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Modeling of the Effect of Radicals on Plasmas Used for Etching in Microelectronics

Plasma etching represents one of the critical steps in manufacturing of integrated circuits. Further optimization of plasma equipment is needed since new generations in technology require different plasma chemistry. In this paper, we will study the influence of radicals on the plasma characteristics, since it was often neglected in plasma models. The radicals dominate attachment of electrons as the basic etching mixture is weakly electronegative and they also affect the drift velocity through modified momentum balance. We have used numerical solutions to the Boltzmann equation and Monte Carlo simulations (MCS) to determine the transport coefficients of electrons.

Keywords: *CF_4, transport coefficients, Global model, Monte Carlo code*

1. INTRODUCTION

The CF_4 has an important role in technological applications such as discharge switches [1], in gaseous detector technology [2] and for the development of particle detectors [3, 4]. The CF_4 belongs to Freon group of gases that unfortunately significantly affect the global warming of our planet. Its atmospheric lifetime is estimated at over 50 000 years and it has one of the largest potentials to global warming. Because of this it is important to continue research related to removal of this Freon from the atmosphere. One technique proposed to achieve this by applying plasma which could be induced by focused microwave radiation [5].

Carbon tetrafluoride is commonly used in today's semiconductor industry for etching of dielectric materials, such as SiO_2 [6, 7] and also for deposition of fluorinated polymer films.

2. CROSS SECTION SETS

In order to achieve further improvements of the high resolution plasma processing for future generations of integrated circuits, empirical development of plasma processing tools has to be replaced by exact modeling of the physics and chemistry of plasmas in real geometries.

A description of electron kinetics in non-equilibrium plasma modeling necessarily includes, either directly or indirectly the calculation of transport coefficients. Such calculations are usually based on compilations of cross sections from various sources [8]. Requirement to establish reliable transport coefficients for CF_4 plasmas is especially demanding since practical conditions include many reactive species. The reactive radicals have often been neglected in plasma models. Free radical species, such as CF_y (y=1-3) and fluorine atoms, play important but complex roles in plasma processing. Electron transport coefficients were calculated for pure CF_4 and in X/CF_4 mixtures (X= F, F_2, CF, CF_2 and CF_3) for the conditions overlapping with those used in plasma technologies for semiconductor production. In this paper we shall only consider CF. Set of cross sections for CF, CF_2 and CF_3 is based on work of Rozum *et al.* [9]**.** Set of cross sections for F_2 is from [10] and for F is according to Gudsmundsson [11].

Attachment and ionization rate coefficients were calculated 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 [12].

3. RESULTS AND DISCUSSION

The basic cross sections of pure CF_4 were used from [8] with a modification made in [13, 14] in order to include production of CF_3^- ions. Complete cross section set is shown in Figure 1.

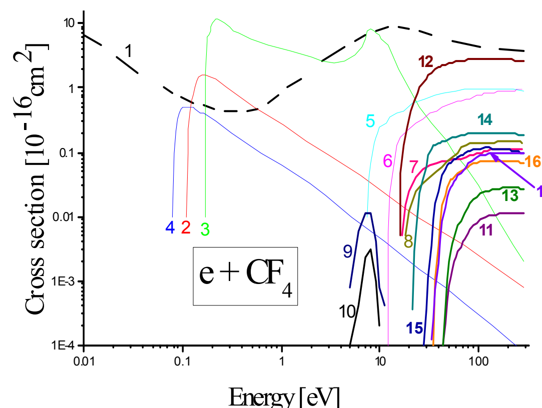

Figure 1. Electron impact cross sections for scattering on CF_4 (1- el. mom. transfer, 2- vib.exc. v=1, 3-vib.exc. v=3, 4 - excitation v=4, 5-electronic excitation, 6-dissociation to products CF_3, 7- dissociation to products CF_2 , 8- dissociation to products CF, 9-diss.el.at. (F), 10-diss.el.at (CF_3^-), 11- ionization CF_3^+ + F + 2e, 12-17 -other channels of ionization.

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In Figure 2 we show the input data for the cross sections for e-CF scattering.

