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MODELING OF HIGH E/N IN MIXTURES OF CF_4 AND ITS RADICALS

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Abstract. We present transport coefficients for electrons in mixtures of CF_4 with its radicals for ratios of the electric field to the gas number density E/N from 1 Td to 1000 Td (1 Td=10^{-21} Vm^2). Our analysis of non-conservative collisions revealed a range of E/N where electron attachment introduced by radicals significantly changes electron kinetics obtained for pure CF_4 gas. Results are obtained by using simple solutions for Boltzmann's equation.

1. INTRODUCTION

Carbon tetrafluoride is one of the most often used gases in todays semiconductor industry. It is primarily applied for etching of substrates of different materials where the most important is SiO_2 . It is also for formation of fluorinated polymer films. CF_4 has an important role in technological applications such as development of gaseous circuit breakers (Hunter et al. 1985) and for development of particle detectors (James et al. 1980, Kopp et al. 1982, Yamashita et al. 1992). CF_4 belongs to freons that unfortunately significantly affect global warming of our planet. Its atmospheric halftime estimated to over 50 000 years and it has a large potential to global warming. Because of that it is important to continue research related to removal of this freon from the atmosphere by applying gas discharges (e.g. by focused microwave radiation (Bzenić et al. 1995). CF_4 has advantage with respect to other gases primarily due to the low level of toxicity and relatively low cost. At room temperature it has low reactivity in its electronic ground state. Because no stable excited states exist it dissociates in plasma treatments where it becomes a source of reactive particles (ions, neutrals, radicals). In CCP (capacitively coupled plasma) (Nakano and Samukawa 1999) and ICP (inductively coupled plasma) (Hioki et al. 2000) etching reactors dominant reactive radical is CF_2. Recent advances in measurements and calculations of electron scattering cross sections (Rozum et al. 2006) on CF_4 radicals in the energy domain relevant to non-equilibrium plasmas have shown that probabilities for many processes are significantly larger than for CF_4 itself. It is even likely that CF_2 radical may reclaim a dominant role for certain processes in plasma. It is now possible to build more precise quantitative picture about rate coefficients in realistic gas mixtures and improve control of radical concentration in order to optimize these processes. In this work we calculated electron transport coefficients for mixtures of CF_4/CF_2 in order

to estimate radical concentrations at which dominant radical influence is achieved in collisions of electrons with CF_4.

2. MONTE CARLO CODE AND TWO TERM APPROXIMATION

A description of electron kinetics in non-equilibrium plasma modeling necessarily includes calculation of transport coefficients which are usually based on compilations of cross sections from different sources (Kurihara et al. 2000). Requirement 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 pure CF4 and in X/CF_4 mixtures (X= F, F_2, CF, CF_2 and CF_3) for the conditions overlapping with those found in plasma technologies for semiconductor production. Set of cross sections for CF, CF_2 and CF_3 is based on the work of Rozum et al. (2006). Set of cross sections for molecular fluorine is from Morgan (1992) and for atomic fluorine is according to Gudsmundsson et al. (2002). We calculated attachment and ionization rate coefficients for 0.01 %, 0.1 %, 1 % and 10 % of the radical species X in CF_4. Transport coefficients are obtained by using numerical solution of Two Term approximation to Boltzmann equation (Morgan et al. 1990).

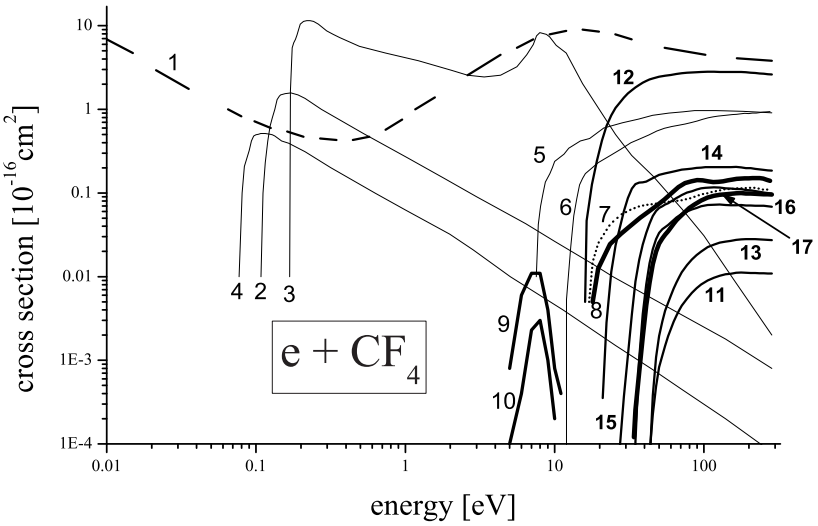

Figure 1: Electron impact cross sections for scattering on CF_4 (1 - elastic momentum transfer, 2 - vibrational excitation v=1, 3 - vib. excitaton v=3, 4 - vib. excitation v=4, 5 - electron excitation, dissociation to products CF_3 (6), CF_2 (7), CF (8), 9 - dissociative electron attachment(DEA) (F^-), 10 - DEA (CF_3^-), 11 - CF_3^+ + F + 2e (ionization), 12-17 other channels of ionization.

