A MONTE CARLO COLLISION MODEL TO STUDY RF DISCHARGES WITH A MIXTURE OF ARGON AND OXYGEN

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Prof. Marisa Roberto was a Visiting Scholar from Brazil with the Plasma Theory and Simulation Group in the EECS Department from late February 1999 until late May 2000. She most graciously volunteered to develop two additions to the Monte Carlo Collision (MCC) part of our PIC-MCC many-particle plasma codes. We are very grateful for these additions, which will be widely useful and are already incorporated into our plasma device codes.

Prof. Charles K. (Ned) Birdsall, for the Plasma Theory and Simulation Group.

A MONTE CARLO COLLISION MODEL TO S- TUDY RF DISCHARGES WITH A MIXTURE OF ARGON AND OXYGEN

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Abstract

A planar one-dimensional particle-in-cell simulation with Monte Carlo Collisions (XPDP1) has been used to study a 13.56 MHz argon/oxygen discharge using a mixture of 1 Torr for argon and 0.05 Torr for oxygen. Reactions such as metastable quenching by O_2, charge transfer between Ar^+ and O_2 and Penning ionization are taken into account. It was found that quenching of argon metastables by molecular oxygen and charge transfer between Ar^+ and O_2 are important in determining the metastable and ion profiles for this gas mixture. A comparison with pure argon plasma and pure oxygen plasma was also made. The effect of applied voltage is also verified.

1. Introduction

Discharges containing O_2 are typically used for industrial materials processing and most processing plasmas are produced using either capacitively or inductively coupled rf discharges. Global models have been used to study O_2/Ar mixtures in inductively rf discharges which results were compared with experimental data (1,2,3). This kind of mixture is also used in sputtering in a DC magnetron discharges (4,5). Argon metastable densities in rf Ar and Ar/O_2 electrical cylindrical discharges were studied using a two-dimensional computer simulation in order to verify the pressure effect over density in the axial direction between electrodes. When O_2 is added the metastable density decreases due to quenching of metastable argon by O and O_2 (6).

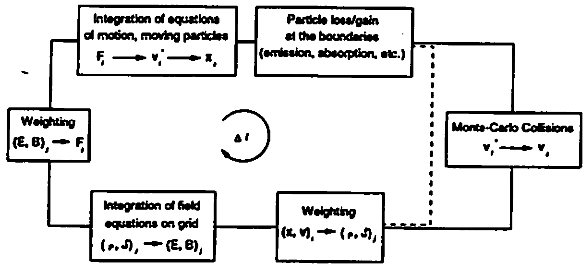

Figure 1: The flow chart for an explicit PIC scheme with the addition of the Monte Carlo condition package, called PIC-MCC.

In this work, the planar one-dimensional particle in cell simulation with Monte Carlo Collision model(7) is used to study a 13.56 MHz rf argon/oxygen discharge. MCC-PIC particle scheme is shown in Figure 1. The effect of applied voltage is studied in the mixture. Reaction such as quenching by O_2, charge transfer, dissociative charge transfer and Penning ionization are taken into account. Results from the mixture are compared with simulations of pure oxygen and argon discharges.

2. Collision Types

The reactions considered in the mixture model are:

(1) $e + O_2 \longrightarrow e + O_2$ (momentum transfer)

(2) $e + O_2 \longrightarrow e + O_2(r)$ (rotational excitation)

(3)-(6) $e + O_2 \longrightarrow e + O_2(v=n, n=1,4)$ (vibrational excitation)

(7) $e + O_2 \longrightarrow e + O_2\ (a^1\ \Delta_g)$ (metastable excitation - 0.98 eV)

(8) $e + O_2 \longrightarrow e + O_2(b^1\ \Sigma_g^+)$ (metastable excitation - 1.63 eV)

(9) $e + O_2 \longrightarrow O + O^-$ (dissociative attachment-4.2 eV)

