Control of particle properties in low-pressure radio frequency gas discharges

Booklet of Doctoral Thesis

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1 Background and motivation

Plasmas are gases containing free charged particles. The electrostatic interactions and the collision processes between the wide range of plasma particles (electrons, ions, neutral gas atoms/molecules, metastables, photons etc.) make the systems complex. In radiofrequency (RF) electrical gas discharges, the energy supply is provided by a RF generator. Capacitively coupled plasmas (CCPs) are one type of RF plasmas, which are widely applied in plasma processing technologies like etching, deposition and cleaning. The substrate located on one of the electrodes is bombarded by plasma particles. Consequently, surface processes are of crucial importance in a RF plasma, and applications can be optimized by the control of particle energies and fluxes at the electrodes.

In the current thesis, the physics of CCPs is investigated, in order to facilitate the optimization of plasma processing applications. The electron power absorption and ionization dynamics and the role of surface processes are central topics. To achieve a fundamental understanding, modelling and simulation of CCPs combined with experiments are performed. The simulations need realistic models for plasma processes, although several assumptions have been applied for plasma–surface interactions. In the frame of this work, the realistic modelling of the surface processes is aimed.

2 Methods

For the studies presented in the thesis, a kinetic particle-based simulation method called particle-in-cell/Monte Carlo collisions (PIC/MCC) and an experimental method called phase-resolved optical emission spectroscopy (PROES) are applied. The simulation is capable of obtaining various local and global quantities of the RF plasma with high resolution in time and space. The flux-energy distributions of the plasma particles at the electrode surfaces can also be calculated, which determine the nature of interaction of these species with the surfaces. Based on this information the plasma operating conditions can be tuned for optimum processing results. The surface processes also influence the plasma characteristics by e.g., modifying the charged species balance. These effects can also be traced in the simulations. The experimental method, PROES provides access to the spatially and temporally resolved dynamics of energetic electrons, revealing information about the excitation processes and aiding the validation of the computational models.

3 Theses

The scientific findings presented in the current work are summarized in the following theses.

1. For neon CCPs with stainless steel electrodes, I determined the unknown effective ion-induced secondary electron emission coefficient (γ) by a revised version of the γ-CAST method, a computationally assisted spectroscopic technique. A γ coefficient of 0.29 provided the best agreement between the Ne $2p_1$ excitation rate obtained from PROES measurement and PIC/MCC simulation [TP1].

2. I demonstrated that PROES measurements does not always probe the operation mode of a CCP. In fact, such measurements are only able to provide information about the excitation rate of the measured excited state from the ground state, which can have different spatio-temporal distribution compared to the ioniza-

tion rate, based on which the operation mode of a discharge can be defined. I found that the reason behind this is the different shape of the electron-impact cross sections of the excitation of the measured excited state and the ionization. In neon CCPs, this difference in the cross sections makes high-energy γ-electrons within the sheath more likely to cause ionization than excitation, resulting in a γ-mode discharge operation unobservable by PROES measurement of the Ne $2p_1$ state [TP1].

3. I implemented a realistic model for the interaction of electrons with the electrode surface into the PIC/MCC simulation code of oxygen CCPs. Based on this, I found that electron-induced secondary electrons (δ-electrons) together with ion-induced secondary electrons (γ-electrons) play a crucial role in the ionization dynamics in high-voltage and low-pressure oxygen CCPs, which significantly increases the charged particle densities and the $O_2(a^1\Delta_g)$ metastable density, leading to the decrease of the electronegativity of the discharge. Parallel to this, the role of the drift-ambipolar mode decreases in the ionization dynamics when electron-induced secondary electron emission is treated realistically in the simula-

tion, and a transition to the α-mode occurs with emergence of an additional ionizing electron beam at the phase of partial sheath collapse [TP2].

4. In addition to electron induced secondary electron emission, I added a realistic implementation of secondary electron emission induced by O_2^+ ions to the PIC/MCC simulation code. This way the effects of secondary electrons on the discharge characteristics were even more pronounced at high driving voltages. The simulations showed that above 800 V, the effective γ^* ion induced secondary electron emission coefficient was higher than 0.4, reaching a value of 0.62 at the highest driving voltage of 1200 V. While the electron density at 1200 V was an order of magnitude higher according to the surface model containing a realistic implementation of the electron–surface interaction compared to a simple model considering constant electron reflection coefficient and neglecting secondary electron emission, a difference by a factor of 50 was found in the electron densities between the simplest model and the realistic model which contained realistic approaches for both O_2^+ ions and electrons. Moreover, I found that the

oxygen discharge became electropositive above 1000 V, when both electron and ion induced secondary electron emission were treated realistically [TP2].

