FK – 128924

Control of ion properties in low-pressure radiofrequency gas discharges relevant for surface processing

Final report

The aim of this project has been the numerical and experimental study of low-temperature, low-pressure capacitively coupled radio-frequency (RF) discharges operated in various gases and gas mixtures in order to solve solve open issues related to discharge operation, control of the ionization dynamics and particle distributions functions at the electrodes by voltage waveform tailoring, and the influence of surface maerials and surface collisional processes on the discharge characteristics. The particle-based computational studies combined with experiments have revealed new details of the electron power absorption and ionization dynamics in capacitively coupled plasmas (CCPs), which aid the basic understanding of such systems and are also essential to the optimization of plasma-based materials processing applications.

The results of this project have been published in international per-reviewed journals and presented at international conferences. Below, the main achievements of the project are summarized.

We have performed Particle-in-Cell/Monte Carlo Collisions (PIC/MCC) simulations to investigate the effects of heavy-particle induced secondary electrons (SEs) on the ionization dynamics and on the control of ion properties at the electrodes in capacitively coupled discharges driven by tailored voltage waveforms. The driving voltage waveform was composed of a maximum of four consecutive harmonics of the fundamental frequency and was tailored by adjusting the identical phases of the even harmonics, θ. The simulations were carried out at low neutral gas pressures and high voltage amplitudes (discharge conditions relevant in plasma processing applications of surfaces), as well as in the collisional high-pressure regime. Different models were implemented in the simulations to describe the heavy-particle induced secondary electron emission (SEE) at the electrodes: (i) constant ion-induced SEE coefficients, γ, were used and (ii) realistic, energy-dependent SE yields for ions and fast neutrals. In the simulations with constant ion-induced SEE coefficients, values of γ between 0.0 and 0.4 were assumed (low γ-coefficients are typically used for metal electrodes, while high γ-coefficients are considered for dielectric surfaces, e.g. SiO2, Al2O3). At low pressures we obtained largely different dependencies of the ion flux at the electrodes on θ, depending on the value of the γ-coefficient. These effects were influenced by the surface conditions as well. We pointed out that adopting realistic, energy-dependent SE yields for heavy particles in the simulations can lead to significantly different results compared to those obtained by assuming constant SEE coefficients.[1]

Based on a PIC/MCC simulation code, in which all surface processes (heavy-particle induced SEE, electron-surface interactions, sputtering) were described realistically, we investigated the influence of voltage waveform tailoring on the surface processes in multi-frequency Ar discharges with Cu electrodes. We focused on the domain of low-pressures (<1 Pa), where at high voltages the plasma particles can reach the electrodes at high energies and can induce

[1] 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.

significant SEE, as well as sputtering of the surface material. The variation of the mean energy of heavy-particles (ions and fast neutrals) at the electrodes by adjusting the phase angle of the driving harmonics (θ) was found to influence the surface processes involving these particles. We have shown that by tuning θ, the flux of sputtered atoms can be controlled at both electrodes – such control is of key importance in plasma sputtering applications. It was found that the domain over which the sputtered atom flux can be controlled is enlarged by adding more harmonics to the driving voltage waveform. We demonstrated that electron induced SEs can play an important role in the ionization dynamics not only in case of dielectric surfaces, but also in case of surfaces characterized by low γ-coefficients (e.g. clean metal surfaces).[2]

We have investigated the charged particle dynamics under discharge conditions relevant for high aspect ratio dielectric plasma etching. In such applications dual-frequency capacitively coupled RF plasmas operated at low pressures of 1 Pa are used. Such plasma sources are often driven by a voltage waveform that includes a low-frequency component in the range of hundreds of kHz with a voltage amplitude of 10 kV to generate highly energetic vertical ion bombardment at the wafer. In such discharges, the energetic positive ions can overcome the repelling potential created by positive wall charges inside the etch features, which allows high aspect ratios to be reached. In order to increase the plasma density a high-frequency driving component at several 10 MHz is typically applied simultaneously. Under such discharge conditions, the boundary surfaces are bombarded by extremely energetic particles, of which the consequences are poorly understood. By including a realistic implementation of plasma-surface interactions in PIC/MCC simulations of argon discharges, the electron induced SEE (δ-electrons) was found to have a strong effect on the ionization dynamics and the plasma density. Due to the high ion energies at the electrodes, very high yields of the ion induced SEE (γ-electrons) were found. These γ- and δ-electrons, as well as electrons created in the plasma bulk and accelerated towards the electrodes to high energies by reversed electric fields during the local sheath collapse were found to induce the emission of a high number of δ-electrons, when they hit the boundary surfaces. Dual-frequency discharges with identical electrode materials were studied at different pressures and high-frequency driving voltages, as well as the effects of using electrodes made of different materials and characterized by different SEE coefficients. The electron dynamics and charged particle distribution functions at the boundary surfaces were determined including discharge asymmetries generated by using different materials at the powered and grounded electrodes.[3]

