Rate Coefficients of F^- Ions in Ar/BF_3 Mixtures

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Transport parameters of F^- ions in mixtures Ar/BF_3 in DC fields were calculated using Monte Carlo simulation technique assuming the scattering cross-section set assembled on the basis of Nanbu's technique separating elastic from reactive collisions. In this work we present characteristic energy and rate coefficients for low and moderate reduced electric fields E/N (N — gas density) and account for the non-conservative collisions.

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1. Introduction

Negative ions are abundant in plasmas containing fluorine molecules and which are also relevant for a wide range of applications. One should bear in mind that electron affinity of F atom is the largest of all atoms and also that electronegative plasmas containing F^- ions are highly reactive. Knowledge of the plasma chemistry and behavior of negative ions in plasmas is thus necessary in order to model plasma processing devices. Additionally, recent progress of discharge modeling and simulation has made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or finding operating conditions.

Plasma enhanced chemical vapour deposition (PECVD) using BF_3 gas is successfully used for the synthesis of cubic boron nitride (cBN) films with extreme properties similar to diamond. In a dominant fluorine environment low pressure PECVD [1, 2] produces the low energy negative ions [3] that affect the chemistry near the surface. The large gaps in understanding of chemical kinetics relevant to the ion–BF_3 collisions make the progress in the synthesis of cBN films almost empirical. BF_3 gas is also a working medium in neutron detectors [4] where electron–ion pairs are produced in neutron encounters. The signal detected due to ion transport produces false counts that should be avoided. In order to trace such signals, cross-sections and rate coefficients are needed for ion transport.

2. Monte Carlo technique

The cross-sections for scattering of BF_4^- ions on Ar and BF_3, and for F^- ions on BF_3 are calculated by using Nanbu's theory [5, 6] separating elastic from detachment collisions. The cross-sections for F^- on Ar [7] are used to calculate rate coefficients for detachment. The dipole polarizability of 3.31×10^{-30} m^3 [8] and 1.64×10^{-30} m^3 [9] is used for BF_3 and Ar target, respectively.

Similar to our recent papers [10, 11] Nanbu's theory is used to separate elastic from reactive endothermic collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [5]. Within the RRK theory internal energy is being distributed among empirical number of s equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

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

$$\sigma_{\mathrm{exo}} = \beta\sigma_{\mathrm{L}}, \tag{1}$$

where σ_{L} is the orbiting cross-section [12] and β is the probability of a specific exothermic reaction. When reactive processes come into play, according to Nanbu's theory elastic collisions are competing with reactive collisions and as a consequence none of cross-sections is following Langevin's cross-section energy dependence. Monte Carlo technique of Ristivojević and Petrović [13] is used to calculate the transport parameters as a function of E/N.

3. Transport coefficients

A correct approach to obtain transport parameters of higher accuracy would be to follow the solutions of quantum mechanical generalization of the Boltzmann equation than to include the effects of inelastic collisions and internal energy states [14, 15]. The Monte Carlo simulation methods are generally built around the same initial principles as the related kinetic equations. In this work we apply the Monte Carlo simulation designed for swarm particles [16].

The calculated transport coefficients are the drift velocity, diffusion coefficients, ionization and attachment coefficients, and chemical reaction coefficients for ions [17]. 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 the collision operator representing only binary collisions.

In this work a Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the

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background gas particles [13] is used to calculate swarm parameters of F^- ions in gas for temperature $T = 300$ K.

Apart from mobility data for F^- in Ar [18], other transport parameters for F^- were measured neither for Ar nor for BF_3.

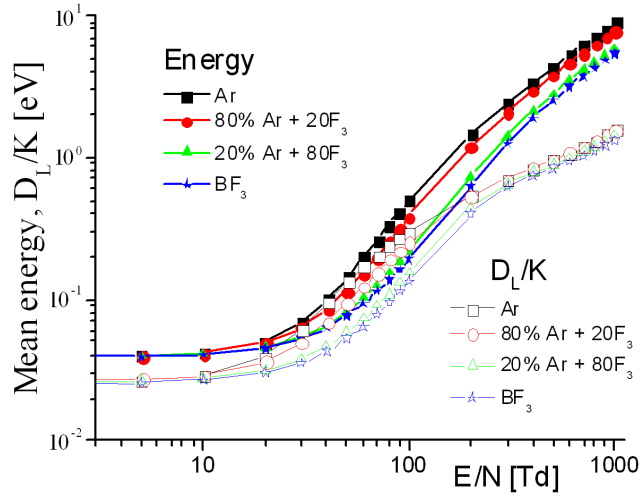

Fig. 1. Mean and characteristic energies of F^- ions in Ar/BF_3 mixtures as a function of E/N.

