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# Development of a global model for $BF_3$ discharge

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## 1. Introduction

Plasma processing has an important role in the electronics industry such as anisotropic etching in the fabrication of micro-electric chips, implantation of many dopants in semiconductors [1]. In the ion implantation technique using boron trifluoride ($BF_3$) gas, the characterization of ion species in the plasma source is of great importance. In this work, we have developed a simplified global model for unmagnetized, low-pressure $BF_3$ plasma. In the particle balance equation, we consider 5 neutral species (B, F, BF, $BF_2$, $BF_3$) and 6 ion species ($B^+$, $B^{++}$, $F^+$, $BF^+$, $BF_2^+$, $BF_3^+$). Not only the primary reactions such as the direct ionization, dissociation, and dissociative ionization but also the surface reactions such as dissociative recombination of $BF_3^+$, $BF_2^+$, and $BF^+$ ions are included in the model. In this paper, the details of the global model and preliminary results are presented.

## 2. Model

In the present model, we consider the ion species ratio without the magnetic field effect and the power balance equations, compared to the Patel's model [1]. We only apply the particle balance equations for ion and neutral species, along with the conservation of charge and atomic number. For the primary reactions, we consider the direct ionization, dissociation, and dissociative ionization. The surface reactions include the dissociative recombination of $BF_3^+$, $BF_2^+$, and $BF^+$ ions. Negative ions and metastables are not considered. Compared to the Patel's model [1], the excitation reactions (including vibrational excitation processes), momentum transfer reactions and charge transfer reactions are not included in the present model. In this present model, we do not consider two step ionization for any of the species, which is similar to Patel's assumption [1]. The present global model is developed based on the models provided by Patel [1], Choe [2] and Fukumasa et al [7]. As an initial trial, a cylindrical chamber with a radius of 1 cm and a length of 10 cm is considered. The assumptions used in the present model is well described elsewhere [1].

From the species and the processes which are expressed above, all of the reactions (primary reactions and surface reactions) of the global model are given in Tables I and II.

Table I : List of primary reactions

| Reaction | Process | Energy [eV] | Ref. |
|---|---|---|---|
| 1. $e + BF_3 \rightarrow BF_3^+ + 2e$ | Ionization | 15.56 | [1], [4] |
| 2. $e + BF_3 \rightarrow BF_2^+ + F + 2e$ | Dissociative ionization | 15.76 | [1], [3] |
| 3. $e + BF_3 \rightarrow BF_2 + F + 2e$ | Dissociation | 10.1 | [1], [3] |
| 4. $e + BF_2 \rightarrow BF_2^+ + 2e$ | Ionization | 9.4 | [1], [4] |
| 5. $e + BF_2 \rightarrow BF + F + e$ | Dissociation | 5.9 | [1], [3] |
| 6. $e + BF \rightarrow BF^+ + 2e$ | Ionization | 11.12 | [1], [4] |
| 7. $e + BF \rightarrow B + F + e$ | Dissociation | 8.1 | [1], [3] |
| 8. $e + B \rightarrow B^+ + 2e$ | Ionization | 8.30 | [1], [4] |
| 9. $e + B \rightarrow B^{++} + 3e$ | Ionization | 33.45 | [1], [3] |
| 10. $e + F \rightarrow F^+ + 2e$ | Ionization | 17.4 | [1], [6] |
| 11. $e + B^+ \rightarrow B^{++} + 2e$ | Ionization | 25.15 | [1], [5] |

Table II : List of surface reactions

| Reaction | Process | Ref. |
|---|---|---|
| 12. $e + BF_3^+ \rightarrow BF_2 + F$ | Dissociative recombination | [1], [3] |
| 13. $e + BF_2^+ \rightarrow BF + F$ | Dissociative recombination | [1], [3] |
| 14. $e + BF^+ \rightarrow B + F$ | Dissociative recombination | [1], [3] |

For the Maxwellian distribution of electron energy, $f_M(E)$, the rate constants are given by [1] :

$$k_i = \left(\frac{2}{m_e}\right)^{1/2} \int_0^\infty \sigma_i(E)\,\sqrt{E}\, f_M(E)\, dE\ ,$$

where $\sigma_i(E)$ is the collision cross-section of $i$th reaction, and $m_e$ is the electron mass, E is the electron energy (eV). The differences between the present rate constants data and Patel's rate constants data [1] in two tables above are : in the ionization reactions of $BF_3$, $BF_2$, BF, B (the reactions of $1^{st}$, $4^{th}$, $6^{th}$, $8^{th}$ processes, respectively), we use the NIST cross section data [4] to calculate the rate constants of these reactions, and for the ionization of F (the $10^{th}$ process), the rate constant is obtained by using the Approximate Analytical Formulas of the recommended cross section [6]. All of the rate constants of the remaining reactions are calculated by using the Patel's data [1]. Figure 1 shows the rate coefficients of all reactions used in the present model depending on the electron temperature.

