On electron heating in a low pressure capacitively coupled oxygen discharge

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We use the one-dimensional object-oriented particle-in-cell Monte Carlo collision code ooppd1 to explore the charged particle densities, the electronegativity, the electron energy probability function (EEPf), and the electron heating mechanism in a single frequency capacitively coupled oxygen discharge when the applied voltage amplitude is varied. We explore discharges operated at 10 mTorr, where electron heating within the plasma bulk (the electronegative core) dominates, and at 50 mTorr where sheath heating dominates. At 10 mTorr the discharge is operated in combined drift-ambipolar (DA) and α-mode and at 50 mTorr it is operated in pure α-mode. At 10 mTorr the effective electron temperature is high and increases with increased driving voltage amplitude, while at 50 mTorr the effective electron temperature is much lower, in particular within the electronegative core, where it is roughly 0.2 – 0.3 eV, and varies only a little with the voltage amplitude.

I. INTRODUCTION

Low temperature low pressure radio frequency (rf) driven capacitively coupled plasma (CCP) discharges have been used for several decades for etching and deposition of thin films. The CCP consist of two parallel electrodes, typically of radius of a few tens of cm, separated by a few cm, and biased by a radio-frequency power supply, often operated at 13.56 MHz. In the CCP a plasma forms between the electrodes, from which it is separated by space charge sheaths. Nearly all the applied voltage appears across the oscillating sheaths. In a single-frequency CCP the ion flux ($\propto$ plasma density) and ion energy ($\propto$ sheath voltage) cannot be varied independently. The plasma parameters such as the electron density, the ion densities, the effective electron temperature, and the electron energy distribution depend on the operating condition of the discharge including the gas composition, gas pressure, applied voltage, reactor geometry and the electrode material. These operating parameters dictate the mechanisms by which power is transferred to the electrons for sustaining the discharge. When operated at low neutral gas pressure collisionless heating mechanism effectively transfers energy to the electrons. This is due to a rapid movement of the electrode sheaths that contributes to the electron heating via stochastic or collisionless heating by the expanding sheaths [1, 2]. As the electrons interact with the moving sheaths, they can be either cooled (collapsing sheath) or heated (expanding sheath). When an energetic electron bounces back and forth between the two sheaths and hits each sheath during its expansion phase, it will be heated multiple times. This effect is referred to as electron bounce resonance heating (BRH) [3]. The sheath motion and thus the stochastic heating can also be enhanced by self-excited non-linear plasma series resonance (PSR) oscillations [4-8]. At higher pressures some of the power is deposited by ohmic heating in the bulk plasma due to collisional momentum transfer between the oscillating electrons and the neutrals. For this mechanism to be dominant the electron mean free path must be smaller than or comparable to the discharge dimensions. When a discharge is sustained through collisional ohmic heating and/or stochastic heating it is commonly referred to as the α-mode [3]. At high applied voltages and pressures secondary electron emission can contribute or even dominate the ionization processes. This operation regime is referred to as γ-mode [3]. In electronegative discharges large electron density gradients with local maxima of the electron density at the sheath edges, can develop within the rf period and lead to generation of ambipolar fields, also drift fields can arise due to the low bulk plasma conductivity. These fields can accelerate the electrons and are thus referred to as drift-ambipolar (DA) mode [10, 11].

