Vol. **126** (2014) *ACTA PHYSICA POLONICA A* No. 3

Transport Parameters of F^- Ions in BF_3

Ž. Nikitović[a],*, V. Stojanović[a], Z. Raspopović[a] and J. Jovanović[b]
[a]Institute of Physics, University of Belgrade, POB 68, 11080 Belgrade, Serbia
[b]Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11000 Belgrade, Serbia

(Received January 22, 2014; in final form June 18, 2014)

In this work we presented the new results for energy dependent cross-sections and transport coefficients as a function of E/N for F^- ions in BF_3 gas. Results were obtained by using the Monte Carlo technique for cross-section set determined on the basis of the Nanbu theory. Monte Carlo method is applied to obtain swarm parameters at temperature of $T = 300$ K.

DOI: 10.12693/APhysPolA.126.724
PACS: 51.10.+y, 52.20.Hv, 52.65.Pp, 52.77.–j

1. Introduction

F^- ions are abundant in plasmas relevant for a wide range of applications. Knowledge of the plasma chemistry and behavior of the negative ions in the plasmas is thus a key to control plasma processing devices. Additionally, the recent progress of discharge modeling and simulation have made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or operating conditions. Boron dopant penetration in silicon is technologically achieved by DC pulsed plasma system (PLAD) most widely applying BF_3 gas [1, 2]. Uniform plasma and implantation with normal ion incidence are the main goals in this technological process. Control over the number density of negative ions, in such a case being F^- and BF_4^-, increase efficiency of implantation. Modeling of such plasmas requires knowledge of transport parameters of all abundant particles [3].

In this work, we employ the Nanbu theory [4] to calculate transport cross-section set for F^- ions scattering on BF_3 molecule appropriate for low energies of F^- ions. By using Monte Carlo technique of Ristivojević and Petrović [5] we calculated transport parameters as a function of E/N (E — electric field, N — gas density).

2. Calculation of the cross-section set

According to the Nanbu theory elastic and reactive endothermic collisions are separated and treated by accounting for the thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [4]. Within the RRK theory an excited molecular complex is treated as excited activated complex where the internal energy is distributed among s equivalent vibrational modes of the complex.

Accounting for long range polarisation forces we exploited polarizability of 3.31×10^{30} m^3 for BF_3 [6]. For $F^- + BF_3$ system characteristic low energy reactive channels are shown in Table.

The cross-section for exothermic reaction (EXO) forming a super halogen molecular ion BF_4^- is commonly represented by ion capture cross-section:

$$\sigma_{\rm exo} = \beta\sigma_L, \tag{1}$$

where σ_L is the orbiting cross-section [7] and β is the probability of a specific exothermic reaction. It is also known that stabilization of the excited activated complex proceeds either radiatively or collisionally [8] for reaction EXO in Table. at room temperatures and pressures of about 0.5 Torr (67 Pa). Similar situation appears in the case where BF_4^- energies from the surface sputtering of cluster BF_3 ions [9]. In Ref. [8] Herd and Babcock concluded that magnitudes of collisional stabilization, radiative stabilization, and unimolecular decomposition back to initial reactants are comparable in these conditions. Since non-associative reactions share the same collisional complex the total probability of all selected reactions equals 1, so one can account cross-section for exothermic reaction as $\sigma_{\rm exo} = \beta\sigma_{e0}$, where β is selected to define elastic cross-section contribution as $\sigma_e = (1-\beta)\sigma_{e0}$. σ_{e0} is the elastic cross-section (EL) obtained by Nanbu theory for endothermic reactions. Now one can determine β by calculating rate coefficient for association reaction and comparing with experimental data.

TABLE

F^-–BF_3 reaction paths considered in the model and the corresponding thermodynamic threshold energies Δ.

No	Reaction path	Δ [eV]
1	F_2^-+BF_2 (CT)	–5.6 [13]
2	F^-+$BF_3 + e^-$ (DET)	–3.4012 [14]
3	BF_4^- EXO)	+3.58 [12]

Thermal rate coefficient for association reaction 3 (Table) is determined experimentally by Babcock and Streit [10] by flowing afterglow technique and has a value 9.4×10^{-11} cm^3/molecule/s for $T = 300$ K. By combining the relation (1) and thermal rate coefficient we determined the probability of exothermic reaction and

---

*corresponding author; e-mail: zeljka@ipb.ac.rs

thus contributions of association cross-section (EXO) and elastic cross-section (EL) (Fig. 1). In the low energy limit the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the nonconservative collisions become efficient for different possible processes.

