fundamentally unstable to instabilities. Though this method is commonly used for fully ionized, magnetized, and fusion plasmas, it is less common for weakly ionized plasmas because the analysis is so sensitive to many collision processes and must be approached numerically.

The steady state solution will be perturbed using a linear stability analysis in 1-D,

$$n_e(x,t) = n_{e0}(x) + n_{e1}\exp(kx - \omega t). \quad (3)$$

where n_{e0} is the steady state electron density and n_{e1} is the small perturbation. The perturbation dynamics will consider the often-ignored Dufour effect in the electron energy transport:

$$\frac{\partial}{\partial t}\left(\frac{3}{2}k_b n_e T_e\right) - \chi_e \frac{\partial n_e}{\partial x} - \kappa_e \frac{\partial T_e}{\partial x} = P_0 - \sum_i^{rxns} \Delta\epsilon n_e N_i k_i \quad (4)$$

where k_B is Boltzmann's constant, T_e is the electron temperature, χ_e thermoelectric transport coefficient, κ_e is the electron thermal conductivity.

The resulting stability criterion will be used to explore the trends in stable and unstable modes over broad ranges of parameter space and gas mixtures which are relevant for semiconductor processing.

4. References

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5. Funding Acknowledgement

This work was funded by Lam Research Foundation.