Oxygen discharges are widely used in plasma materials processing including oxidation of silicon [12, 13], ashing of photoresist [14, 15], and surface modification of polymer films [16]. The properties of the oxygen discharge depend heavily on the accumulation of the singlet metastable oxygen molecules, which are known to play a significant role in the oxygen discharge [17, 18]. Earlier we have demonstrated that these singlet metastable molecular states influence the electron kinetics and the electron heating mechanism in the capacitively coupled oxygen discharge operated at a single frequency of 13.56 MHz [14, 22] as well as the ion energy distribution in both single and dual frequency discharges [22]. We found that at low pressure (10 mTorr), electron heating in the bulk plasma (the electronegative core) dominates, while at higher pressures (50 – 500 mTorr) the electron heating occurs mainly in the sheath region. We demonstrated that the detachment by the singlet molecular metastable states is the process that has the most influence on the electron heating process in the higher pressure regime (50 mTorr), while it has only a small influence at lower...
The one-dimensional object-oriented particle-in-cell Monte Carlo collision (PIC/MCC) code oopd1 \cite{24,25} is here applied to study the capacitively coupled oxygen discharge. In 1d-3v PIC codes the model system has one spatial dimension and three velocity components. Earlier we discussed the capability of the oopd1 code, the advantages and improvements compared to the well-established xpd1 code, and benchmarked it against the xpd1 code for a capacitively coupled discharge with a simplified oxygen discharge model \cite{26}. The xpd1 code included only reaction set for oxygen molecules in the ground state $O_2(X^{3}Σ_g^−)$, $O_2^+$-ions, $O^-$-ions and electrons and the neutral particles were not treated kinetically \cite{27}. Particle weight is the number of real particles each superparticle represents, i.e. the ratio of the number of physical particles to computational particles. In oopd1 the various particles can have different weights. As the neutral gas density is much higher than the densities of charged species, different weights allow us to treat both charged particles and neutral particles kinetically. In our earlier work we added oxygen atoms in the ground state $O(^3P)$ and ions of the oxygen atom $O^+$ and the relevant reactions to the oopd1 discharge model \cite{26}. In subsequent studies we added the singlet metastable molecule $O_2(a^1Δ_g)$ and the metastable oxygen atom $O(^1D)$ \cite{19}, and the singlet metastable molecule $O_2(b^1Σ_g^+)$ \cite{21}, to the reaction set. Furthermore, the discharge model now includes energy dependent secondary electron emission coefficients for oxygen ions and neutrals as they bombard the electrodes \cite{21}. For this current work the discharge model contains nine species: electrons, the ground state neutrals $O(^3P)$ and $O_2(X^{3}Σ_g^−)$, the negative ion $O^-$, the positive ions $O^+$ and $O_2^+$, and the metastables $O(^1D)$, $O_2(a^1Δ_g)$ and $O_2(b^1Σ_g^+)$ . The full oxygen reaction set and the cross sections used have been discussed in our earlier works and will not be repeated here \cite{14,21,26,20}.

We assume a capacitively coupled discharge where one of the electrodes is driven by an rf voltage

$$V(t) = V_0 \sin(2\pi ft)$$

while the other is grounded. Here $V_0$ is the voltage amplitude, $f$ the driving frequency and, $t$ is the time. For this study we allow the applied voltage amplitude $V_0$ to vary from 100 to 500 V while the electrode separation is kept fixed at 4.5 cm, the driving frequency is 13.56 MHz, and a capacitor of 1 F is connected in series with the voltage source. We assume discharges operated at pressures of 10 and 50 mTorr and assume geometrically symmetric electrodes. The discharge electrode separation is assumed to be small compared to electrode diameter so that the discharge can be treated as one dimensional. The time step $Δt$ and the grid spacing $Δx$ resolve the electron plasma frequency and the electron Debye length of the low-energy electrons, respectively, according to $ω_{pe}Δt < 0.2$ where $ω_{pe}$ is the electron plasma frequency, and the simulation grid is uniform and consists of 1000 cells. The electron time step is $3.68 \times 10^{-11} \text{ s}$. The simulation was run for $5.5 \times 10^6$ time steps or 2750 rf cycles. It takes roughly 1700 rf cycles to reach equilibrium for all particles and the time averaged plasma parameters shown, such as the densities, the electron heating rate, and the effective electron temperature, are averages over 1000 rf cycles. All particle interactions are treated by the Monte Carlo method with a null-collision scheme \cite{28}. For the heavy particles we use a sub-cycling and the heavy particles are advanced every 16 electron time steps and we assume that the initial density profiles are parabolic \cite{29}.