5. By PIC/MCC simulations of CCPs driven by multifrequency waveforms (a sinusoidal waveform containing additional harmonics of the base harmonic) in argon at high voltage and low pressure, I found that the DC self-bias between the electrodes can be modulated between a negative and a positive peak of ≈ 500 V by changing the phase angle of the even (second and fourth) harmonics. Via the modulation of the self bias, the mean energy of heavy particles (argon ion and argon fast atom) at the electrodes can also be tuned within a range of a factor of 7 in the current study. With the use of a realistic surface model treating heavy particle induced and electron induced secondary electron emission with energy-dependent coefficients and accounting for the sputtering of the copper electrodes with a realistic coefficient as well, I demonstrated that the sputtering yield of copper atoms caused by heavy particle impact can also be efficiently controlled by changing the phase angle of the even harmonics between 0° and

180° in the driving voltage waveforms. The domain over which the sputtered atom flux can be varied is enlarged by adding more harmonics to the driving voltage waveform. When two harmonics are used, the sputtering varies between the two electrodes by a factor of 3, while this difference rises up to a factor of 5 in case of four harmonics [TP3].

4 Conclusions

The thesis aimed the fundamental understanding of the electron power absorption and ionization dynamics and the role of plasma–surface interactions in CCPs. In order to reach these goals, particle-based computational studies were combined with experiments. The accurate modelling of surface processes in PIC/MCC simulations was a key issue in this work. Various surface models were developed and incorporated to the simulation model. This way new details of the electron power absorption and the ionization dynamics were discovered in CCPs operated in electropositive and electronegative gases, and the role of various surface processes in such systems was revealed. Moreover, efficient control of the sputtering yield was achieved in low-pressure CCPs, which can facilitate the optimization of plasma processing applications.

List of publications

Publications corresponding to theses

1. Thesis Paper 1

   B Horváth, A Derzsi, J Schulze, I Korolov, P Hartmann, Z Donkó: Experimental and kinetic simulation study of electron power absorption mode transitions in capacitive radiofrequency discharges in neon. *Plasma Sources Science and Technology* **29** 055002, 2020. *https://doi.org/10.1088/1361-6595/ab8176*

2. Thesis Paper 2

   B Horváth, Z Donkó, J Schulze, A Derzsi: The critical role of electron induced secondary electrons in high-voltage and low-pressure capacitively coupled oxygen plasmas. *Plasma Sources Science and Technology* **31** 045025, 2022.

   https://doi.org/10.1088/1361-6595/ac64bd

3. Thesis Paper 3

   A Derzsi, B Horváth, Z Donkó, J Schulze: Surface processes in low-pressure capacitive radio frequency discharges driven by tailored voltage waveforms. *Plasma Sources Science and Technology* **29** 074001, 2020. *https://doi.org/10.1088/1361-6595/ab9156*

Other publications

1. B Horváth, M Daksha, I Korolov, A Derzsi, J Schulze: The role of electron induced secondary electron emission from SiO_2 surfaces in capacitively coupled radio frequency plasmas operated at low pressures. *Plasma Sources Science and Technology* **26** 124001, 2017. *https://doi.org/10.1088/1361-6595/aa963d*

2. B Horváth, J Schulze, Z Donkó, A Derzsi: The effect of electron induced secondary electrons on the characteristics of low-pressure capacitively coupled radio frequency plasmas. *Journal of Physics D: Applied Physics* **51** 355204, 2018. *https://doi.org/10.1088/1361-6463/aad47b*

3. A Derzsi, B Horváth, I Korolov, Z Donkó, J Schulze:

Heavy-particle induced secondary electrons in capacitive radio frequency discharges driven by tailored voltage waveforms. *Journal of Applied Physics* **126** 043303, 2019. *https://doi.org/10.1063/1.5100508*

4. Z Donkó, A Derzsi, M Vass, B Horváth, S Wilczek, B Hartmann, P Hartmann: eduPIC: an introductory particle based code for radio-frequency plasma simulation. *Plasma Sources Science and Technology* **30** 095017, 2021. *https://doi.org/10.1088/1361-6595/ac0b55*

5. M Vass, S Wilczek, A Derzsi, B Horváth, P Hartmann, Z Donkó: Evolution of the bulk electric field in capacitively coupled argon plasmas at intermediate pressures. *Plasma Sources Science and Technology* **31** 045017, 2022. *https://doi.org/10.1088/1361-6595/ac6361*

6. A Derzsi, P Hartmann, M Vass, B Horváth, M Gyulai, I Korolov, J Schulze, Z Donkó: Electron power absorption in capacitively coupled neon-oxygen plasmas: a comparison of experimental and computational results. *Plasma Sources Science and Technology* **31** 085009, 2022. *https://doi.org/10.1088/1361-6595/ac7b45*