The influence of F and F_2 on kinetics of electrons in BF_3

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Abstract

We present transport coefficients for electrons in mixtures of BF_3 with its radicals (specifically F and F_2) for ratios of the electric field to the gas number density *E/N* from 1 to 1000 Td (1 Td = 10^{-21} V m^2). Our analysis of non-conservative collisions revealed a range of *E/N* where electron attachment to radicals significantly changes the electron kinetics compared to pure gaseous BF_3. The results were obtained using simple solutions for Boltzmann's equation and Monte Carlo simulation.

Keywords: BF_3 • F • F_2 • Elendif • Monte Carlo code

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The interest in the research of electron transport phenomena in molecular gases arises from the contribution of electron-assisted processes in modeling phenomena of today's advanced technologies. For example, understanding electron transport in low temperature BF_3 plasmas [1] is necessary in modeling ion implantation devices.

To gain full understanding of plasma devices one needs to model them almost exactly [2,3]. Application of transport coefficients in plasma modeling is not trivial as swarm parameters are measure and calculated for pure buffer gas. At the same time, real plasmas have all the products of collisions of electrons in large numbers that may affect the energy distribution function [4,5] and plasma chemistry [6]. Thus, it is important to determine swarm data for the actual conditions that occur in plasma devices. One example of such work is our previous study of transport in CF_4 [7].

In this work we have calculated the electron transport coefficients for mixtures of BF3/F_2/F in order to estimate when radicals begin to play a significant role in the electron kinetics. In order to optimize plasma processing for future generations of integrated circuits, the empirical development of the plasma processing tools has to be replaced by quantitative, predictive models containing all of the relevant physics and chemistry of plasmas. These results will be useful for such plasma models. In realistic plasmas, large abundances, sometimes even several percent, of fluorine radicals are present.

NUMERICAL METHOD

Calculations were performed by using our Monte Carlo technique for electron transport that has been verified against basic swarm benchmarks [8,9]. Calculations were also made by a two term approximation of the Boltzmann's equation [10].

We also pay attention to non-conservative transport in presence of ionization and attachment. For example, the distinction should be made between [8,9] the so called bulk (*b*) and flux (*f*) transport properties such as drift velocity:

$$\vec{v}_b = \frac{\mathrm{d}}{\mathrm{d}t}\sum_{i=1}^{n}\vec{r}_i \; ; \; \vec{v}_f = \sum_{i=1}^{n}\vec{v}_i \qquad (1)$$

The drift velocities obtained by Monte Carlo simulation calculated in real space (bulk) and in velocity space (flux) values which are obtained as <*v*> and d*x*/d*t*, respectively. The differences are a result of the time varying number of electrons which, when differentiated, produces an additional term to the standard flux definition <v>. The differences occur only when non-conservative processes are present.

The null collision technique has been applied to model the basic experiment where spatial profiles of absolute emission (excitation) have been measured to provide the data on excitation coefficients, contribution of fast ions and neutrals, non-equilibrium processes (such as equilibration distance), secondary electron yields at the cathode surface and back diffusion [11].

Monte Carlo simulations were mainly used to test the two term approximation to the Boltzmann's equation (TTA). The test of cross sections for low energies was performed by comparing the calculated and experimental drift velocities and characteristic energies (eD_T/μ, where D_T is the transverse diffusion coefficient and μ is mobility). The test at higher energies was made by using the ionization rate, while assuming that the ionization cross section is very accurately measured or calculated and therefore should not be modified further.

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RESULTS AND DISCUSSION

The basic set of cross section data for BF_3 was compiled by Biagi [12] and we have used this set in our previous work [13]. Some of the preliminary data along similar lines were already presented [14]. The electron drift velocity in pure BF_3 exhibits regions of negative differential conductivity (NDC) [15] similar to but smaller in magnitude than those in CH_4 and CF_4. Results for mean energy shown in Figure 1 obtained by TTA are compared to MCS results at T = 0 K. We show results for drift velocity obtained by different methods in Figure 1b. Agreement between Monte Carlo and TTA results are obtained below 20 Td. Large vibrational cross sections significantly affect region of negative differential conductivity (NDC) up to about 80 Td. Results obtained by TTA show effect of NDC that is slightly smaller than observed in experiment [16]. At higher E/N excellent agreement exist between results obtained by two Monte Carlo techniques and TTA.