(10) $e + O_2 \longrightarrow e + O_2\ (c^1\ \Sigma_u^-, A^3\ \Sigma_u^+)$ (metastable excitation - 4.5 eV)

(11) $e + O_2 \longrightarrow e + O(3P) + O(3P)$ (dissociation - 6.0 eV)

(12) $e + O_2 \longrightarrow e + O(3P) + O(1D)$ (dissociation - 8.4 eV)

(13) $e + O_2 \longrightarrow e + O(1D) + O(1D)$ (dissociation - 10.0 eV)

(14) $e + O_2 \longrightarrow e + O_2^+ + e$ (ionization - 12.06 eV)

(15) e + $O_2 \longrightarrow$ e + O + $O^*(3p^3P)$ (dissociative excitation- 14.7 eV)

(16) e + $O_2^+ \longrightarrow$ O + O (dissociative recombination)

(17) e + $O^- \longrightarrow$ e + O + e (electron impact detachment)

(18) O^- + $O_2{}^+ \longrightarrow$ O + O_2 (mutual neutralization)

(19) O^- + $O_2 \longrightarrow$ O + O_2 + e (detachment)

(20) O^- + $O_2 \longrightarrow O^-$ + O_2 (scattering)

(21) O_2^+ + $O_2 \longrightarrow O_2$ + O_2^+ (charge exchange)

(22) O + $O_2 \longrightarrow$ O + O_2 (scattering)

plus reactions with mixtures -

(23) Ar^m + $O_2 \longrightarrow$ Ar + O$*$ + O (quenching)

(24) Ar^+ + $O_2 \longrightarrow O_2^+$ + Ar (charge transfer)

(25) Ar^+ + $O_2 \longrightarrow O^+$ + O + Ar (dissociative charge transfer E = 10 eV)

(26) Ar^* + $O_2 \longrightarrow$ Ar + O_2^+ + e (Penning Ionization E=15 eV)

plus reactions with argon

(27) e + Ar $\longrightarrow$ e + Ar (elastic scattering)

(28) e + Ar $\longrightarrow$ e + Ar^* (excitation E=11.83eV)

(29) e + Ar $\longrightarrow$ e + Ar^m (metastable excitation E=11.55 eV)

(30) e + Ar $\longrightarrow$ 2e + Ar^+ (ionization E = 15.76 eV)

(31) e + $Ar^m \longrightarrow$ 2e + Ar^+ (ionization of metastable E=4.21 eV)

(32) Ar^m + $Ar^m \longrightarrow Ar^+$ + Ar + e (metastable pooling)

(33) Ar^m + e $\longrightarrow Ar^r$ + e (quenching to resonant)

(34) Ar^+ + Ar $\longrightarrow$ Ar + Ar^+ (charge exchange)

(35) Ar^+ + Ar $\longrightarrow Ar^+$ + Ar (elastic scattering)

Particle in Cell simulations for modeling rf capacitve discharges with O_2 have been made by Vahedi and Surendra[8]. The first 22 reactions were considered in Vahedi's model.

In this work reactions (23-26) between argon and oxygen plus reactions between the charged species and argon neutrals were also taken into account (27-35). The cross section for quenching by O_2 (reaction 23) is in ref. (9), charge transfer and dissociative charge transfer (reactions 24 and 25) are in ref. (10) and Penning ionization (reaction 26) is in ref. (11). For collisions with argon, cross sections for reactions (27), (28), (30), (34) and (35) are in ref. (8) and reactions (29) and (31) are in refs. (12) and

(13). For reactions (32) is in ref. (14) and for reaction (33) is in ref. (15).

It is assumed that the argon and oxygen densities (the neutral species) remain constant and uniform in space. Therefore the neutral particles are not followed as particles. All the other species are followed as particle species. The electrons in this model collide with five species (O_2, O_2^+, O^-, Ar, Ar^m), three of which are modelled as particles. The algoritm for determining collisions between charged and neutral species used the same method discussed by Vahedi and Surendra[8]. For collisions with metastable excited argon and ion argon with O_2 was followed the same procedure used in reactions with O_2 and O_2^+, given that both species have approximately the same temperature. The density of target particle O_2 is constant which makes collisions with Ar^m and Ar^+.

