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Transport Coefficients For Electrons in Mixtures $CF_4/Ar/O_2$ and CF, CF_2 or CF_3 Radicals

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Transport coefficients for electrons in mixtures of CF_4 with Ar and O_2 for ratios of the electric field to the gas number density E/N from 1 Td to 1000 Td (1Td = 10^{-21} V m^2) are presented. The analysis of non-conservative collisions revealed a range of the reduced electric field $E/N$where electron attachment introduced by radicals significantly changes electron kinetics obtained for mixtures without dissociation of CF_4 gas. The results obtained by using a simple, Two Term solutions for Boltzmann's equation are verified by Monte Carlo simulations. It was found that three body attachments for oxygen is not significant for pressures that are standard in plasma etching equipment i.e. below 1 Torr. Furthermore, the attachment to CF, CF_2 and CF_3 at low mean energies is significant, several orders of magnitude. At the same time the mean energy and energy distribution functions for the given E/N are the same as in unperturbed gas mixture. The large changes of the attachment rate are sufficient to change the nature of plasmas and turn them into ion-ion plasmas with very few electrons for realistic abundances.

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1. Introduction

In addition to semiconductor industry, carbon tetrafluoride is widely used in other technological applications such as development of gaseous circuit breakers [1] and for development of particle detectors [2–4]. CF_4 belongs to freons that unfortunately significantly affect the global warming of our planet. Its atmospheric halftime has been estimated to over 50 000 years and it has a large potential to global warming. Because of all these arguments it is important to continue research related to the kinetics of CF_4 in order to improve plasma etching applications and facilitate removal of this gas from the atmosphere by applying gas discharges (e.g. by focused microwave radiation [5, 6]). Pure CF_4 plasmas are rarely used in material processing and instead are diluted with Ar and O_2 to control the production of fluorocarbons and provide selectivity in etching. Oxygen plasmas are widely used in material processing such as photo resist aching, surface modification, chemical vapor deposition and oxidation. In oxygen plasma, the density of atomic oxygen and its distribution are significant since the processing speed and the process uniformity in a wafer depend on the flux distribution of atomic oxygen onto a wafer. Kitajima *et al.* [7] showed that the density of metastable atomic oxygen O (^{1}D) increases in highly Ar diluted oxygen plasma in CCP.

2. Monte Carlo code and Two Term approximation

Electron kinetics in pure CF_4 is well described by the set of cross sections of Kurihara *et al.* [8] which represents our starting point. The need to establish reliable transport coefficients for CF_4 plasmas is especially demanding for conditions that include many reactive species.

Free radical species, such as CF_y (y=1-3) and fluorine atoms, play important but complex roles in plasma processing. We calculated electron transport coefficients for a binary mixture of 80% Ar, 10% CF_4 and 10% O_2. In order to determine the role of radicals, we added 1% of radical X species (X = F, F_2, CF, CF_2 and CF_3) replacing the equivalent amount of CF_4. Calculations were made for conditions overlapping with those found in plasma technologies for semiconductor device manufacturing. Sets of cross sections for CF, CF_2 and CF_3 are based on the work of Rozum *et al.* [9]. The set of cross sections for F_2 is from [10] and for F is from Gudsmundsson [11]. The cross sections for Ar are from Hayashi [12] and for O_2 from Phelps [13].

We calculated attachment and ionization rate coefficients for 1% of the radical species X in Ar/CF_4. Transport coefficients are obtained by using a Two Term approximation (TTA) to the electron Boltzmann equation [14] and by a Monte Carlo simulations [15, 16] (MCS). The TTA technique is very frequently used in plasma modeling in spite of its limited accuracy [17]. The TTA results are sufficiently good for most modeling purposes. We however use two term approximation to provide extrapolation to very low E/N where it is sufficiently accurate while MC results become very difficult to obtain. It is also used to give a general guidance to plasma modelers which effects may be expected and to determine rates of some specific collisional channels that have exceedingly small cross sections. Finally presenting the TTA data gives a guidance of how much the approximate theory differs from the exact results.

The basic cross sections of pure CF_4 from [8] were used, with a modification made in [18, 19] in order to include production of CF_3^- ions.

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3. Results and discussion

The electron mean energy and the electron drift velocity in mixtures Ar/CF_4/O_2 as a function of E/N(E-electric field, N-gas density) are shown in Fig. 1. Based on our earlier studies [8] we estimated that the difference between Monte Carlo and Boltzmann equation solution results is significant above 10 Td (1 Td = 10^{-21} V m^2) and does not exceed a few percent for the characteristic energy and is even less for drift velocities. The drift velocities obtained by Monte Carlo simulation calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and dx/dt respectively.

The effect of radicals in Ar/CF_4/O_2 mixture is observed by forming a ternary mixture consisting of 80% Ar, 10% O_2, 9% CF_4 and 1% of radicals. The influence of radicals on the drift velocity is noticeable only below 5 Td where CF_3 and CF radicals play a dominant role. Rate coefficient in the mixture is not affected appreciably by the changes of the electron energy distribution function (EEDF) and the shape of the cross section. In Fig. 1b one can see that for the mixture without radical CF the difference between flux and bulk is zero at low E/N, hardly observable at moderate E/N and large for large E/N where ionization becomes significant. When CF is added a large difference between the two drift velocities is observed at low E/N due to attachment to CF and also the drift velocity is slightly changed for mean energies where Ar has Ramsauer Townsend minimum.