The kinetics of the charged particles (electrons, $O_2^+$, $O^+$ and $O^-$-ions) was followed for all energies. The neutral gas density is much higher than the densities of charged species, so that the neutral species at thermal energies (below a certain cut-off energy) are treated as a background with fixed density and temperature and maintained uniformly in space. These neutral background species are assumed to have a Maxwellian velocity distribution at the gas temperature (here $T_n = 26$ meV). We used a volume averaged (global) model \cite{32} to determine the partial pressure for each of the thermal neutral species at 50 mTorr only and use these values at 10 mTorr as well. These calculations give atomic oxygen partial pressure of 0.519 % which corresponds to atomic oxygen density of $8.3 \times 10^{18} \text{ m}^{-3}$ at 50 mTorr and $1.6 \times 10^{18} \text{ m}^{-3}$ at 10 mTorr. These are somewhat higher than the values of $0.5 - 3.2 \times 10^{18} \text{ m}^{-3}$, increasing with increased applied power up to 200 W, reported by Kitajima et al. \cite{33} at 50 mTorr. At 75 mTorr Katsch et al. \cite{34} find the atomic density to be $5 \times 10^{18} \text{ m}^{-3}$ using TALIF, which is lower than $1.4 \times 10^{19} \text{ m}^{-3}$ if based on oxygen partial pressure of 0.519 %. Also Kechkar
et al. measured the atomic oxygen density, by TALIF and actinometry in a slightly asymmetric capacitively coupled discharge at 100 mTorr and 100 W, to be $1.4 \times 10^{20}$ m$^{-3}$, which is higher than $1.9 \times 10^{19}$ m$^{-3}$ if based on oxygen partial pressure of 0.519%. Thus this atomic oxygen partial pressure can both be over and under estimate. However, it is clear that at these densities the role of atomic oxygen in these discharges is not very significant. All the neutral species are treated kinetically as particles if their energy exceeds a preset threshold value. The threshold values used here for the various neutral species are listed in Table I. As a neutral species hits the electrode it returns as a thermal particle with a given probability and atoms can recombine to form a thermal molecule with the given probability. Table I lists all the wall recombination and quenching coefficients used for the neutral species here. The wall recombination coefficient for the neutral atoms in ground state O($^3P$) is assumed to be 0.5 as measured by Booth and Sadeghi for a pure oxygen discharge in a stainless steel reactor at 2 mTorr. The choice of the wall recombination coefficient for atomic oxygen has a significant influence on the atomic oxygen density and the type of electrode material may explain the discrepancy in the experimental results discussed above. As the metastable atom O($^1D$) hits the electrode we assume half of the atoms are quenched forming O($^3P$) and the other half recombines to form the ground state molecule O$_2$(X$^3\Sigma_g^-$). For O$_2$(a$^1\Delta_g$) we use a quenching probability of 0.007 estimated by Sharpless and Slanger for iron while for aluminium they estimate the quenching probability to be $< 10^{-3}$ [30]. A value of 0.006 is suggested by Derzsi et al. [37], found by comparing PIC/MCC simulation with experimental findings which in their system (aluminium electrodes and L = 2.5 cm) leads to $[O_2(a^1\Delta_g)]/[O_2(X^3\Sigma_g^-)]$ density ratio that is on the order of 0.1. They point out that there are significant changes in the electronegativity as this parameter is varied. Using a 1D fluid model Greb et al. demonstrated that the electronegativity depends strongly on the O$_2$(a$^1\Delta_g$) surface quenching probability. They argue that increased quenching coefficient leads to decreased O$_2$(a$^1\Delta_g$) density and thus decreased detachment by the O$_2$(a$^1\Delta_g$) state and thus higher negative ion density. We assume that the quenching coefficient for O$_2$(b$^1\Sigma_g^+$) at the electrodes to be 0.1. This assumption is based on the suggestion that the quenching coefficient for the b$^1\Sigma_g^+$ state is about two orders of magnitude larger than for the a$^1\Delta_g$ state [30]. We neglect the reflection of electrons from the electrodes. The electrodes are assumed to be identical, made of stainless steel, and the surface coefficients are kept the same at both electrodes.

