PD – 121033

Reactive gas discharges excited by tailored voltage waveforms

Final report

The aim of this project has been the numerical study of low-temperature, low-pressure capacitively coupled radio-frequency (RF) discharges operated in various gases and gas mixtures in order to uncover the connections between the discharge operating conditions and the charged particle dynamics and particle distribution functions, to reveal the possibilities and limitations of the efficient control of plasma parameters by voltage waveform tailoring, as well as the effect of surface processes on the discharge characteristics. Most of the studies in this project have been accomplished within an international collaboration network. The simulation studies planned in this project have been complemented by experimental studies in some cases.

The results of this project have been published in international per-reviewed journals and presented at international conferences. These results aid the basic understanding of low-pressure capacitively coupled RF discharges and are also relevant for applied research by providing a scientific basis for enhanced process control in plasma processing applications of surfaces. Below, the main achievements of the project are summarized.

By using our Particle-in-Cell/Monte-Carlo Collisions (PIC/MCC) simulation code, we have investigated the electron heating and ionization dynamics in capacitively coupled oxygen discharges driven by tailored voltage waveforms at different fundamental frequencies and at different pressures. We have studied the amplitude asymmetry effect as well as the slope asymmetry effect in such discharges by performing simulations for pulse-type and sawtooth-type voltage waveforms that consist of up to four consecutive harmonics of the fundamental frequency. We have found transitions of the discharge electron heating mode from the drift-ambipolar mode to the α-mode induced by changing the number of consecutive harmonics included in the driving voltage waveform or by changing the gas pressure. We have found that changing the number of harmonics in the waveform has a strong effect on the electronegativity of the discharge, on the generation of the DC self-bias and on the control of ion properties at the electrodes. We have investigated the effect of the surface quenching rate of oxygen singlet delta metastable molecules on the spatio-temporal excitation patterns. We have obtained good agreement between the spatio-temporal distributions of the excitation rates obtained from the simulations and those derived from phase resolved optical emission spectroscopy (PROES) measurements.[1]

We have developed a realistic model for the description of the electron-surface interaction in capacitively coupled plasmas and incorporated this model into our PIC/MCC simulation code. This realistic model considers the elastic reflection and the inelastic backscattering of electrons, as well as the emission of electron induced secondary electrons (SEs). The emission coefficients corresponding to these elementary processes are determined as a function of the electron energy and angle of incidence, taking the properties of the surface into account. By using this model,

[1] Derzsi A, Bruneau B, Gibson R, Johnson E, O'Connell D, Gans T, Booth J-P, Donkó Z: *Power coupling mode transitions induced by tailored voltage waveforms in capacitive oxygen discharges*, Plasma Sources Sci. Technol. 26, 034002 (2017)

we have studied the influence of the electron induced secondary electrons (δ-electrons) on the plasma density, the electron power absorption, and the ionization dynamics in argon gas at low pressures, for SiO_2 electrodes. Compared to the results obtained by using a simplified model for the electron-surface interaction, widely used in PIC/MCC simulations of capacitively coupled plasmas, which includes only elastic electron reflection at a constant probability, we have found strongly different electron power absorption and ionization dynamics, and complex dynamics of the secondary electrons, including multiple reflections between the boundary sheaths. We have demonstrated that the realistic description of the electron-surface interaction is essential at low pressures, especially at high voltage amplitudes, and the emission of electron induced secondary electrons has to be included in discharge models in order to obtain realistic results.[2, 3, 4]

We have performed systematic investigation of the influence of various surface processes - such as the SE emission induced by ions and electrons, electron reflection at the electrodes - on the discharge characteristics in low-pressure capacitively coupled RF discharges. By using the realistic model for the description of the electron-surface interaction presented above, we have studied the effect of the electron-induced SEs on the discharge characteristics in the 0.5 Pa–3 Pa pressure range, for voltage amplitudes between 100 V–1500 V, assuming different SE yields for ions (γ–coefficient). Such discharge conditions are typical in industrial applications, such as plasma etching, sputtering and plasma immersion ion implantation. We have found that both the gas pressure and the value of the γ-coefficient affect the role of electron induced SEs in shaping the discharge characteristics at different voltage amplitudes. Their effect on the ionization dynamics has been found to be most striking at low pressures, high voltage amplitudes and high values of the γ-coefficient. We have pointed out that the realistic description of the electron-surface interaction significantly alters the computed plasma parameters, compared to results obtained based on a simple model for the description of the electron-surface interaction, widely used in PIC/MCC simulations of low-pressure capacitively coupled plasmas.[5]

We have proposed an ab-initio model based on Hagstrum's theory on Auger emission for the calculation of the ion induced SE emission coefficients (γ) at metal surfaces with a wide range of surface conditions and for a variety of ion species. We have performed PIC/MCC simulations of 13.56 MHz, single-frequency argon and helium capacitive discharges by assuming γ to be a constant 0.1, or by implementing the functional forms for "clean" and "dirty" metals that is dependent on the ion energy but independent on the specific metal type. We have compared the outcome of these simulations to the simulation results obtained by utilizing different γ coefficients for calcium, gold, molybdenum, copper and platinum based on Hagstrum's model. We have observed that, depending on the assumed surface conditions, the plasma properties change dramatically. We have pointed out that a realistic, material dependent implementation