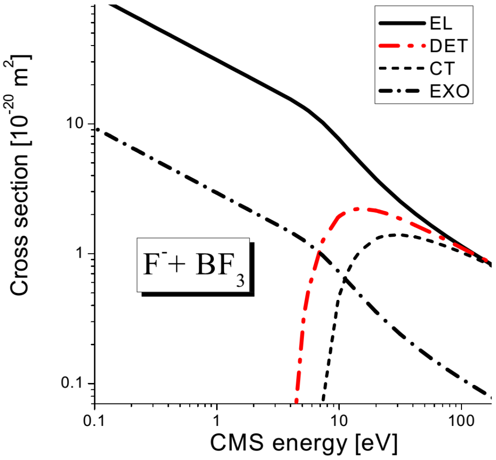

Fig. 1. Cross section set for F^- ions in BF_3.

3. Transport parameters

The transport coefficients include the drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [3]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with collisional operator representing only binary collisions.

In this work a Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the background gas particles [5] is used to calculate swarm parameters of F^- ions in gas for temperature $T = 300$ K.

The critical review of experimentally obtained transport properties of gaseous halogen ions is presented in [11].

In Fig. 2 we show characteristic energies (diffusion coefficient normalized by mobility D/K in units eV) longitudinal (L) and transverse (T) to the direction of electric field. We also show the mean energy, which cannot be directly measured in experiments but a map of mean energy versus E/N may be used directly to provide the data in fluid models especially when local field approximation fails. As visible in the figure the energy increases from 10 Td.

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under unit electric field. One often exploits the reduced

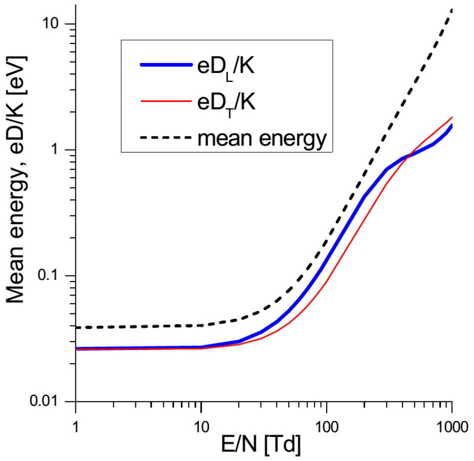

Fig. 2. Mean and characteristic energy of F^- ions in BF_3 as a function of E/N.

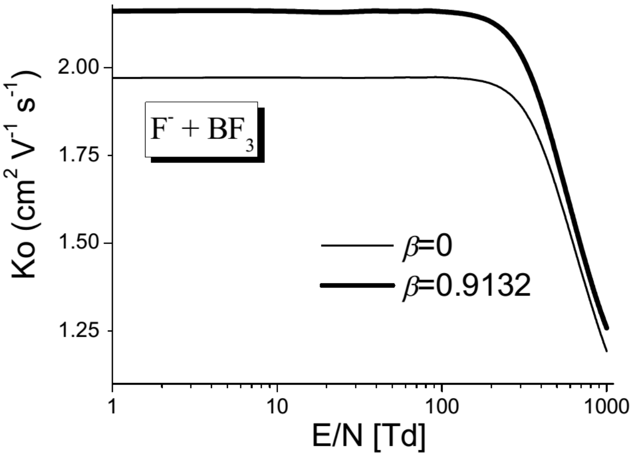

Fig. 3. Reduced mobility of F^- ions in BF_3 as a function of E/N.

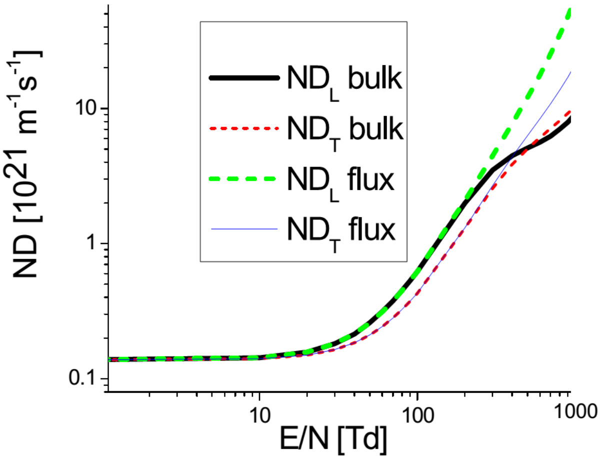

Fig. 4. The diffusion coefficients for F^- ions in BF_3 gas as a function of E/N at $T = 300$ K.

or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0} NE, \tag{2}$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T, E is the electric field.