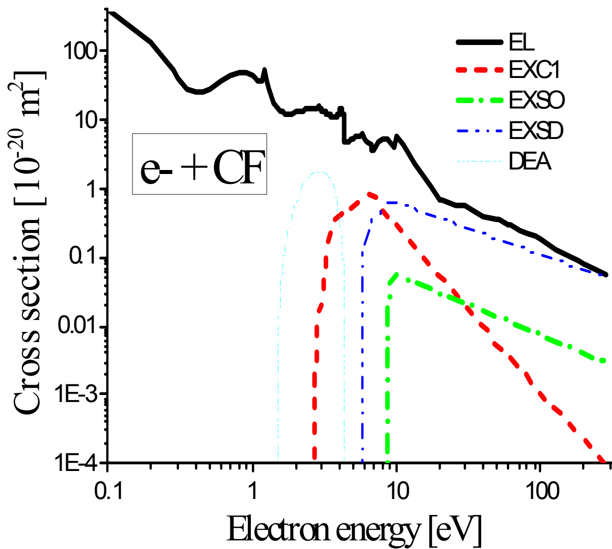

Figure 2. Electron impact cross sections for scattering on CF (EL-elastic momentum transfer. EXC1, EXCM-excitation to first exc.state, EXSB-exc.to bound and radiative state, EXSO-exc.to other dissociative states, EXSD-exc to dissociative A and B states,DEA-dissociative attachment).

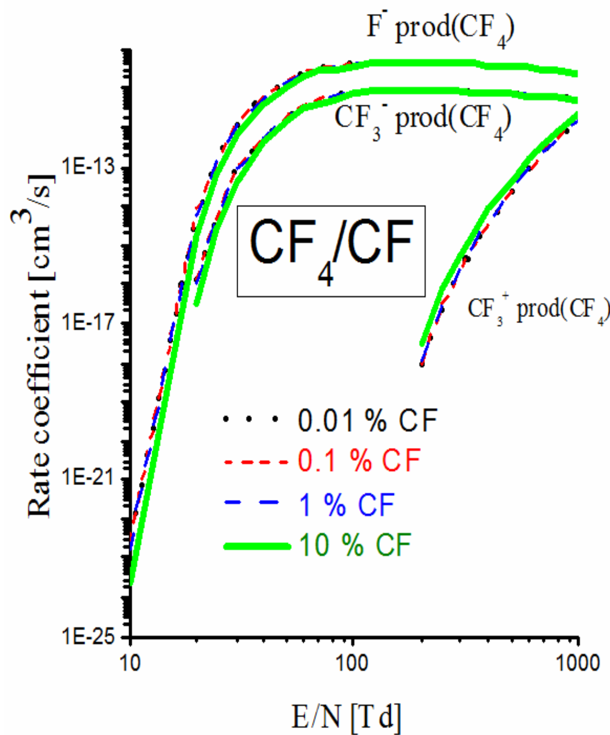

Figure 3. Total rate coefficients for attachment in CF_4/ CF mixture.

We present transport coefficients for electrons in mixtures of CF_4 with its radicals (specifically CF) 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).

The rate coefficients for the formation of F^-, CF_3^- and CF_3^+ ions calculated for the CF_4/CF mixture are presented in Figure3. In principle almost negligible differences between low and higher abundance data indicate a very small perturbations of the EEDF as those ions are produced in collisions of electrons with CF_4 molecule.

In the Figure 4. we show the Electron Energy Distribution Function (EEDF) in mixtures of CF_4/ CF.

Even the large attachment introduced by CF for electron energies around 1 eV only causes minor differences in the EEDF shape for energies below 0.5 eV and insignificant changes at higher energies.

The electron mean energy and electron drift velocity in mixtures of CF_4/ CF as a function of *E/N* is shown in Figure5 and Figure6. Adding 1% or less of CF did not significantly change the mean energy, although the effect on the momentum balance is significant as can be observed in the disappearance of the high velocity peak (enhanced drift velocity) and of the negative differential conductivity (NDC). This change on its own is sufficient to warrant taking into account radicals when one models realistic plasma devices.