### III. RESULTS AND DISCUSSION

Figure 1 shows the spatio-temporal behavior of the electron heating rate $J\cdot E$, where $J$ and $E$ are the spatially and temporally varying electron current density and electric field, respectively, for a discharge operated at 10 mTorr and 50 mTorr for voltage amplitude $V_0 = 300$ V. For each of the figures the abscissa covers the whole inter-electrode gap, from the powered electrode on the left hand side to the grounded electrode on the right hand side. Similarly the ordinate covers the full rf cycle. Note that the color scale differs in magnitude between the two figures. Figure 1(a) shows the spatio-temporal behavior of the electron heating rate when operating at 10 mTorr and Figure 1(b) shows the heating when operating at 50 mTorr. For both pressures the electron heating is most significant during the sheath expansion phase at each electrode (the red areas). We also note that cooling in the sheath region during the sheath collapse is always apparent (note the different scale). At 10 mTorr a significant energy gain (red and yellow areas) and small energy loss (dark blue areas) are also evident in the plasma bulk region as seen in Figure 1(a). The electron heating appears during the sheath collapse on the bulk side of the sheath edge while there is cooling...
(electrons lose energy) on the electrode side (the lower left hand corner and upper center on the right hand side). At 50 mTorr the electron heating rate in the sheath region has increased and there is almost no electron heating in the plasma bulk as seen in Figure 1(b). We note that there are high frequency oscillations in the electron heating rate at both pressures adjacent to the expanding sheath edge similar to those reported by Vender and Boswell [10]. These are due the generation of an energetic electron beam during sheath expansion that in turn can trigger a beam-plasma instability at the electron plasma frequency. Remains of excess negative charges from the sheath collapse leads to a build up of an electric field that is large enough to accelerate bulk electrons toward the powered electrode. As the rf sheath expands again, the electrons are accelerated back into the bulk plasma with high kinetic energy. This leads to an electron-electron two-stream instability between the bulk electrons and the electrons accelerated by the moving sheath that is the cause of the oscillations [14]. These oscillations were first predicted computationally [10, 12] but have been more recently been confirmed experimentally using phase resolved optical emission spectroscopy (PROES) [41, 42]. The origins of the electric fields and the kinetics of multiple electron beams and the interactions of cold and hot electrons have been explored further more recently by Wilczek et al. [8]. Figure 2 shows the time averaged electron heating rate profile \( \langle \mathbf{J}_e \cdot \mathbf{E} \rangle \) at 10 and 50 mTorr. We see in Figure 2(a) that when the discharge is operated at 10 mTorr electron heating in the electronegative core dominates. This is in agreement with our earlier findings that at low pressures electron heating within the electronegative core dominates and the presence of the metastable molecules has only a minor influence on the heating mechanism [20, 22]. We see in Figure 2(a) that the time averaged heating rate in the electronegative core increases with increased voltage amplitude. There is both electron heating and electron cooling apparent in the sheath regions. At \( V_0 = 100 \) V the cooling cancels out the heating in the sheath region. With an increase in the voltage amplitude we see that the time averaged heating rate as well as the cooling rate in the sheath region increases. When the discharge is operated at 50 mTorr the time averaged electron heating rate in the electronegative core is roughly zero, and the time averaged electron heating is almost entirely located in the sheath regions. We also see that the time averaged electron heating rate in the sheath region increases with increased voltage amplitude. We have earlier demonstrated how adding the singlet metastable molecules to the reaction set drives the electron heating in the electronegative core to zero such that all the electron heating occurs only in the sheath regions at operating pressures of 50 mTorr and higher [13, 20, 22]. We see that the sheath width increases with increased voltage amplitude at both 10 and 50 mTorr. The different heating mechanisms at 10 and 50 mTorr results in different shape of the electron energy distribution. This can be seen in Figure 3 that shows the electron energy probability function (EEPF) for discharges operated at 10 and 50 mTorr. We see that when the discharge is operated at 10 mTorr the EEPF is concave as seen in Figure 3(a) while at 50 mTorr it is convex or bi-Maxwellian, characterized by the two distinct low and high energy electron groups. It is well known that when sheath heating or stochastic heating dominates in the capacitively coupled discharges the electron energy distribution can be described as a bi-Maxwellian. We see that at both 10 and 50 mTorr increasing the voltage amplitude increases the number of higher energy electrons. In all cases we also note a high energy tail, high energy electrons that are due to the secondary electron emission. These secondary electrons are emitted from the electrodes and are accelerated within the sheath and cause ionization as they travel through the plasma. The spatio-temporal behavior of the effective electron temperature \( T_{\text{eff}} = (2/3) \langle \mathbf{E} \rangle \) where \( \langle \mathbf{E} \rangle \) is the average electron energy) is shown in Figure 4 for voltage amplitude of \( V_0 = 300 \) V. It shows the effective electron temperature as a function of position between the electrodes within one rf period. At 10 mTorr seen in Figure 4(a) we see that the effective electron temperature is high within the plasma bulk (the electronegative core) throughout the rf period. Furthermore, we see that the effective electron temperature peaks within the plasma bulk during the sheath collapse phase. At 50 mTorr, seen in Figure 4(b)
FIG. 2: The time averaged electron heating profile for various voltage amplitudes for a parallel plate capacitively coupled oxygen discharge with a gap separation of 4.5 cm driven at 13.56 MHz operated at (a) 10 mTorr, and (b) 50 mTorr.

