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Cross sections and transport properties of positive ions in BF_3 plasmas

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ABSTRACT

Boron produced in plasma devices continues to be the main p-type dopant in ion implantation of semiconductor devices. Yet plasma parameters of most frequently used Boron rich gas, BF_3, are not well established. Time resolved measurements of ion energy distributions in the cathode boundary [1] of a pulsed dc plasma doping system revealed possible role of the charge-transfer collisions between singly charged ions of various mass. The cross sections for scattering of B^+, BF^+ and BF_2^+ ions on BF_3 molecule are calculated by using Nanbu's theory [2] separating elastic from reactive collisions. A Monte Carlo simulation technique was applied to perform calculations of transport parameters in DC electric fields.

1. Introduction

Boron is widely used as the main p-type dopant in ion implantation of semiconductor devices. The ion implantation is a process by which ionized atoms are accelerated directly into a substrate to selectively add dopant atoms. Plasma parameters of the most frequently used boron rich gases (BF_3, B_2F_6, $B_{10}H_{14}$) that determine the plasma content and beam quality are still not well understood. Most commonly used gas, BF_3, which belongs to the group of hard acids, is non-flamable and does not support combustion. However, it is toxic when inhaled and corrosive to the skin. Although the emissions of BF_3 must be controlled because of an immediate danger its decomposition to neutral and/or charged constituents has seldom been addressed.

Optimization and performance of plasma devices for boron production demand knowledge of the role of gas and surface processes in disintegration of the precursor molecules. Such system is capable of high dose rates at energies ranging from ultra low to moderate (0.02–10 kV). It was previously found that BF_2^+ is the dominant ion species, with BF^+ as the second most abundant ion species [3] followed by BF_3^+ and B^+. Lack of cross-section data for many colliding species especially ions and radicals and poor knowledge of complex surface processes are difficulties limiting modeling of ion source plasmas.

Time resolved measurements of ion energy distributions in cathode boundary [1] of a pulsed dc plasma doping system revealed possible role of charge-transfer collisions between singly charged ions of various masses. The goal of this work is to determine most important energy dependent scattering probabilities of positive ions in BF_3 gas and to explore effects of non-conservative processes on transport properties of the ions.

2. Cross sections sets

The cross sections for scattering of F^+, B^+, BF^+ and BF_2^+ ions on BF^3 molecule are calculated by using Nanbu's theory [2,4] separating elastic from reactive endothermic collisions. In Nanbu's theory reactive collision is treated by accounting for thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [2]. In the RRK theory of unimolecular reaction rates excited molecular complex is treated as excited activated complex where internal energy is distributed among s equivalent oscillators–vibrational modes of the complex. For example $s = 3$ for $B^+ + BF_3$ system. Our procedure is an implementation of this theory and approximation. We have used value 3.31×10^{-30} m^3, for polarizability of BF_3 recommended by Szmytkowski et al. [5], ionization potentials for B, BF, BF_2 from [6], F_2 and F from [7], and BF_3 from [8] and the bond values between atoms in Ref. [9]. A preferred procedure would be to unfold the cross sections from the measured transport coefficients and thermochemical data in a separate drift tube experiment but to our knowledge no such data are available. Thus we have resorted to

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using Nanbu's procedure that was shown to give very good results for a number of ions relevant to plasma processing [10,11]. Elastic scattering in the low energy limit is controlled by polarization force and thus for the same target, the cross sections as a function of relative energy are almost identical. The calculated scattering cross sections are shown in Fig. 1 for B^+ (a) and BF^+(b) and in Fig. 2 for BF_2^+ in BF_3.

2.1. B^+ ions in BF_3

Most probable reactions, based on thermochemical values are shown in Table 1 where distinction between the collisional induced dissociation (CID) reactions (inelastic) and dissociative charge transfer (DCT) reactions is made. Negligibly low probability for B^+ reactions with BF_3 [6] producing B_2^+ and B_2 compounds is assumed. Similar conclusion holds for F_2^+ production that is neither found in analysis in Ref. [3] nor in scattering measurements in Ref. [12]. Only for B^+ ions we included reactions producing F_2 molecules, while other association reactions with projectile are not included in calculations assuming low probability of complex formation at low gas densities in processing plasmas. Some authors [13] suggest 2F formation instead of F_2 since only 1.602 eV is needed to break the bond [7] that is not too far from the total uncertainties related to some endothermicities. The cross section set is shown in Fig. 1(a). B^+ ion is known by two distinctive states in which it is often found, ground $B^+(^1S,2s^2)$ [assigned further as B^+(g)] and metastable state $B^+(^3P,2s2p)$ [further B^+(m)] with 4.63 eV energy above the ground state. A significant production of B^+(m) may be achieved by dissociative electron excitation [12].

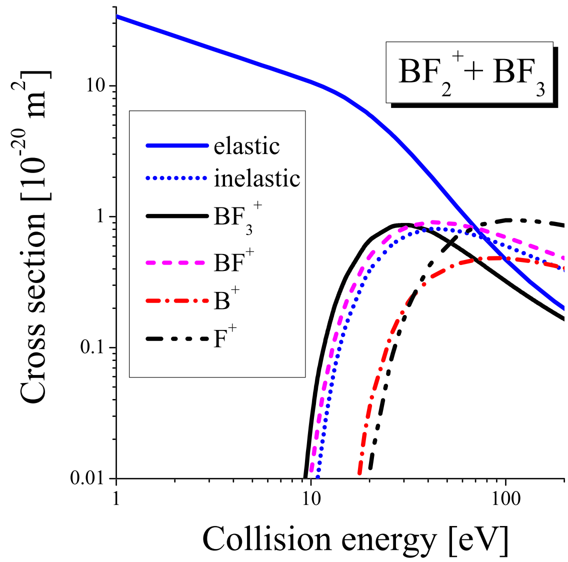

Fig. 2. Cross section set for scattering of BF_2^+ ions in BF_3 gas.