In Fig. 3 we show the results of Monte Carlo simulation for reduced mobility as a function of E/N. Nonconservative collisions of F^- ions producing BF_4^- ions are only slightly modifying mobility curve obtained for two values of parameter β.

Longitudinal and transverse bulk and flux diffusion coefficients for F^- ions in BF_3 as a function of E/N are shown in Fig. 4. Note that the difference between flux and bulk values of diffusion coefficients which have the same origin have the same initial value as drift velocities. There are no published experimental data for the longitudinal and transverse diffusion coefficients of F^- in BF_3.

4. Conclusion

In this paper we show predictions for the low energy cross-sections and transport coefficients of negative F^- ions in BF_3 which did not exist in literature.

Monte Carlo technique was applied to carry out calculations of the mean energy, drift velocity and diffusion coefficients as a function of reduced electric field in DC electric fields.

In Monte Carlo technique used in presented study collision frequency in case of thermal collisions of a test ion particle is not calculated by Monte Carlo integration technique [15] but by using piecewise calculation [16]. The piecewise calculation is based on assumption that most cross-sections are defined numerically at limited number of points with linear interpolation for mid points.

The cross-section set have been determined by using a simple theory and transport data for gas BF_3, which is technologically very important. There results are a good base for modeling, but it could be further improved by adding a data base of the measured values of transport coefficients and then perform the analysis again.

Acknowledgments

Results obtained in the Laboratory of Gaseous Electronics Institute of Physics University of Belgrade under the auspices of the Ministry of Education, Science and Technology, projects No. 171037 and 410011.

References

[1] B.-W. Koo, Z. Fang, L. Godet, S.B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet, D. Lenoble, *IEEE Trans. Plasma Sci.* **32**, 456 (2004).

[2] Ž. Nikitović, S. Radovanov, L. Godet, Z. Raspopović, O. Šašić, V. Stojanović, Z. Lj. Petrović, *EPL* **95**, 45003 (2011).

[3] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Rađenović, *J. Phys. D: Appl. Phys.* **42**, 194002 (2009).

[4] K. Denpoh, K. Nanbu, *J. Vac. Sci. Technol. A* **16**, 1201 (1998).

[5] Z. Ristivojević, Z. Petrović, *Plasma Sources Sci. Technol.* **21**, 035001 (2012).

[6] C. Szmytkowski, M. Piotrowicz, A. Domaracka, L. Klosowski, E. Ptasinska-Denga, G. Kasperski, *J. Chem. Phys.* **121**, 1790 (2004).

[7] E.W. McDaniel, V. Čermak, A. Dalgarno, E.E. Ferguson, L. Friedman, *Ion–Molecule reactions*, Wiley-Interscience, New York 1970.

[8] C.R. Herd, L.M. Babcock, *J. Phys. Chem.* **91**, 2372 (1987).

[9] X.L. Zhao, A.E. Litherland, *Nucl. Instrum. Methods Phys. Res. B* **259**, 223 (2007).

[10] L.M. Babcock, G.E. Streit, *J. Phys. Chem.* **88**, 5025 (1984).

[11] L.A. Viehland, E.A. Mason, *At. Data. Nucl. Data Tables* **60**, 37 (1995).

[12] G.L. Gutsev, P. Jena, R.J. Bartlett, *Chem. Phys. Lett.* **292**, 289 (1998).

[13] K.A.G. MacNeil, J.C.J. Thynne, *J. Phys. Chem.* **74**, 2257 (1970).

[14] E.W. Mc Daniel, *Atomic Collisions-Electron, Photon Projectiles*, Willey & Sons, New York 1989.

[15] T. Simko, V. Martisovits, J. Bretagne, G. Gousset, *Phys. Rev. E* **56**, 5908 (1997); S. Longo, P. Diomede, *European Phys. J. Applied Physics* **26**, 177 (2004).

[16] Z.Lj. Petrović, J.V. Jovanović, V. Stojanović, Z.M. Raspopović, Z. Ristivojević, *Eur. Phys. J. D* **48**, 87 (2008).