(b), we see a peak in the effective electron temperature within the plasma bulk in the sheath expansion phase. At 50 mTorr the effective electron temperature is low within the plasma bulk throughout the rf period. The profiles of the time averaged effective electron temperature are shown in Figure 5. The time averaged effective electron temperature changes significantly when the pressure is varied as seen by comparing Figure 5 (a) for 10 mTorr and Figure 5 (b) for 50 mTorr. When the discharge is operated at 10 mTorr the electron temperature is high and increases with increased voltage amplitude as seen in Figure 4 (a). For $V_0 = 100$ V the effective electron temperature in the discharge center is $T_{\text{eff}} = 4.1 \text{ eV}$ and for $V_0 = 500$ V it is $T_{\text{eff}} = 5.9 \text{ eV}$. When operated at 50 mTorr the electron temperature is low, highest in the sheath region and drops to roughly 0.2 – 0.3 eV within the electronegative core. In the sheath region the effective electron temperature increases with increased voltage amplitude from roughly 1.5 eV when $V_0 = 100$ V to roughly 2.5 V when $V_0 = 500$ V. These results are consistent with the Langmuir probe measurements of the effective electron temperature reported by Kechkar et al. in a slightly geometrically asymmetric capacitively coupled oxygen discharge with electrodes made of aluminum alloy [36, 44], where the driven electrode was 205 mm in diameter and the grounded electrode was 295 mm in diameter with electrode separation of 45 mm. In the discharge center at 10 mTorr and 200 W ($V_0 = 338$ V) they find $T_{\text{eff}} = 4.5 \text{ eV}$ and in the pressure range 50 – 100 mTorr, $T_{\text{eff}} \approx 0.7 \text{ eV}$ ($V_0 = 290$ V at 50 mTorr) [36, 44, 45].

We would expect collisionless (stochastic) heating at low pressures when the electron-neutral mean free path $\lambda_{\text{en}}$, is comparable or greater than the gap between the electrodes $L$ or the width of the plasma bulk $L_{\text{bulk}}$ or $\lambda_{\text{en}} > L_{\text{bulk}}$. At high pressures the electron-neutral mean free path $\lambda_{\text{en}}$ is small so that electrons collide more frequently with the neutral background gas or $\lambda_{\text{en}} < L_{\text{bulk}}$. The electron-neutral mean free path is $\lambda_{\text{en}} \approx 50$ mm at 10 mTorr for effective electron temperature in the range 4 – 6 eV. These electrons have a mean free path that is
FIG. 4: The spatio-temporal behavior of the effective electron temperature for a parallel plate capacitively coupled oxygen discharge with a gap separation of 4.5 cm driven at 13.56 MHz with $V_0 = 300$ V operated at (a) 10 mTorr, and (b) 50 mTorr.

much larger than the width of the plasma bulk $L_{\text{bulk}} \approx 20$ mm. At 50 mTorr $\lambda_{en} \approx 12$ mm for effective electron temperature of 0.5 eV and $\lambda_{en} \approx 9$ mm for effective electron temperature of 2 eV. Thus electron neutral collisions are rare in these discharges. For the secondary electrons $\lambda_{en} \approx 217$ mm at 10 mTorr and $\lambda_{en} \approx 43$ mm at 50 mTorr if we assume acceleration up to 100 eV, and these values increase with increased acceleration voltage. At both 10 and 50 mTorr these high energy electrons have a mean free path that is larger than the width of the plasma bulk. Thus we would not expect the secondary electrons to have much influence at 10 and 50 mTorr and to be mostly lost to the electrodes without collisions with the neutral molecules. These calculations are based on the momentum transfer cross section given by Itikawa [46]. Electron-neutral collisions are thus not a very efficient heating mechanism at these pressures so something more has to come to play, in order to explain the observed electron heating within the plasma bulk at 10 mTorr.