This model does not include ionization of atomic oxygen and this assumption is justified in conventional capacitive rf discharge, where the electrons density is relatively low ($n_e \simeq 10^{-9} cm^{-3}$). Consequently, this model is adequate only for modeling weakly dissociated oxygen discharges where O_2^+ is the dominant positive species and O_2 is dominant neutral species in the pure oxygen discharge. The inclusion of argon and the resultant reactions between Ar^m and Ar^+ and O_2 completely changes the behaviour of the discharge as will be showed next.

3. Results and Discussion

The simulations modelled a rf capacitive discharge with external circuit elements R=L=0, C=1 F, electrode spacing L=5 cm, electrode area A=0.2 cm, initial densities for electrons, O_2^+, O^-, Ar^+ and Ar^m of $3x10^{15}m^{-3}$, $3x10^{15}m^{-3}$, $7x10^{15}m^{-3}$, $7x10^{15}m^{-3}$ and $1.0x10^{14}m^{-3}$, respectively. Discharge properties are compared for V = 500 V and V = 200 V, using p = 0.05 Torr for oxygen and p = 1 Torr for argon. The simulation was run for 300 rf cycles, until to reach the equilibrium for electrons and ions, which corresponds to time around 3 x 10 $^{-5}$ s.

Figure 2 shows O_2^+, O^-, electron, Ar^+ and Ar^m densities for V = 200 V and Fig. 3 shows these densities for V = 500 V. The average electron energy is KE = 1.00 eV for V = 200 V and KE = 0.45 eV for V = 500 V. It can be seen as voltage increases the electron density increases and O^- density decreases. Electrons are lost by dissociative attachment and dissociative recombination reactions and they are

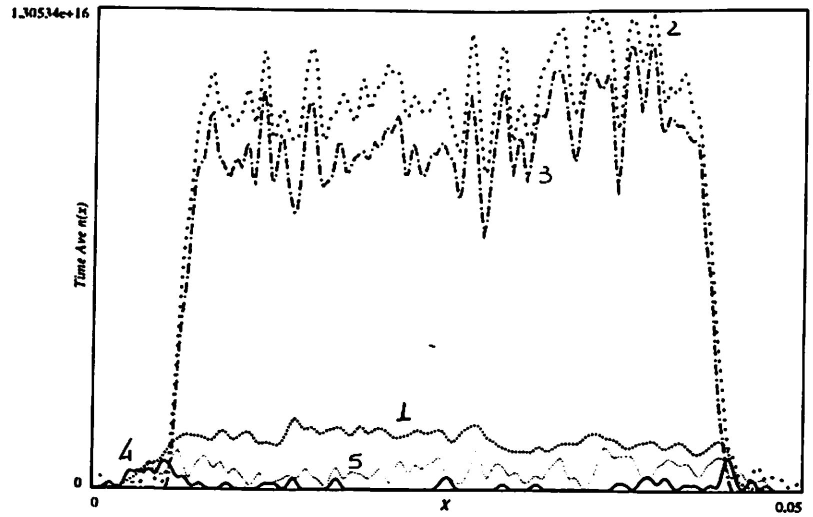

Figure 2: Electron (1), O_2^+ (2), O^- (3), Ar^+ (4) and Ar^m (5) densities for V=200 V, p = 1 Torr for argon and 0.05 Torr for oxygen.

created by ionization reactions, electron impact detachment and detachment. The ion O^- is created through dissociative attachmnent reaction and is lost by electron impact detachment, mutual neutralization and detachment. For V = 200 V, the relation between gain and loss of O^- is $\approx$ 1.0, considering peak values for these reactions. However, for V = 500 V, more O^- is lost by detachment and mutual neutral reactions than is gained, i.e., gain/loss $\approx$ 0.80. For this reason one have more electrons produced by detachment at V = 500 V than for V = 200 V.