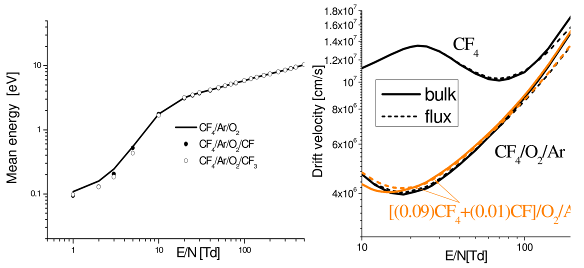

Fig. 1. a) Mean energy and b) drift velocity as a function of the reduced electric field E/N for Ar/CF_4 mixture. Drift velocity for 80% Ar, 9% CF_4, 10% O_2 and 1% radicals CF in the mixture. Results for the pure CF_4 are also shown.

In Fig. 2. total attachment coefficients for mixtures CF_4/Ar/O_2 are compared to the values obtained by TTA for 80% of Ar, 9% CF_4 and 10% O_2 with 1% of radicals CF, CF_2, CF_3, F and F_2. The effect of added radicals on attachment coefficients is considerable, especially at low mean energies (E/N). Before discussing radicals we had to establish whether the addition of oxygen affects the results through the effect of three body attachment in oxygen at low energies.

The influence of CF_2 radicals on: a) EEPF (Electron Energy Probability Functions) and b) the density of electrons is displayed in Fig. 3. The simulation results were obtained by using a one-dimensional Particle-in-cell/Monte Carlo collision code (PIC/MCC) [20, 21] for pure CF_4 (solid line), for addition of 1% CF_2 (dot line) and 10% CF_2 (dash line). As expected, EEPF increases with increasing concentration of CF_2 radicals, while the electron density decreases as the concentration of radicals increases due to attachment process.

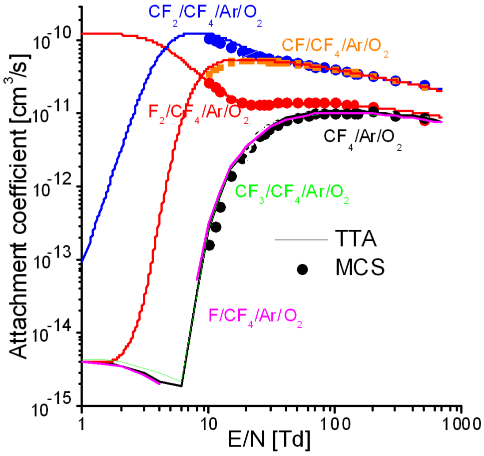

Fig. 2. The dependence of the total attachment rates for electrons in Ar/CF_4/O_2 mixture on the reduced electric field E/N when 1% of radicals are added.

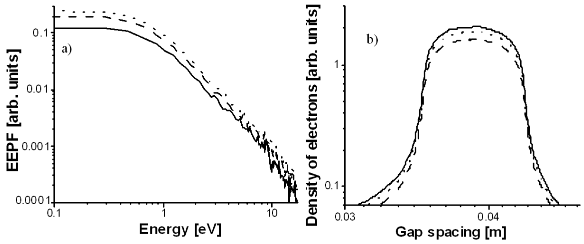

Fig. 3. PIC/MCC simulation results for: a) Electron Energy Probability Function (EEPF) and b) spatial profile of the electron density. The results for pure CF_4 are shown by solid line, while dot and dash lines correspond to addition of 1% CF_2 and 10% CF_2, respectively. Calculations were carried out for high frequency plasma that includes a large albeit typical population of radicals.

It was thus shown that even at small abundances some rate and transport coefficients may change drastically and the best example is the attachment rate. The most abundant radical in plasmas containing CF_4 is CF_2 [16, 22] and it can be found even at abundances of the order of several%. As CF and possibly CF_2 have attachment at low energies with thresholds considerably smaller than that of the dissociative electron attachment for electrons in CF_4 the overall attachment rate is enhanced and extended to lower energies. The attachment rate at low mean energies increases by many orders of magnitude, even the peak value is increased considerably.

Adding Ar in CF_4 mixture causes the increase of the mean energy while the addition of radicals decreases the mean energy mainly at low E/Nvalues. The effect on other transport coefficients is small except at low E/N.

Relatively strong influence of radicals on the drift velocity or to be more precise on the NDC effect is observed only at E/N below about 5 Td. It is mainly due to filling of the Ramsauer Townsend minimum of both Ar and CF_4 by a relatively high momentum transfer cross section of the radicals.

4. Conclusion

The presence of radicals has a considerable effect on the attachment rates especially at low mean energies. As the distribution functions suffer only a minor change due to the presence of the radicals we may conclude that the observed change of the attachment rate is predominately due to introduction of the low energy attachment to the radicals.

As discussed above, the effect of radicals on transport coefficients may be important in understanding possible discrepancies between experiments and models that do not include the cross sections for electron collisions with radicals. It is also of importance for understanding electronegative plasmas and for reducing charging damage by using double layers to accelerate negative ions into the charged high aspect ratio structures in dielectrics [23].

Acknowledgments

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