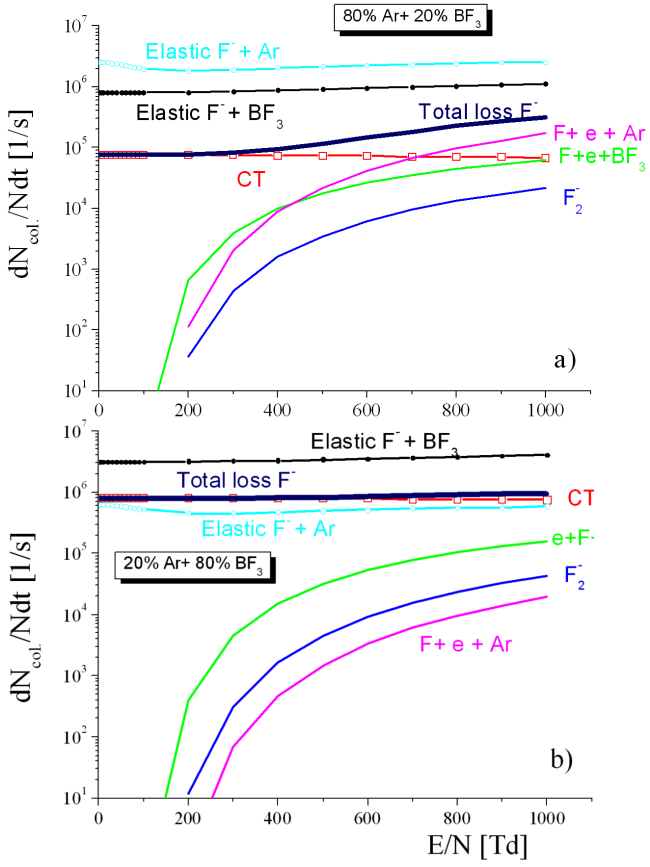

Fig. 2. Rate coefficients for F^- ions in Ar/BF_3 mixtures as a function of E/N.

In Fig. 1 we show the characteristic energies (diffusion coefficient normalized by mobility D/K in units of 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 the 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 Fig. 1 the mean energy and the characteristic energies increase from about 20 Td.

In order to test the Monte Carlo code [13] for the case of mixtures we calculated mean energy and characteristic energy at lowest E/N. Obtained values for all mixtures converged exactly to the thermal mean energy $(3/2)kT = 0.038778$ eV and the thermal $eD/K = kT$ i.e. to 0.025852 eV (longitudinal ($D = D_\mathrm{L}$) and transverse ($D = D_\mathrm{T}$) diffusion coefficients) as expected.

Calculated rate coefficients for processes are presented in Fig. 2. Rate coefficients are important for applications of the global model to Ar/BF_3 mixtures. We are presenting rate coefficients for charge transfer (CT), elastic scattering of F^- in Ar, elastic scattering of F^- in BF_3, and total loss of F^- for (a) 80% Ar + 20%BF_3 and (b) 20% Ar + 80%BF_3.

Transversal diffusion coefficients for F^- ions in Ar/BF_3 mixtures as a function of E/N are shown in Fig. 3. Note that the difference between the 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 Ar/BF_3.

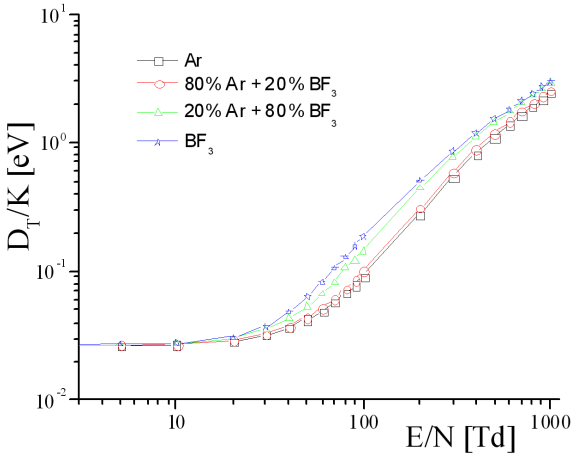

Fig. 3. The transversal diffusion coefficients for F^- ions in Ar/BF_3 mixtures as a function of E/N.

4. Conclusion

In this paper we show transport properties for the F^- in mixtures Ar/BF_3 which do not exist in the literature. The complete cross-section set has been determined by extending Nanbu's theory.

The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then perform the analysis again.

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