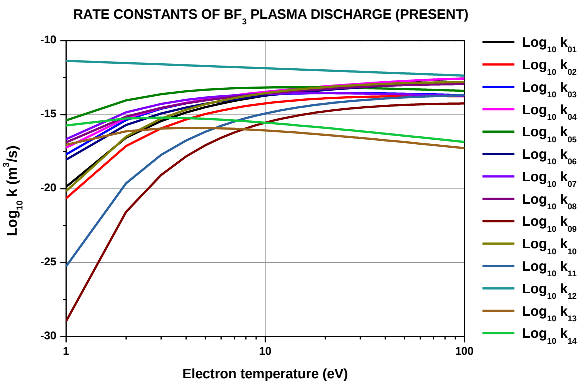


Fig. 1. Rate coefficients of reactions used in the present model.

According to the assumptions in the present model, we formulate the particle balance equations for all neutral and ion species as following [1,2,7] :

$N_3 n_e k_{07} + k_{14} n_4 n_e - N_1 n_e k_{08} - N_1 n_e k_{09} - \gamma\, N_1/T_1 = 0$ (1)

$N_5 n_e k_{02} + N_5 n_e k_{03} + N_4 n_e k_{05} + N_3 n_e k_{07} + k_{14} n_4 n_e + k_{13} n_5 n_e + k_{12} n_6 n_e - N_2 n_e k_{10} - \gamma\, N_2/T_2 = 0$ (2)

$N_4 n_e k_{05} + k_{13} n_5 n_e - N_3 n_e k_{06} - N_3 n_e k_{07} - \gamma\, N_3/T_3 = 0$ (3)

$N_5 n_e k_{03} + k_{12} n_6 n_e - N_4 n_e k_{04} - N_4 n_e k_{05} - \gamma\, N_4/T_4 = 0$ (4)

$N_1 n_e k_{08} - n_1 n_e k_{11} - n_1/\tau_1 = 0$ (5)

$N_1 n_e k_{09} + n_1 n_e k_{11} - n_2/\tau_2 = 0$ (6)

$N_2 n_e k_{10} - n_3/\tau_3 = 0$ (7)

$N_3 n_e k_{06} - n_4/\tau_4 - k_{14} n_4 n_e = 0$ (8)

$N_5 n_e k_{02} + N_4 n_e k_{04} - n_5/\tau_5 - k_{13} n_5 n_e = 0$ (9)

$N_5 n_e k_{01} - n_6/\tau_6 - k_{12} n_6 n_e = 0$ . (10)

The charge and particle number conservations are [1,2,7] :

$n_1 + \frac{1}{2} n_2 + n_3 + n_4 + n_5 + n_6 = n_e$ (11)

$N_1 + n_1 + n_2 + N_3 + n_4 + N_4 + n_5 + N_5 + n_6 = N_0 = p/kT_0$ (12)

$N_2 + n_3 + N_3 + n_4 + 2N_4 + 2n_5 + 3N_5 + 3n_6 = 3N_0 = 3\,p/kT_0$ (13)

where $N_1$, $N_2$, $N_3$, $N_4$, $N_5$ are the densities of B, F, BF, $BF_2$, $BF_3$, respectively; $n_1$, $n_2$, $n_3$, $n_4$, $n_5$, $n_6$ are the densities of $B^+$, $B^{++}$, $F^+$, $BF^+$, $BF_2^+$, $BF_3^+$, respectively; $T_1$, $T_2$, $T_3$, $T_4$ are the transit times of B, F, BF, $BF_2$ across the chamber, respectively; $\tau_1$, $\tau_2$, $\tau_3$, $\tau_4$, $\tau_5$, $\tau_6$ are the containment times of $B^+$, $B^{++}$, $F^+$, $BF^+$, $BF_2^+$, $BF_3^+$, respectively; and the containment times of B, F, BF, $BF_2$ would be $T_1/\gamma$, $T_2/\gamma$, $T_3/\gamma$, $T_4/\gamma$; γ is the sticking factor of B, F, BF, $BF_2$ at the wall; p is the $BF_3$ gas pressure; $T_0$ is the ion and neutral temperature (= 600 K); $n_e$ is the electron density; $N_0$ is the density of $BF_3$ molecules before discharge.