Figure 6 shows the axial electric field at $t/\tau_f = 0.5$ for both 10 and 50 mTorr. At 10 mTorr (Figure 6 (a)) we see that there is a significant electric field strength within the electronegative core. The electric field strength and its gradient increase with increased voltage amplitude. This strong electric field within the plasma bulk (the electronegative core) indicates a drift-ambipolar heating mode [10]. This electric field is a combination of a drift field and an ambipolar field. The ambipolar field is due to local maxima of the electron density at the sheath edge and a steep electron density gradient and yields the local maxima in the electric field observed at the sheath edges [10]. The drift electric field is due to low bulk conductivity, as we see later the electron density in the electronegative core is indeed very low. This high electric field accelerates the electrons to high average energies and thus causes ionizations within the plasma bulk. Thus when the discharge is operated at 10 mTorr the electron heating consists of stochastic heating in the sheath region and DA-heating within the electronegative core. We saw in Figure 1 (a) that the electron heating maxima occurs within the plasma bulk and close to the collapsing sheath edge. The DA-mode is characterized by a high ionization rate and high electron energy within the plasma bulk. Thus we can say that at 10 mTorr the discharge is operated in a combined DA- and $\alpha$-mode. The DA-heating mode has been observed in electronegative discharges,
including a dual frequency oxygen discharge \[47\], single frequency silane discharge \[48\] and \(\text{CF}_4\) discharge \[10,49\], but also in dusty plasmas including single frequency argon discharge \[50\] and hydrogen diluted silane discharge \[51\]. Furthermore, ohmic heating (drift) mode (\(\Omega\) mode) has been observed in an atmospheric-pressure diffuse dielectric barrier discharge in helium \[52\]. It is referred to as the DA mode when there is a simultaneous presence of both this ohmic heating (\(\Omega\) mode) and the heating due to the ambipolar field in electronegative discharges. When the discharge is operated at 50 mTorr (seen in Figure 6 (b)) the electric field is zero within the electronegative core. We saw in Figure 1 (b) that electron heating is almost solely in the sheat regions at 50 mTorr. Hence, at 50 mTorr the discharge is operated in a pure \(\alpha\)-mode. The transition from combined DA-\(\alpha\)-mode to pure \(\alpha\)-mode coincides with a significant decrease in the electronegativity as discussed below. Transitions between the DA- and the \(\alpha\)-mode have been demonstrated by both simulations and experiments on \(\text{CF}_4\) discharges \[11\] \[49\]. By increasing the pressure at a fixed voltage, a transition from the \(\alpha\)-mode to the DA-mode is induced. Note that the \(\text{CF}_4\) discharge is weakly electronegative at 75 mTorr while it is strongly electronegative at 600 mTorr \[11\]. Also by increasing the voltage at a fixed pressure, a transition from the DA-mode to the \(\alpha\)-mode is observed in a \(\text{CF}_4\) discharge \[10\]. Here we show the opposite, that by increasing the pressure at a given voltage a transition from the DA-\(\alpha\)-mode to the \(\alpha\)-mode is observed in the oxygen discharge. This is a similar transition as reported by Derzsi et al. \[53\] which observe an operation mode transition from DA-\(\alpha\)-mode to \(\alpha\)-mode in an oxygen discharge as harmonics are added to the voltage waveforms for 10 and 15 MHz driving frequency, which also coincides with a strong decrease in the electronegativity. Earlier we have demonstrated a transition from the DA-\(\alpha\)-mode to pure \(\alpha\)-mode, for a discharge operated at 50 mTorr, when the singlet metastables were added to the reaction set \[22\].