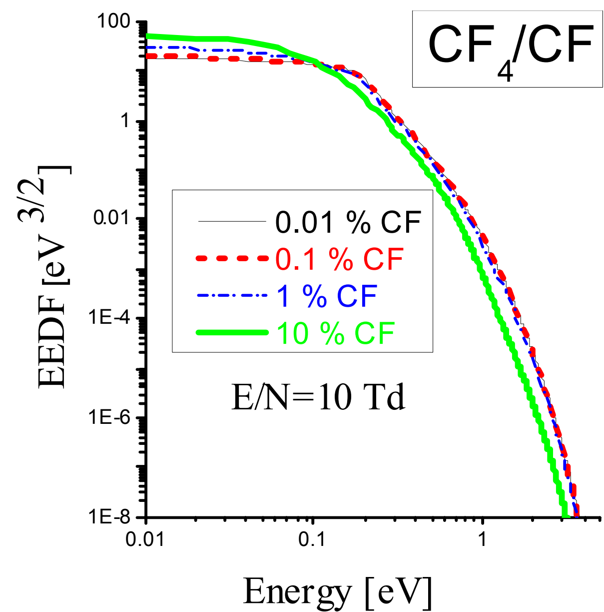

Figure 4. EEDF in CF_4/ CF mixture.

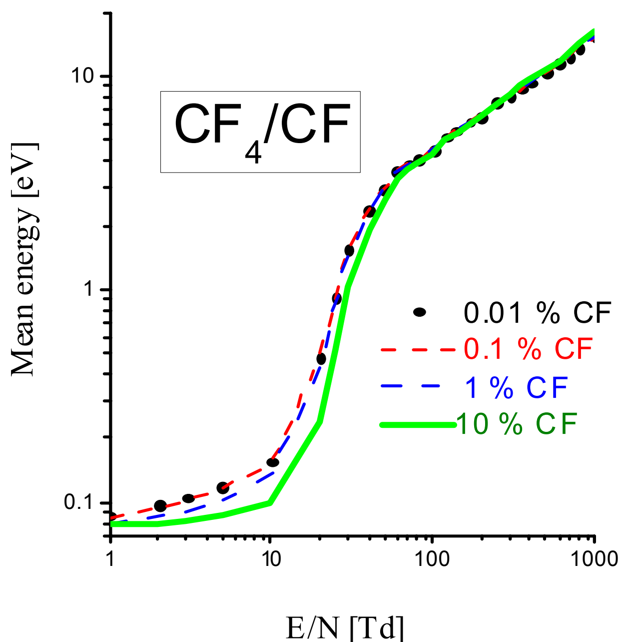

Figure 5. Mean energy in CF4/ CF mixture.

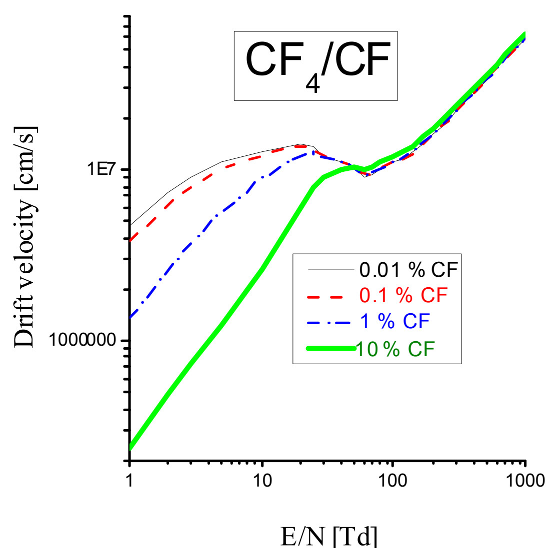

Figure 6. Drift velocity in CF_4/ CF mixture.

4. REMARKS

It was shown in this paper 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 [15, 16] and it can be found even at abundances of the order of several %. As CF 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. Attachment rate at low mean energies increases many orders of magnitude, even the peak value is considerably increased. Also it was found that even a small amount of radicals affects the plasma and makes it more electronegative.

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ЕФЕКТИ РАДИКАЛА У МОДЕЛИРАЊУ ПЛАЗМИ КОРИШЋЕНИХ ЗА НАГРИЗАЊЕ У МИКРОЕЛЕКТРОНИЦИ

Жељка Д. Никитовић, Јасмина В. Јовановић, Урош Цвелбар, Миран Мозетич, Владимир Д. Стојановић

Плазма нагризање представља један од критичних корака у изради интегрисаних кола. Даља оптими–зација плазма уређаја је потребна јер нове генерације у технологији захтевају различиту плазма хемију. У овом раду бавимо се утицајем радикала на плазма карактеристике, што је често занемаривано у плазма моделима. Радикали доминирају захватом електрона чинећи да је базна смеша за нагризање слабо електронегативна, а они такође модификују брзину дрифта преко модификованог баланса момента. Ми смо користили нумеричка решења Болцманове једначине и Монте Карло симулације (МЦС) за одређивање транспортних коефицијената електрона.