In the equations which are expressed above, we consider the ratio of $\tau_1$, $\tau_2$, $\tau_3$, $\tau_4$, $\tau_5$, $\tau_6$ to be the ratio of the square root of the respective ion masses, and also consider the ratio of $T_1$, $T_2$, $T_3$, $T_4$ to be the ratio of the square root of the respective atomic or molecular masses [2,7]. $\tau_1$ and $T_1$ are calculated as two unknown variables.

## 3. Preliminary results

As preliminary results, we calculate the dependence of ion species fractions on plasma density, gas pressure without considering the relation between pressure and electron temperature. Figure 2 illustrates the ion species fractions when changing the plasma density from $10^{15}$ $m^{-3}$ to $10^{19}$ $m^{-3}$ at fixed operating pressure p = 20 mTorr, the recombination coefficient and the electron temperature are set as γ = 0.1 and $T_e$ = 3 eV, respectively [2]. We can see that the ion species fraction is greatly influenced by the plasma density. When the plasma density increases, the ion species fractions of $B^+$, $F^+$, $BF^+$, and $BF_2^+$ increase, while the ion species fraction of $BF_3^+$ decreases significantly, indicating the $BF_3^+$ is negligible at very high plasma density regime. The ion species fraction of $BF_2^+$ is always higher than that of $B^+$, $B^{++}$, $F^+$, and $BF^+$.

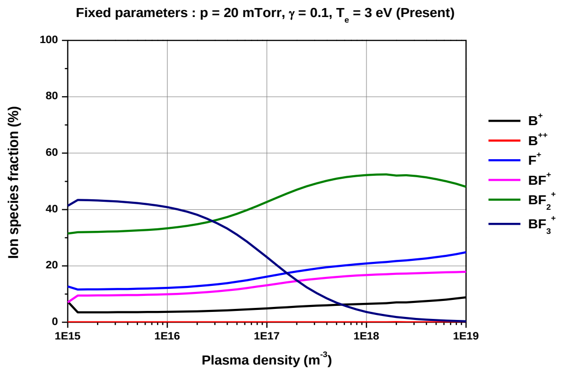


Fig. 2. The dependence of ion species fractions on plasma density.

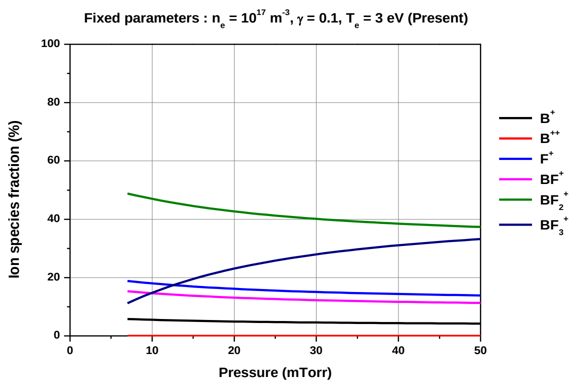

Fig. 3. The dependence of ion species fractions on gas pressure.

Figure 3 shows the ion species fractions when the operating pressure is changed from 7 to 50 mTorr. The setup parameters are : $n_e = 10^{17}$ $m^{-3}$, $\gamma = 0.1$, $T_e = 3$ eV. We can see that when the gas pressure increases, the ion species fractions of $B^+$, $F^+$, $BF^+$, and $BF_2^+$ decrease, while the ion species fraction of $BF_3^+$ increases dramatically. The ion species fraction of $BF_2^+$ is still higher than that of $B^+$, $B^{++}$, $F^+$, and $BF^+$ for all gas pressure values.

## 4. Conclusions and Future work

In this paper, we have developed the global model for $BF_3$ plasma discharge which is widely used in plasma processing. The preliminary results show the great dependency of ion species fraction on the change of the conditions such as the plasma density (while the setup parameters are operating pressure, recombination coefficient and electron temperature) and the operating pressure (while the setup parameters are plasma density, recombination coefficient and electron temperature). In the future, we will add the power balance equation for determining the plasma parameters self-consistently and consider the effect of the external magnetic field.

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