[2] Horváth B, Daksha M, Korolov I, Derzsi A, Schulze J: *The role of electron induced secondary electron emission from SiO2 surfaces in capacitively coupled radio frequency plasmas operated at low pressures*, Plasma Sources Sci. Technol. 26, 124001 (2017)
[3] Horváth B: *Rádiófrekvenciás gerjesztésű gázkisülések numerikus szimulációja*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, Fizika BSc, 2017 - BSc dissertation
[4] Horváth B: *Az elektron-elektróda kölcsönhatás szerepe alacsony nyomású rádiófrekvenciás gázkisülésekben*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, Fizikus Tudományos Diákköri Konferencia (TDK), 2017 - TDK dissertation
[5] Horváth B, Schulze J, Donkó Z, Derzsi A: *The effect of electron induced secondary electrons on the characteristics of low-pressure capacitively coupled radio frequency plasmas*, J. Phys. D: Appl. Phys. 51, 355204 (2018)

of the ion induced SE yield is required to obtain realistic simulation results and that the proposed model suits this purpose.[6]

We have investigated the energy and angular distributions of ions reaching the electrodes in low-pressure, capacitively coupled oxygen radio-frequency discharges by PIC/MCC simulations. These distributions, as well as the possibility of the independent control of the ion flux and the ion energy at the electrodes have been analysed for different types of excitation: single- and classical dual-frequency (DF), as well as valley- and sawtooth-type waveforms. Besides numerical simulations, we have applied analytical models as well to understand the features of the energy and angular distribution functions. We have studied oxygen discharges characterized by weakly collisional to highly collisional domains of ion transport via the electrode sheaths. The effects of the ion induced SEs on the discharge characteristics and control of ion properties under such discharge conditions have been also explored. In the case of the classical DF excitation, the application of the low-frequency voltage component was found to increase the width of the electrode sheaths significantly, thereby increasing their collisionality. In the case of the valley-type waveforms, the enhancement of the mean ion energy was found to occur without this effect, and as a result a more confined beam of ions (in terms of angular spread) was found to reach the electrode surfaces. Hence, applying valley-type waveforms allows for control of the ion energy without strongly affecting the narrow ion angular distribution function. In the case of sawtooth-type waveforms, a weak effect of the waveform shape on the angular distributions was found. We have demonstrated that using complex waveforms, especially the classical DF waveform is advantageous whenever a smooth ion flux-energy distribution function is preferred in the applications.[7]

We have investigated the effects of changing the electrode gap on important plasma characteristics such as the central electron density, electronegativity, mean electron energy, and ion flux-energy distribution functions in low-pressure single-frequency capacitively coupled oxygen plasmas operated at 13.56 MHz. We have also studied the time averaged optical emission from atomic oxygen lines and the spatio-temporal ionization dynamics. These investigations have been performed based on a synergistic combination of experiments and PIC/MCC simulations. The simulations allowed us to obtain a fundamental understanding of the changes of the plasma characteristics as a function of the electrode gap. In particular, a decrease of the mean electron energy and the electronegativity were observed, indicating a change from a plasma with electronegative character at short gaps to a plasma with electropositive character at long gaps. The numerical results indicated a complex trend of the O_2^+ ion flux to the electrodes as a function of the gap length. We have explained these findings by mode transitions of the electron power absorption dynamics from the Drift-Ambipolar mode at low gap distance to the α-mode at larger electrode gaps. Comparison of the simulation results to measured discharge characteristics also served as an experimental benchmark of our simulation code for oxygen discharges.[8]

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[6] Dakhsa M, Derzsi A, Donkó Z, Schulze J: *Material dependent modeling of secondary electron emission coefficients and its effects on PIC/MCC simulation results of capacitive RF plasmas*, Plasma Sources Sci. Technol. 28, 034002 (2019)
[7] Donkó Z, Derzsi A, Vass M, Schulze J, Schuengel E, Hamaguchi S: *Ion energy and angular distributions in low-pressure capacitive oxygen RF discharges driven by tailored voltage waveforms*, Plasma Sources Sci. Technol. 27, 104008 (2018)
[8] You K H, Schulze J, Derzsi A, Donkó Z, Yeom H J, Kim J H, Seong D J, Lee H C: *Experimental and computational investigations of the effect of the electrode gap on capacitively coupled radio frequency oxygen discharges*, Physics of Plasmas 26, 013503 (2019)

We have performed PIC/MCC simulations to investigate the effects of heavy-particle induced 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 4 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 SE emission at the electrodes: (i) constant ion-induced SE emission coefficients, γ, were used and (ii) realistic, energy-dependent SE yields for ions and fast neutrals. In the simulations with constant ion-induced SE emission 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. SiO_2, Al_2O_3). 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. For γ=0.2, the ion flux was found to remain nearly constant as a function of θ, independently of the choice of the number of harmonics, i.e., the mean ion energy can be controlled separately from the ion flux by adjusting θ. However, for values of γ different from 0.2, the quality of the separate control of the ion properties was found to change significantly. These effects were influenced by the surface conditions as well. We have 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 SE emission coefficients.[9]