Phase Resolved Optical Emission Spectroscopy (PROES) is a powerful technique for the spatio-temporal observation of the optical emission of plasmas at specific wavelengths. With the appropriate choice of an emission line resulting from electron-impact excitation with a high threshold energy, one can gain insight into the dynamics of high-energy electrons. As ionization is also caused by high-energy electrons, PROES is often applied to reveal the discharge operation mode. We have performed PC/MCC simulations and PROES measurements in neon CCPs and provided a detailed comparison of simulated and experimental results in a wide parameter regime. We examined the applicability of PROES (which provides information about the spatio-temporal distribution of the electron-impact excitation dynamics) to probe the

---

[2] A. Derzsi, B. Horváth, Z. Donkó, J. Schulze: *Surface processes in low-pressure capacitive radio frequency discharges driven by tailored voltage waveforms*, Plasma Sources Sci. Technol. 29, 074001, 2020.

[3] P. Hartmann, L. Wang, K. Nösges, B. Berger, S. Wilczek, R. P. Brinkmann, T. Mussenbrock, Z. Juhasz, Z. Donkó, A. Derzsi, E. Lee, J Schulze: *Charged particle dynamics and distribution functions in low pressure dual-frequency capacitively coupled plasmas operated at low frequencies and high voltages*, Plasma Sources Sci. Technol. 29, 075014, 2020.

discharge operation mode (which is determined by the spatio-temporal distribution of the ionization dynamics). We found that the spatio-temporal excitation rates measured by PROES are in a good agreement with the excitation rates obtained from the PIC/MCC simulations for all discharge conditions studied. However, the ionization dynamics was found to be significantly different from the excitation dynamics under most of the discharge conditions studied, especially at high values of the driving frequency and low values of the pressure, when energetic heavy particle induced SEs (γ-electrons) are more likely to ionize than to excite. We pointed out that, while PROES measurements clearly provide very important information about the charged particle dynamics in the discharge, one should generally be careful with predicting the operation mode of the discharge based on this technique. The agreement between the experiments and simulations over a wide range of operation conditions confirmed that the discharge model developed for neon CCPs properly captures the main physical phenomena.[4,5]

Based on PIC/MCC simulations and PROES measurements, we have investigated the charged-particle power absorption dynamics in CCPs operated in CF4/Ar, driven by tailored voltage waveforms. The studies were performed at different pressures. It was found that the drift electric field in the plasma bulk is reduced substantially as the electronegativity of the discharge is decreased, both as a function of increasing argon content and decreasing pressure. This was identified as the main mechanism that induces a mode transition from the DA-mode to the α-mode. Based on these results, the physical origin of the generation of a DC self-bias as a function of the argon content in the case of 'peaks'- and 'valleys'-waveforms was revealed, which is valuable knowledge for plasma process optimization in multifrequency discharges in mixtures of electropositive and electronegative gases.[6]

We have studied the influence of applying a uniform magnetic field parallel to the electrodes on radio frequency capacitively coupled oxygen discharges driven at 13.56 MHz at a pressure of 100 mTorr by PIC/MCC simulations. We found that increasing the magnetic field from 0 to 200 Ga results in a drastic enhancement of the electron and the O_2+ ion density due to the enhanced confinement of electrons by the magnetic field. The time and space averaged O^- ion density was found to remain almost constant, since both the dissociative electron attachment (production channel of O^-) and the associative electron detachment rate due to the collisions of negative ions with oxygen metastables (main loss channel of O^-) are enhanced simultaneously. We performed a detailed analysis of the spatio-temporal electron dynamics in order to understand this effect. The nearly constant O^- density in conjunction with the increased electron density was found to cause a significant reduction of the electronegativity and a pronounced change of the electron power absorption dynamics as a function of the externally applied magnetic field. A local enhancement of the electron power absorption at high magnetic fields was revealed, caused by a strong electric field reversal generated near each electrode during the local sheath collapse. Based on a model of the electric field generation we demonstrated that the reversed electric field is the consequence of the reduction of the electron flux to the