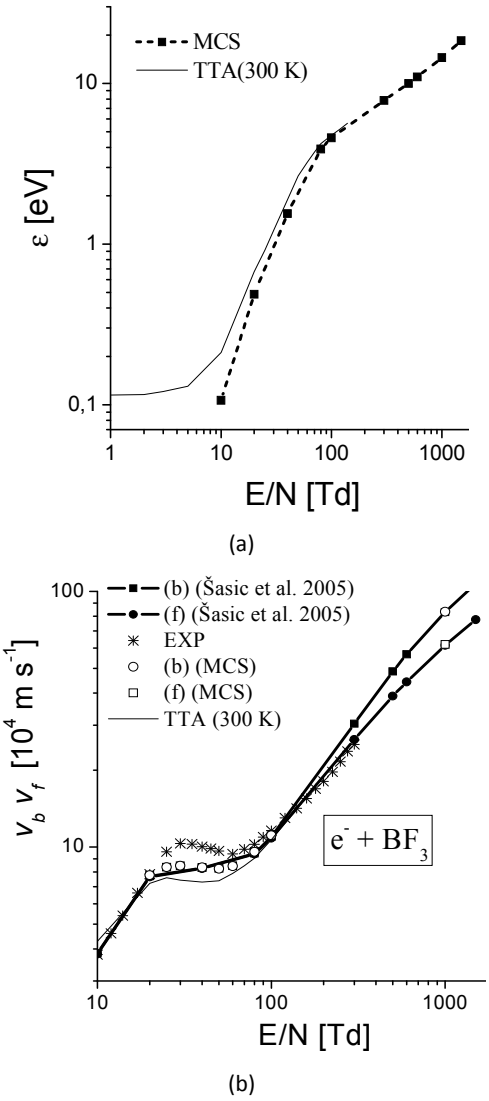

Figure 1. a) Mean energy and b) drift velocity as a function of E/N for BF_3. The data for BF_3 from ref. 15 is denoted as EXP.

The electron mean energy and electron drift velocity in the mixture BF_3/F_2 as a function of E/N are shown in Figure 2. Adding less than 0.01, 0.1, 1 and 10% of other constituents does not change significantly the drift velocities or mean energies.

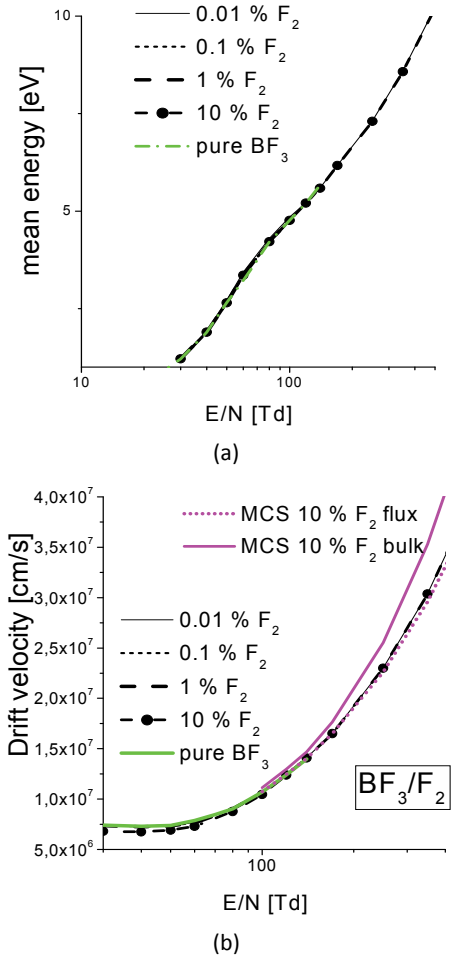

Figure 2. a) Mean energy and b) drift velocity as a function E/N for mixtures BF_3 and 0.01%, 0.1%, 1% and 10% F_2. Results for the pure BF_3 are also shown.

In Figure 3 we show total attachment coefficients and effective ionization coefficient for the mixture BF_3/F_2 as a function of E/N accounting for total electron production in the mixture. Ionization of BF_3 affects electron kinetics from about 100 Td. The effect of radicals on ionization is small at higher E/N. It is important to note that due to a large threshold of attachment in BF_3 addition of a radical with small threshold for attachment will lead to considerable changes, turning the otherwise electropositive plasma into electronegative. Thus, one needs to test the cross sections for BF_x radicals in the same way as it was done for CF_4 [7].

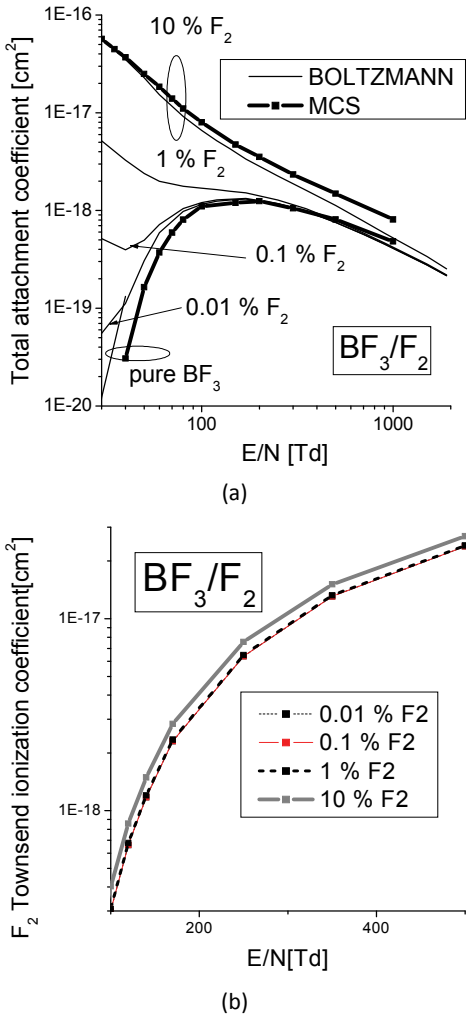

Figure 3. a) Total attachment coefficients and b) ionization coefficients in BF_3/F_2 mixtures (0.01, 0.1, 1 and 10% of F_2). Total attachment results for the pure BF_3 are also shown.