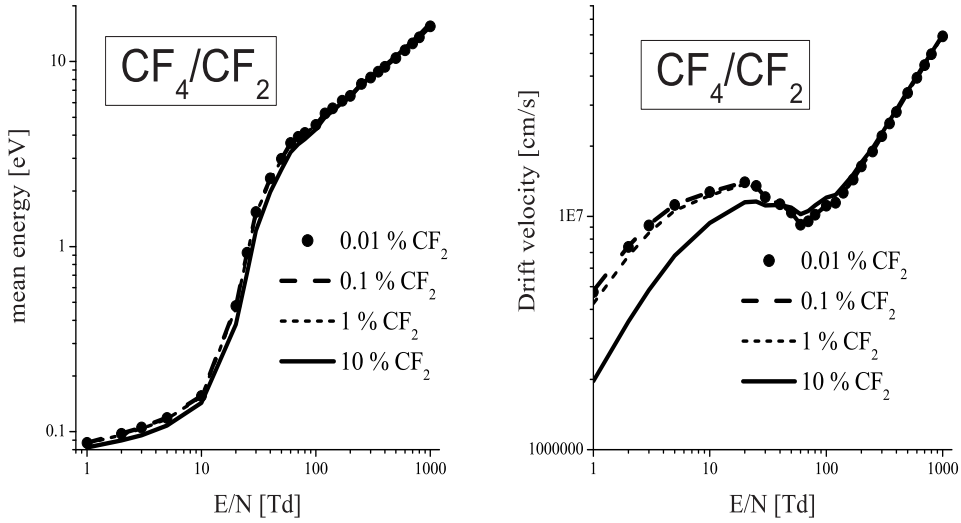

Figure 2: Mean energy and drift velocity as a function of E/N for CF_4/CF_2 mixture.

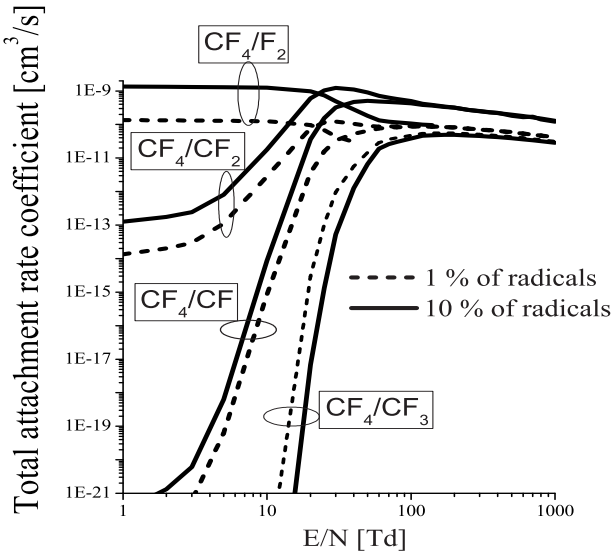

Figure 3: Comparison of total attachment rate coefficient for 1 % s and 10 % of radicals.

3. RESULTS AND DISCUSSION

The basic cross sections of pure CF_4 were used from Kurihara et al. (2000) and are modified (Donko 2006) in order to include production of CF_3^- ions. Complete cross section set is shown in Fig. 1.

Electron mean energy and electron drift velocity in mixtures CF_4/CF_2 as a function of E/N are shown in Fig. 2. Effect of adding less than 0.01 %, 0.1 %, 1 % and 10 % is significant only at the level of few percent.

Total rate coefficient for electron attachment, obtained as a sum of electron attachment contributions to CF_4 and one of its radicals according to the assumed abundance is shown in Fig. 3.

Large variations of attachment coefficient are observed below 10 Td even for concentrations of added radicals below 1 %. In these conditions one should not expect large changes in electron kinetics. Adding CF_3 radical in mixture with CF_4 decreases total attachment rate coefficient due to the increased rate for elastic collisions and lack of attachment for the radical. Total attachment rate coefficient for both CF_2 and CF radicals in 10 % mixture with CF_4 are quite similar in magnitude for $E/N > 100$ Td which is the result of CF_4 ionization.

Acknowledgments

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