[4] 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 Sci. Technol. 29, 105004, 2020.
[5] C-W Park, B. Horváth, A. Derzsi, J. Schulze, J. H. Kim, Z. Donkó, H-C Lee: *Experimental validation of particle-in-cell/Monte Carlo collisions simulations in low-pressure neon capacitively coupled plasmas*, submitted to Plasma Sources Science and Technol., 2023.
[6] S. Brandt, B. Berger, Z. Donkó, A. Derzsi, E. Schuengel, M. Koepke, J Schulze: *Control of charged particle dynamics in capacitively coupled plasmas driven by tailored voltage waveforms in mixtures of Ar and CF_4*, Plasma Sources Science and Technol. 28, 095021, 2019.

electrodes due to their trapping by the magnetic field. This work pointed out that the influence of the magnetic field on the plasma properties can significantly affect the applications of such discharges in etching, deposition and other semiconductor processing technologies.[7]

We have successfully implemented our one-dimensional electrostatic PIC/MCC simulation code used for the study of low-pressure capacitively coupled plasmas (CCPs) on GPU. We have introduced efficient, massively parallel GPU implementation approaches for speeding up the simulations and examined the performance and scalability of the developed algorithms. We used four standard plasma benchmark cases to verify the accuracy and correctness of the CUDA and OpenCL implementations and analysed their performance properties on a number of NVIDIA and AMD cards. Plasma parameters computed with both GPU implementations were found to differ not more than 2% from each other and respective literature reference data. Our final implementations showed speed up values from few 10x to 200x depending on the number of particles. We demonstrated that GPUs can be very efficiently used for simulating collisional plasmas and pointed out that their further use will enable performing more accurate simulations in shorter time, increase research productivity and help in advancing the field of PIC/MCC plasma simulations. We also highlighted that traditional porting of existing codes is not guaranteed to provide good performance; for the efficient use of GPUs, new programming approaches and new algorithms are required that take architectural characteristics into consideration and provide the level of parallelism needed for these massively parallel systems.[8]

We have performed a systematic multi-diagnostic experimental validation of one-dimensional PIC/MCC simulations for argon CCPs operated at 13.56 MHz, at pressures between 1 Pa and 100 Pa. The measurements were performed in a specifically designed, custom built geometrically symmetric reference reactor. The simulations included a careful treatment of various plasma-surface interactions. In the experiment, stainless steel electrodes were used and multiple diagnostics were applied to measure the driving voltage waveform at the powered electrode, the central plasma density, the ion flux-energy distribution function at the grounded electrode, the spatio-temporally resolved electron impact excitation dynamics, and the gas temperature as a function of the gas pressure and driving voltage amplitude. We found that the simulations can describe the experiments quantitatively correctly, if the correct gas temperature and appropriate surface coefficients are used in the simulations. From a systematic comparison of experimental and computational results the effective electron reflection probability at the electrodes was determined. If the gas temperature is known, surface coefficients for different electrode materials can be determined in this way by computationally assisted diagnostics. This work corresponds to one of the first successful systematic multi-diagnostic experimental validations of PIC/MCC simulations of CCPs. We demonstrated that PIC/MCC simulations can yield realistic results that are in quantitative agreement with experiments for a variety of plasma parameters and over a wide range of discharge conditions. This however, necessitates using realistic gas temperatures and surface coefficients in the simulation.[9]

---

[7] L. Wang, D. Q. Wen, P. Hartmann, Z. Donkó, A. Derzsi, X. W. Wang, Y. H. Song, Y. N. Wang, J. Schulze: *Electron power absorption dynamics in magnetized capacitively coupled radio frequency oxygen discharges*, Plasma Sources Sci. Technol. 29, 105004, 2020.
[8] Z. Juhasz, J. Durian, A. Derzsi, S. Matejcik, Z. Donkó, P. Hartmann: *Efficient GPU implementation of the Particle-in-Cell/Monte-Carlo collisions method for 1D simulation of low-pressure capacitively coupled plasmas*, Computer Phys. Commun. 263, 107913, 2021.
[9] D. A. Schulenberg, I. Korolov, Z. Donkó, A. Derzsi, J. Schulze: *Multi-diagnostic experimental validation of 1d3v PIC/MCC simulations of low pressure capacitive RF plasmas operated in argon*, Plasma Sources Sci. Technol. 30, 105003, 2021.