Ionization rate from ground state profiles for argon and oxygen have a peak near the plasma sheath interface, as shown in Figs. 4 and 5, for V = 200 V, while reactions such as dissociative attachment, electron impact detachment and detachment occurs in almost whole discharge volume. This means that although the ratio of Ar ionization is higher than other reactions for electrons production, electrons are lost in whole volume due to dissociative attachment reaction in the higher ratio than are created. However, for V = 500 V, electrons production in reaction such as detachment is higher than electrons lost by dissociative attachment. As voltage increases, average electron energy decreases. Dissociative attachment needs 4.2 eV to occur and for V = 500 V one has less energetic electrons than for V = 200 V.

Figure 6 shows Ar^+ and Ar^m densities profiles for V = 500 V. Argon ions are created by ionization from ground-state and from metastable and are lost mainly by charge transfer with O_2. For metastable species one has gain/loss $\approx$ 1.0. They are

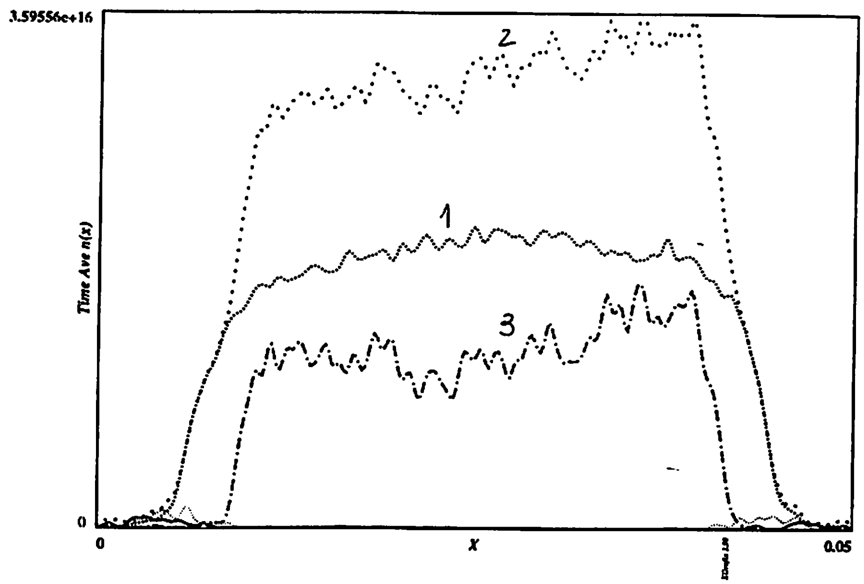

Figure 3: Electron (1), O_2^+ (2), O^- (3), Ar^+ (4) and Ar^m (5) densities for V=500 V, p = 1 Torr for argon and 0.05 Torr for oxygen.