The center density of the dominating charged particles is shown in Figure 7. When operating at 10 mTorr the \(\text{O}_2^+\)-ion density and the \(\text{O}^-\)-ion density are similar and the electron density is significantly smaller as seen in Figure 7 (a). The electron density \(n_e\) is only \(0.6 \times 10^{14}\) m\(^{-3}\) at \(V_0 = 100\) V and increases to \(1.3 \times 10^{14}\) m\(^{-3}\) at \(V_0 = 500\) V. Thus the conductivity \(\sigma_{dc} \propto n_e\) is low in the plasma bulk. When operating at 50 mTorr the \(\text{O}_2^+\) ion density and the electron density are similar and the \(\text{O}^-\)-ion density is significantly smaller as seen in Figure 7 (b). At 50 mTorr the electron density is much higher than at 10 mTorr and increases from \(0.5 \times 10^{16}\) m\(^{-3}\) at \(V_0 = 100\) V and \(1.6 \times 10^{16}\) m\(^{-3}\) at \(V_0 = 500\) V. For comparison Kechkar et al. \[32\] \[44\] \[45\] measured the electron density in a slightly asymmetric capacitively coupled oxygen discharge to be \(6.5 \times 10^{14}\) at 30 W (\(V_0 = 90\) V) and \(2.7 \times 10^{15}\) at 200 W (\(V_0 = 338\) V) when operated at 10 mTorr, and \(1.6 \times 10^{15}\) at 30 W (\(V_0 = 85\) V) and \(3 \times 10^{16}\) at 200 W (\(V_0 = 290\) V) when operated at 50 mTorr. As seen by comparing Figures 7 (a) and (b) the negative ion density is higher at 10 mTorr than at 50 mTorr. At 10 mTorr and 100 V the \(\text{O}^-\)-ion density is \(3.6 \times 10^{15}\) m\(^{-3}\) at 100 V and increases to \(5.5 \times 10^{15}\) m\(^{-3}\) at 500 V. At 50 mTorr the \(\text{O}^-\)-ion density is \(2.7 \times 10^{14}\) m\(^{-3}\) at 100 V and increases to \(9.2 \times 10^{14}\) m\(^{-3}\) at 500 V. So as the pressure is increased the electron density increases and the negative ion density decreases so that the electronegativity decreases significantly. We know from global (volume averaged) model studies of the oxygen discharge that at low pressure (\(<10\) mTorr) the destruction of negative ions is dominated by electron impact detachment while at higher pressure detachment by oxygen atoms and singlet metastable oxygen molecules and charge exchange with the ground state molecule take over and their role increases with increased discharge pressure and the negative ion density decreases as the discharge pressure is increased \[54\]. At 10 mTorr the negative \(\text{O}^-\)-ions are effectively created by the dissociative attachment processes as the effective electron temperature is high, and the detachment by electrons is dominating. At 50 mTorr due to the low effective electron temperature dissociative attachment is not very effective in creating the neg-

![Figure 6](image_url)
ative $O^-$-ions while they are effectively eliminated by the detachment processes which are roughly independent of the electron temperature. The center electronegativity $\alpha_0 = n_{-0}/n_{e0}$, where $n_{-0}$ is the center negative ion density and $n_{e0}$ is the center electron density, is shown versus the voltage amplitude in Figure 8. The electronegativity is significantly higher when operating at 10 mTorr than when operating at 50 mTorr. We see that the electronegativity at 10 mTorr decreases with increased voltage amplitude from 58 for $V_0 = 100$ V to 40 for $V_0 = 500$ V. At 50 mTorr the electronegativity is 0.05 for $V_0 = 100$ V, 0.08 for $V_0 = 300$ V, and 0.06 for $V_0 = 500$ V. Figure 8 also shows the average electronegativity

$$\alpha_{ave} = \frac{\int_0^L n_-(x)dx}{\int_0^L n_e(x)dx}$$

versus the voltage amplitude, where $n_-$ is the $O^-$-ion density, $n_e$ is the electron density and $L$ is the electrode separation. We see that the average electronegativity is somewhat lower than the center electronegativity at 10 mTorr while at 50 mTorr the two are very similar. Experimentally, Katsch et al. [55] estimated the electronegativity in the discharge center of a capacitively coupled oxygen discharge to be roughly 2 at 103 mTorr and 150 V and to fall below unity as the applied voltage was increased to 280 V. Also, Berezhnoj et al. [56] determined the electronegativity in a capacitively coupled oxygen discharge to be roughly 10 in the pressure range 22.5 – 225 mTorr.

IV. CONCLUSION

The one-dimensional object-oriented particle-in-cell Monte Carlo collision code oopdi was applied to explore the evolution of the electron heating mechanism, the EEFP, and the effective electron temperature, in a capacitively coupled oxygen discharge with the applied voltage. We compare operation at 10 mTorr and 50 mTorr. We demonstrate that there is a significant difference, the electron heating mechanism is different, which leads to very different electron energy probability function and then very different time averaged electron temperature profile for the two different operating pressures. There is a significant electron heating in the electronegative core and high effective electron temperature that increases with increased applied voltage when operating at 10 mTorr. At 50 mTorr the effective electron temperature is very low (roughly 0.2 – 0.3 eV) in the electronegative core at all voltages. Furthermore, there is significant difference in electronegativity. We observe a strong electric field within the plasma bulk when operating at 10 mTorr while the electric field is zero within the plasma bulk when operating at 50 mTorr. At 10 mTorr the discharge is operated in combined drift-ambipolar and $\alpha$-mode and at 50 mTorr it is operated in a pure $\alpha$-mode.
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