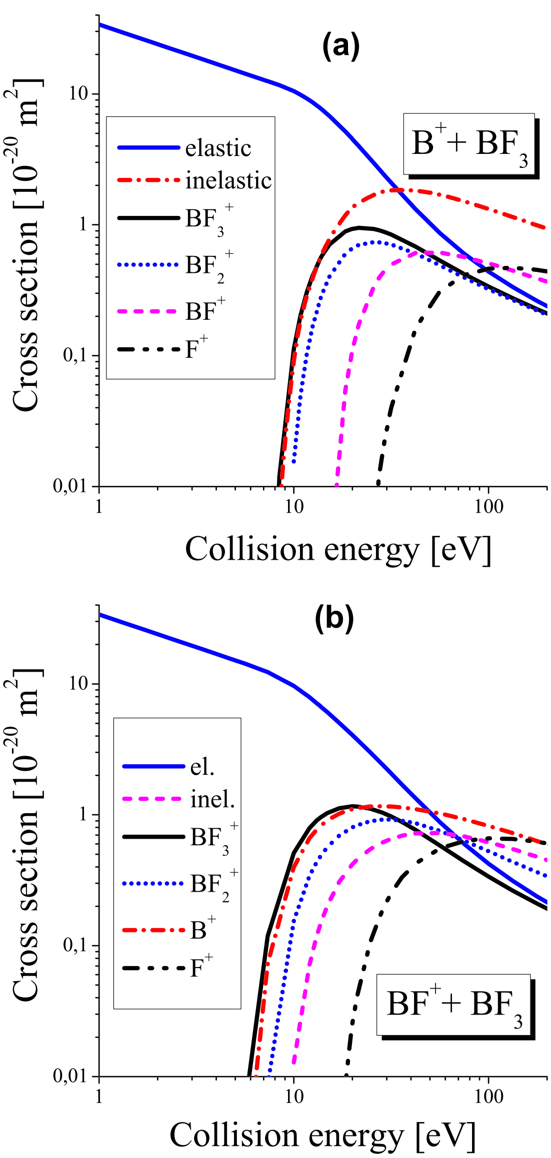

Fig. 1. Cross section set for scattering, (a) B^+ ions, (b) BF^+ ions, in BF_3 gas.

Table 1
$B^+ - BF_3$ endothermic reaction paths considered in the model and the corresponding thermodynamic threshold energies (data were taken from Refs. [6–9], CT denotes charge transfer reaction).

	$B^+ - BF_3$	Δ(eV)		$B^+ - BF_3$	Δ(eV)
1	$BF_3^+ + B$ (CT)	−7.26	7	$F^+ + 2B + F_2$(DCT)	−27.49
2	$BF_2^+ + B + F$ (DCT)	−8.44	8	$B^+ + B + 3F$ (CID)	−19.97
3	$BF^+ + B + F_2$(DCT)	−13.66	9	$B^+ + B + F + F_2$(CID)	−18.37
4	$BF^+ + B + 2F$ (DCT)	−15.26	10	$B^+ + BF + 2F$ (CID)	−12.44
5	$F^+ + BF + B + F$ (DCT)	−21.56	11	$B^+ + BF + F_2$(CID)	−10.84
6	$F^+ + 2B + 2F$ (DCT)	−29.09	12	$B^+ + BF_2 + F$ (CID)	−7.34

2.2. BF^+ ions in BF_3

The scattering probability of BF^+ ions is studied by including processes shown in Table 2. The cross section set for scattering BF^+ ions on BF_3 for 4 processes producing B^+, BF^+ and BF_3^+ ions is shown in Fig. 1(b). Significant reduction of inelastic cross section intensity is observed with respect to scattering of B^+ on BF_3. Significantly lover thresholds for charge transfer reactions are observed for this ion than for other two ions.

Table 2
$BF^+ - BF_3$ endothermic reaction paths considered in the model and the corresponding thermodynamic threshold energies [6–9].

	$BF^+ - BF_3$	Δ(eV)		$BF^+ - BF_3$	Δ(eV)
1	$BF_3^+ + BF$ (CT)	−4.44	9	$B^+ + 3F + BF$	−17.15
2	$BF_2^+ + BF + F$	−5.62	10	$B^+ + 4F + B$	−24.65
3	$BF_2^+ + 2F + B$	−13.15	11	$F^+ + B + BF_3$	−13.73
4	$BF^+ + BF_2 + F$	−7.34	12	$F^+ + BF + BF_2$	−13.64
5	$BF^+ + BF + 2F$	−14.87	13	$F^+ + 2BF + F$	−20.98
6	$BF^+ + B + 3F$	−19.97	14	$F^+ + BF + B + 2F$	−28.51
7	$B^+ + BF_3 + F$	−4.71	15	$F^+ + 2B + 3F$	−36.04
8	$B^+ + BF_2 + 2F$	−12.05			