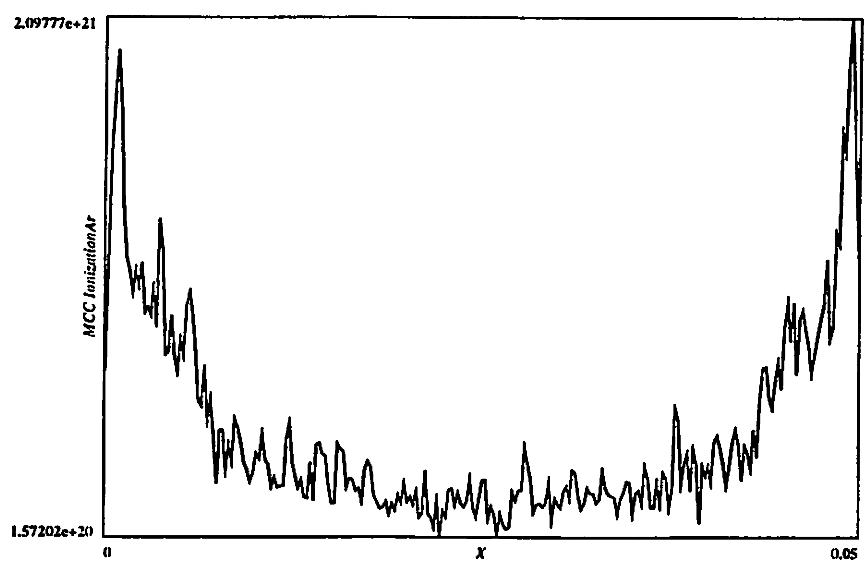

Figure 4: Ionization profile for argon ionization from ground state for V = 200 V (reaction 30).

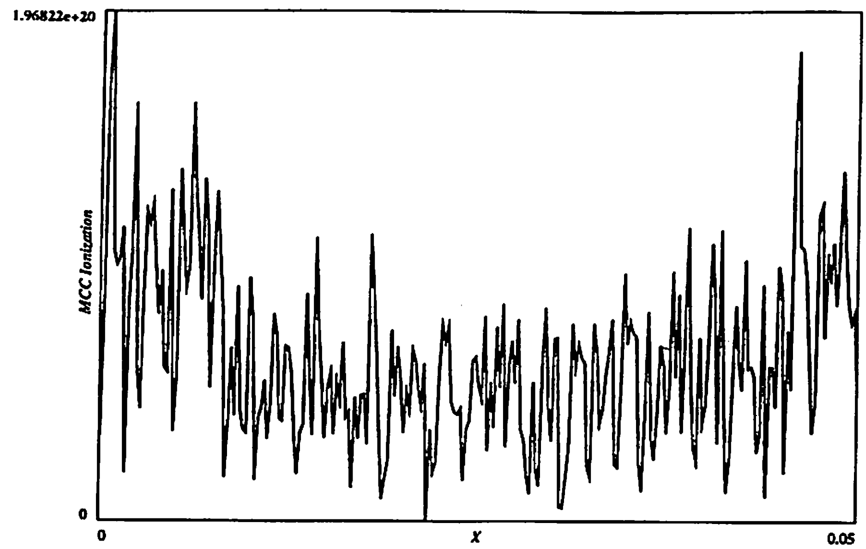

Figure 5: Oxygen rate profile for O_2 ionization from ground state for V = 200 V. (reaction 14)

lost mainly by quenching by O_2.

Fig. 7 shows electrons, O_2^+ and O^- densities for a discharge with O_2 for p = 0.05 Torr and V = 500 V. The initial conditions are n_e=0.3x$10^{16} m^{-3}$, $n_{O_2^+} = 1.0x10^{16} m^{-3}$ and n_{O^-}=0.7x$10^{16} m^{-3}$. In this case, average electron energy is 4.5 eV and reactions such as dissociative attachment occurs more easily and it is the main bulk negative ion creation and bulk electrons loss mechanisms. Electron impact detachment, mutual neutralization and detachment are responsabile by loss of O^-.

Fig. 8 shows a pure argon plasma, for p = 1 Torr and V = 500 V. In this case the metastable density is larger than for the mixture and has a peak near the plasma/sheath interface due to high production of energetic electrons there. The average electron energy is 0.57 eV, in this case. A small quantity of O_2 modifies completely the metastable and ion argon profiles which depends on the reactions (23) and (24). This indicates quenching Ar^m by O_2 and charge transfer between Ar^+ and O_2, have a very high reaction rates.