We have implemented simulation models for Ar/CF_4, Ar/O_2, CF_4/O_2 RF discharges into our PIC/MCC simulation code and developed the related diagnostic modules of the code for the processes taking place in gas mixture plasmas. We have performed a rigorous test of our models based on the comparison of the simulation results with experimental benchmark data. The studies of the electron power absorption modes have indicated that our present models perform reasonably well.[10] Based on PIC/MCC simulations and PROES measurements, we have investigated the charged-particle power absorption dynamics in CCPs operated in CF_4/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. These findings are expected to be highly valuable for knowledge-based plasma process optimization in multifrequency discharges containing mixtures of electropositive and electronegative gases.[11] Systematic investigations of $Ar/CF_4/O_2$ gas mixture discharges with focus on the control of particle properties at the electrodes are currently in progress.

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[9] Derzsi A, Horváth B, Korolov I, Donkó Z, Schulze J: *Heavy-particle induced secondary electrons in capacitive radio frequency discharges driven by tailored voltage waveforms*, Journal of Applied Physics, 126, 043303 (2019)

[10] Donkó Z, Derzsi A, Korolov I, Hartmann P, Brandt S, Schulze J, Berger B, Koepke M, Bruneau B, Johnson E, Lafleur T, Booth J-P, Gibson A, O'Connell D, Gans T: *Experimental benchmark of kinetic simulations of capacitively coupled plasmas in molecular gases*, Plasma Phys. Control. Fusion 60, 014010 (2018)

[11] Brandt S, Berger B, Donkó Z, Derzsi A, Schuengel E, Koepke M and Schulze J: *Control of charged particle dynamics in capacitively coupled plasmas driven by tailored voltage waveforms in mixtures of Ar and CF4*, Plasma Sources Sci. Technol. 28, 095021 (2019)

We have developed a realistic model for the description of the sputtering of the surface material in low-pressure capacitively coupled plasmas, implemented this model into our PIC/MCC simulation code, and used this model in combination with other realistic models previously developed for the description of the interaction of plasma particles with the boundary surfaces (heavy-particle induced SE emission, electron-surface interactions). By using this code (in which all surface processes are described realistically), we have investigated the influence of voltage waveform tailoring on the surface processes in multi-frequency Ar discharges with Cu electrodes. We have focused on the domain of low-pressures, where at high voltages the plasma particles can reach the electrodes at high energies and can induce 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.[12]

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During the 3 years period of the project, besides the research planned originally new interesting questions came up and efforts have been made to extend the investigations into these directions. For instance, we have investigated the limitations of the PROES measurements to probe the discharge operation mode. 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 capacitively coupled plasmas and provided a detailed comparison of simulated and experimental results in a wide parameter regime. Neon is widely used for the spectroscopy of RF discharges operated in different gases and gas mixtures by adding neon as a trace gas to the background gas in a low concentration. Both in simulations and experiments, a transition of the discharge operation mode was found by increasing the voltage amplitude at a fixed frequency and pressure, as well as by increasing the pressure at a fixed frequency and voltage amplitude. However, the simulations and the experiments resulted in different voltage amplitudes/pressures at which the transition happens. This work revealed the applicability of PROES (which provides the spatio-temporal distribution of the excitation dynamics of the Ne 2p1 state) to probe the discharge operation mode (which is determined by the spatio-temporal distribution of the ionization dynamics) under various discharge conditions.[13,14]

A student (B Horváth) has been involved in the research activities in this project. He prepared his BSc (2017) and MSc (2019) thesis related to the realistic description of the electron-surface interactions in PIC/MCC simulations and the investigation of the applicability of PROES to probe the discharge operation mode, and presented the results at national and international

[12] Derzsi A, Schulze J: *Surface processes in capacitive radio frequency discharges driven by tailored voltage waveforms*, 72nd Annual Gaseous Electronics Conference (GEC2019), October 28–November 1, 2019, College Station, Texas

[13] Horváth B: *Electron Power Absorption Mode Transitions in Capacitively Coupled Radiofrequency Plasmas*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, Fizika MSc, 2019 - MSc dissertation

[14] Horváth B, Derzsi A, Schulze J, Hartmann P, Korolov I, Donkó Z: *Experimental confirmation of transitions in the discharge operation mode in low-pressure capacitively coupled Ne plasmas*, 72nd Annual Gaseous Electronics Conference (GEC2019), October 28–November 1, 2019, College Station, Texas

conferences. He received a poster prize at the Symposium on the Application of Plasma Processes (SAPP) 2019 Conference, second prize at the ELTE TDK Conference and Morgan Stanley Award (2017), and third prize in the National TDK (OTDK) Conference (2019).

During the 3 years period of the project the PI has been on unpaid leave for 3 months, during which she was involved in research on topics different from those of the present project.

The results of the work in this project have been published in 9 research articles in leading scientific journals, with a total impact factor of 30.4. The PI have given 4 invited lectures at international conferences that resulted in a good visibility of the project at the international scene.

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

Aranka Derzsi, PI