We have performed a detailed analysis of the surface processes and the complex dynamics of fast electrons in capacitively coupled plasmas excited by RF voltage waveforms at low pressures. Prominent features in a number of physical parameters were found inside the sheath regions. We have successfully associated these features with distinct mechanisms of energetic electron generation and the motion of these electrons in the spatiotemporally varying electric field as well as their reflection at boundary surfaces and sheaths. It was found that they primarily originate from energetic ion induced SEs, as these have a high enough energy to be able to penetrate deeply into the sheath region at the opposite electrode. It was inferred that the features do not correspond to trajectories, but are envelopes of the turning points of these electrons within the sheath region. Each feature was associated with particular groups of energetic electrons and their non-local dynamics in the plasma. This was revealed by a procedure where the electrode surface processes were turned on/off and all possible combinations have been scanned. This approach enabled a deeper understanding of the complex and non-local spatiotemporal dynamics of energetic electrons in technological plasmas.[10]

We have performed PIC/MCC simulations to study the effects of electron induced SEs in single-frequency (13.56 MHz) oxygen CCPs operated in the low-pressure regime (<1 Pa). Oxygen plasma sources operated at low pressures are often used for the etching of graphene and polycyclohexene carbonate, as well as highly oriented pyrolytic graphite and polydimethyl siloxane films, for resist stripping and multilayer lithography. Fundamental understanding of the plasma processes in such systems is required for further process optimization in current and next generation plasma processing. In our study, two different approaches were used to model the interaction of electrons with the electrode material: (i) a simple, "conventional" approach, which takes into account only elastic reflection of the electrons at the boundary surfaces with a constant probability, independently of the discharge conditions and the surface properties, and (ii) a complex, more realistic approach, which includes elastic and inelastic reflection of electrons, as well as electron induced SEE - emission of δ- electrons -, with surface coefficients that are functions of the energy and the angle of incidence of the electrons and depend on the surface properties. Simple and realistic approaches were considered also for the description of SEE induced by ions (emission of γ-electrons) at the electrodes: (i) in the simple approach, a constant SEE coefficient was used for O_2^+ ions, while (ii) in the more realistic approach, the SE yield due to O_2^+ ions was a function of the energy of the ions. The simulation results obtained based on the different models were compared to each other. A significant increase of the electron density and the formation of a complex electron emission and ionization dynamics driven by δ-electrons and γ-electrons together were observed as a consequence of including electron induced SEE in the discharge model. Besides that, specific effects of SEs were found in oxygen: the $O_2(a1\Delta g)$ metastable density increased parallel to the increase of the electron density, which caused the decrease of the electronegativity in two ways: directly, by the increase of the electron density and indirectly through the increased associative detachment rate, which is the primary loss channel of O^- ions. It was found that the SEE induced by both electrons and O_2^+ ions is a critical process at low pressures and high driving voltages in oxygen CCPs, which can seriously influence the discharge characteristics and control of particle properties at the electrodes.[11]

---

[10] M. Vass, A. Derzsi, J. Schulze, Z. Donkó: *Intrasheath electron dynamics in low pressure capacitively coupled plasmas*, Plasma Sources Sci. Technol. 30, 03LT04, 2021.
[11] 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 Sci. Technol. 31, 045025, 2022.