Fig. 9 shows electron energy distribution function (eedf) for oxygen only, for p = 0.05 Torr, for argon only, for p= 1 Torr and for a mixture with 1 Torr for argon and 0.05 Torr for oxygen with V = 500 V. For all cases the eedf are non-Maxwellian. This is typical of eedfs in molecular gases, and has also been seen in Boltzmann simulations and is due to relatively large cross sections of low energy inelastic collisions, such as

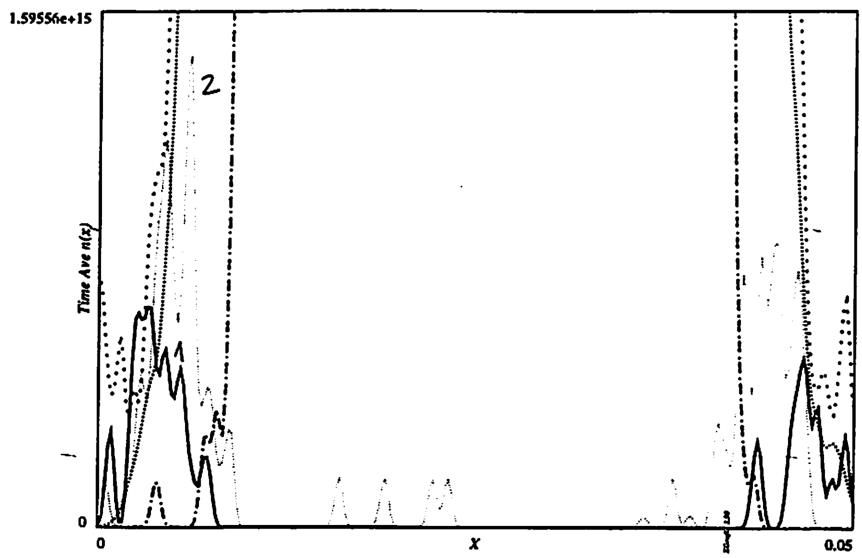

Figure 6: Ar^+ (1) and Ar^m (2) densities for V = 500 V.

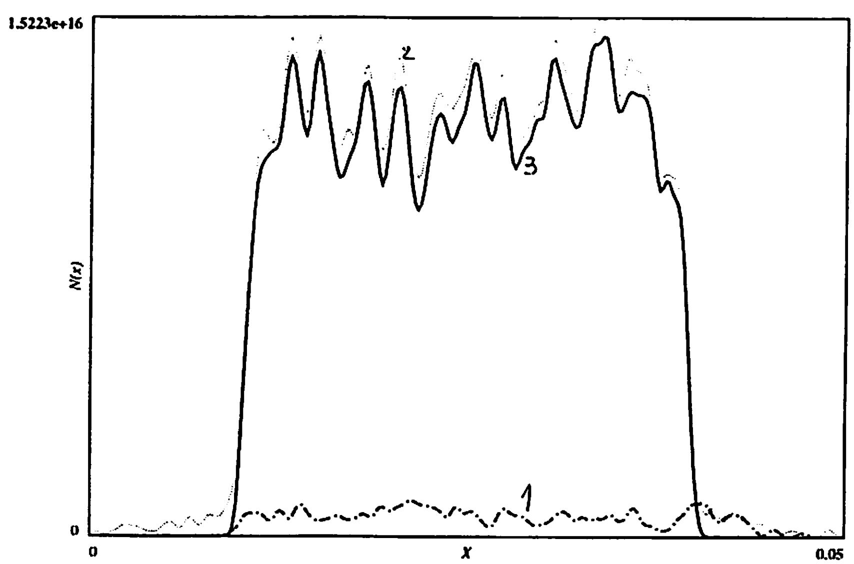

Figure 7: Electron (1), O_2^+ (2) and O^- (3) densities considering oxygen only, for p=0.05 Torr and V=500 V.