CONCLUSION

We have presented electron transport coefficients in mixture of BF_3, F and F_2. Effect of F_2 radicals on electron kinetics is relatively small for all abundances up to 10%. Only if a significant fraction of F_2 is added, one may expect changes in ionization and attachment rate although effective ionization rate may not be changed.

As discussed above, the effect may be important in understanding possible discrepancies between experiments and models that do not include the cross sections for electron collisions with radicals, as well as for understanding electronegative plasmas and reducing charging damage by using double layers to accelerate negative ions into charged high aspect ratio structures in dielectrics.

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REFERENCES

[1] B.-W. Koo, Z. Fang, L. Godet, S.B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet, D.Lenoble, Plasma diagnostics in pulsed plasma doping (P^2LAD) system. IEEE Trans. Plasma Sci. **32** (2004) 456–463.

[2] T. Makabe, Z.Lj. Petrović, Plasma Electronics: Applications in Microelectronic Device Fabrication, Taylor and Francis, New York, 2005.

[3] N. Nakano, N. Shimura, Z.Lj. Petrović, T. Makabe, Simulations of rf glow discharge in SF_6 by the relaxation continuum model: physical structure and function of the narrow-gap reactive-ion etcher, Phys Rev. E **49** (1994) 4455–4465.

[4] Ž. Nikitović, V. Stojanović, J.P. Booth, Z.Lj. Petrović, Electron transport coefficients in mixtures of CF_4 and CF_2 radicals, Plasma Sources Sci. Technol. **18** (2009) 035008.

[5] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Rađenović, Measurement and interpretation of swarm parameters and their application in plasma modeling, J. Phys. D: Appl. Phys. (2009) 42194002.

[6] S. Radovanov, L. Godet, R. Dorai, Z. Fang, B.W. Koo, C. Cardinaud, G. Cartry, D. Lenoble, A. Grouillet, J. Appl. Phys. **98** (2005) 113307.

[7] Ž. Nikitović, V. Stojanović, Z.Lj. Petrović, U. Cvelbar, M. Mozetič, Transport coefficients for electron scattering in $CF_4/Ar/O_2$ mixtures with a significant presence of F_x or CF_x radicals, EPL **91**(5) (2010) 55001.

[8] Z. Raspopović, S. Sakadžić, Z.Lj. Petrović, T. Makabe, Diffusion of electrons in time-dependent $E(t)\times B(t)$ fields, J. Phys. D: Appl. Phys. **33** (2000) 1298–1302.

[9] Z.Lj. Petrović, V.D. Stojanović, The role of heavy particles in kinetics of low current discharges in argon at high electric field to gas number density ratio. J. Vac. Sci. Technol. A **16** (1998) 329–336.

[10] W.L. Morgan, B.M. Penetrante, ELENDIF: A time-dependent Boltzmann solver for partially ionized plasmas, Comp. Phys. Commun. **58** (1990) 127–152.

[11] M. Radmilović, Z.Lj. Petrović, Modeling of back diffusion of electrons in argon. Eur. Phys. J. AP **11** (2000) 35–42.

[12] S. Biagi, Private communication, 2005.

[13] Ž. Nikitović, O. Šašić, Z. Raspopović, V. Stojanović, S. Radovanov, M. Mozetič, U. Cvelbar, Modeling of electron kinetics in BF_3, Acta Phys. Pol. A **117** (2010) 748–751.

[14] O. Šašić, Z.Lj. Petrović, Z. Raspopović, L. Godet, S. Radovanov, 58th Annual Gaseous Electronics Conference, October 16-20, 2005, San Jose, California, 28, Bul. Am. Phys. Soc. **50** (2005) 28 UH2 4.

[15] S.B. Vrhovac, Z.Lj. Petrović, Momentum transfer theory of nonconservative particle transport in mixtures of gases: General equations and negative differential conductivity Phys. Rev. E **53** (1996) 4012–425.

[16] S.R. Hunter, J.G. Carter, L.G. Christophorou, Electron attachment and ionization coefficients and electron drift velocities in BF_3 and SiF_4, J. Appl. Phys. **65** (1989)1858––1865.

IZVOD

UTICAJ F I F_2 NA KINETIKU ELEKTRONA U BF_3

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(Naučni rad)

U ovom radu prikazani su elektronski transportni koeficijenti za smešu F i F_2 sa BF_3 u funkciji redukovanog električnog polja od 1 Td do 1000 Td (1 Td = 10^{-21} V m^2). Analiza nekonzervativnih sudara je izvršena za promene koeficijenta elektronskog zahvata, sa i bez prisustva radikala i kada je prisutan samo čist gas BF_3. Rezultati su dobijeni korišćenjem jednostavnih rešenja Bolcmanove jednačine i Monte Carlo simulacija.

Ključne reči: BF_3 • F • F_2 • Elendif • Monte Karlo kod