We have performed PROES measurements combined with PIC/MCC simulations to study the electron power absorption and excitation/ionization dynamics in neon-oxygen CCPs. We have covered a wide pressure range (15 Pa – 500 Pa) and a wide mixing range (the neon/oxygen concentration was changed between 10% and 90%) of the two gases for a geometrically symmetric plasma reactor operated at a driving frequency of 10 MHz. For all discharge conditions, the spatio-temporal distributions of the electron-impact excitation rate measured by PROES and obtained from PIC/MCC simulations resulted in good qualitative agreement, which supported the validity of our discharge model developed for neon–oxygen CCPs. Based on the emission/excitation patterns, multiple operation regimes were identified. Transitions between different discharge operation modes were found to be induced by changing the gas pressure and varying the neon/oxygen concentration ratio in the discharge. It was found that the localized bright emission features at the bulk boundaries at high pressures and high O_2 concentrations are caused by local maxima in the electronegativity. The relative contributions of the ambipolar and the Ohmic electron power absorption were found to vary strongly with the discharge parameters: the Ohmic power absorption was enhanced by both the high collisionality at high pressures and the high electronegativity at low pressures. The simulation revealed that the temperature of the electrodes increases significantly compared to the initial wall temperature with increasing the gas pressure. It was found that the power deposition within the gas causes only a slight increase of the gas temperature above the temperature of the electrodes, which was, however, found to be significant due to the heating of the electrodes by the particles from the plasma. This finding pointed out the importance of the thermal balance of the electrode construction in determining the electrode and gas temperatures under operating conditions at moderate electrical power levels.[12]

PROES measurements combined with PIC/MCC simulations have been performed also in argon-oxygen mixtures. In this case, the geometrically symmetric CCP reactor was operated in 70% Ar - 30% O_2 mixture, at fixed pressure (120 Pa) and peak-to-peak voltage (350 V), with a wide range of driving RF frequencies (2 MHz $\leq f \leq$ 15 MHz). The measured and calculated spatio-temporal distributions of the electron impact excitation rates from the Ar ground state to the Ar 2p1 state showed significant frequency dependence. Three frequency ranges could be defined with profoundly different characteristic excitation features: (i) in the low frequency range ($f \leq$ 3 MHz), the excitation is strong at the sheaths and weak in the bulk region; (ii) at intermediate frequencies (3.5 MHz $\leq f \leq$ 5 MHz), the excitation rate in the bulk region is enhanced and shows striation formation; (iii) above 6 MHz, the excitation in the bulk gradually decreases with increasing frequency. Based on Boltzmann term analysis, the mechanisms behind the excitation characteristics at different frequencies were analyzed. It was found that despite the significantly different excitation maps seen in the different frequency regimes, the dominant power absorption mechanisms are basically the same in the low and intermediate frequency ranges. The present results clearly showed that it is not straightforward to infer the power absorption mode transitions based on the excitation rate alone. It was found that the same electron power absorption mechanisms could be associated with excitation patterns of significantly different characteristics. [13]

---

[12] 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 Sci. Technol. 31, 085009, 2022.
[13] A. Derzsi, M. Vass, R. Masheyeva, B. Horváth, Z. Donkó, P. Hartmann: *Frequency-dependent electron power absorption mode transitions in capacitively coupled argon-oxygen plasmas*, submitted to Plasma Sources Science and Technol., 2023.

*

Due to the challenges faced during the Covid-19 pandemic, which significantly affected international collaborations and participation in scientific conferences, the PI requested a 9-month extension for the 4-year research project. The request for extension was approved.

The results of the work in this project have been summarized in 13 research articles (with 11 articles published and 2 articles recently submitted for publication) in leading scientific journals, with a total impact factor of 47.6 The PI has given 5 invited lectures at international conferences that resulted in a good visibility of the project at the international scene.

A student (B. Horváth) has been actively involved in the research activities of this project. In 2019, he prepared his MSc thesis based on experimental and simulation study of electron power absorption mode transitions in low-presurre capacitively coupled plasmas. For his PhD work, he focused on the role of surface processes and the control of particle propetries in low-pressure radio frequency gas discharges (his PhD thesis is scheduled to be submitted to the Doctoral School of Physics of Eötvös Loránd University in the fall of 2023). He has also presented the results at both national and international conferences.[14,15]

The support of NKFIH, which has been the basis of all the accomplishments described above, is highly appreciated.

Aranka Derzsi, PI

[14] B. Horváth: *Electron Power Absorption Mode Transitions in Capacitively Coupled Radiofrequency Plasmas*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, MSc thesis, 2019.

[15] B. Horváth: *Control of particle properties in low-pressure radio frequency gas discharges*, Eötvös Loránd Tudományegyetem, Fizika Doktori Iskola, PhD thesis to be submitted, 2023.