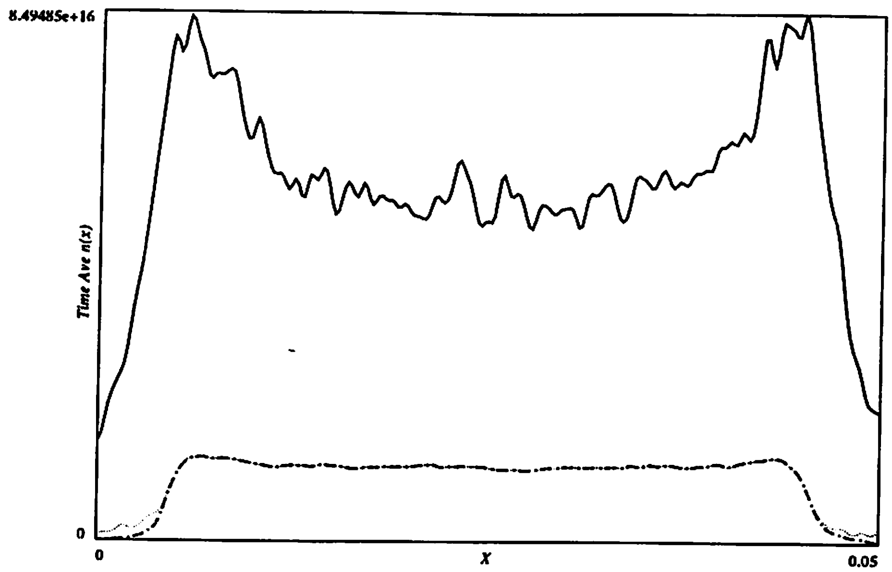

Figure 8: Electron, ion and metastable and ion argon densities for p=1 Torr and V = 500 V in a pure argon plasma. Metastable density has a peak near plasma/sheath interface.

vibrational excitation[8]. A small quantity of oxygen (0.05 Torr) changes the eedf if is compared to eedf in a pure argon plasma.

4. Conclusion

One-dimensional planar simulation with PIC/MCC model has been used to study rf discharge with argon and oxygen. It was found that a small quantity of oxygen, 0.05 Torr in this case, completely changes the argon metastable profile and argon ion profile, due to quenching of Ar^m and Ar^+ by O_2 in quenching (reaction 23) and charge transfer (reaction 24).

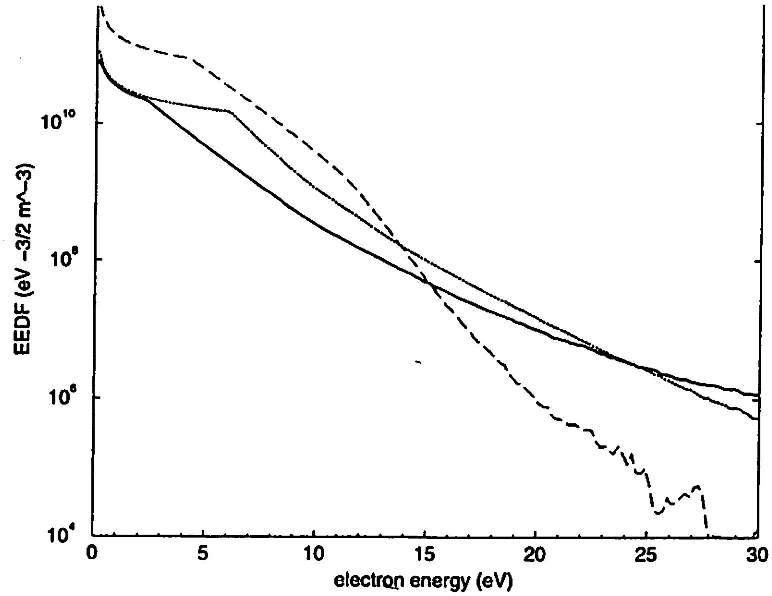

Figure 9: Electron Energy Distribution Function for V = 500 V in a pure 1 Torr argon plasma (dashed line), a pure oxygen 0.05 Torr oxygen plasma (solid line) and for a mixture 1 Torr argon and 0.05 Torr oxygen (dotted line). The knees were not identified.

5. Acknowledgments

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