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# Kinetic Modeling of the Decomposition of PFCs in Electron-Beam-Generated Atmospheric-Pressure Plasmas
# 電子ビーム生成大気圧プラズマによる PFC 分解のモデル

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A kinetic model demonstrating the decomposition of $CF_4$ by using atmospheric-pressure low-temperature argon plasma generated by pulsed electron beam is developed. The validity of the model is verified by comparison of the removal efficiencies of $CF_4$ using the kinetic simulation with the recent experiment [Jpn. J. Appl. Phys. **47**, 5681 (2008)]. The result shows that the principal processes of $CF_4$ decomposition are the reactions of ion and metastable argon not impacting electron.

## 1. Introduction

The electron-beam (e-beam) generated plasmas have been widely used for control of the fuel gases and volatile organic compounds [1, 2, 3]. Recently, the removal of perfluoro compounds (PFCs) such as $CF_4$ and $C_2F_6$ becomes important for the abatement of greenhouse gases from semiconductor facilities. Non-thermal plasma technology by discharges has been applied for the decomposition of PFCs [4]. Atmospheric plasma abatement system for PFCs using microwave has been used commercially. In addition, various methods have been investigated, for example high temperature plasmas such as water plasmas [5] and additional fuel hybrid plasmas [6, 7].

The decomposition of $CF_4$, which is the most difficult compounds in PFCs, by using atmospheric-pressure, non-thermal plasmas generated by pulsed electron beam was experimentally demonstrated [8, 9]. The results show that the removal efficiencies of the pulsed-electron-beam method are comparable to or higher than those of corona discharge methods.

The reactions of ions and excited atoms with PFCs is the principal decomposition process in e-beam-generated plasmas because most energetic electrons interact with the buffer gas due to dilute concentration of PFC. The reaction of $CF_4$ with metastable argon is also important in e-beam generated argon plasmas [10, 11].

Based on the assumption of the above decomposition reactions, we have developed a kinetic model demonstrating the decomposition of $CF_4$ in argon gas [12, 13]. The simple kinetic models are commonly used for the treatment of the excimer lasers [14] and flue gas cleaning by irradiation with e-beams [1]. The validity of the kinetic model of the decomposition of $CF_4$ has not yet been verified by the experimental data. It is impossible to consider every chemical reaction in kinetic model. In addition, all rate coefficients generally include uncertainties. Therefore, the verification of the model is important by experimental data. It is also important to optimize the concentration of additives such as $H_2O$, $O_2$ in gas phase reaction.

In this paper, we apply the kinetic model to the previously reported experimental $CF_4$ decomposition using atmospheric-pressure non-thermal argon plasma generated by pulsed electron beam [8]. We compare the removal efficiencies of $CF_4$ obtained in this experiment with those using the kinetic model simulation.

## 2. Verification of simulation model

A computational method based on the kinetic model of $CF_4$ in argon gas, using $H_2O$ as an additive gas under pulsed-e-beam irradiation, was used. This method employs a zero-dimensional kinetic model of a gas phase reaction. The details of the kinetic model are provided in our previous papers [12, 13]. However, the validity of the kinetic model has not yet been verified by the experimental data. The decomposition of $CF_4$ by using atmospheric-pressure, non-thermal argon plasma generated by pulsed e-beams was experimentally reported [8]. In this section, we verify the model by comparing the $CF_4$ removal efficiencies of the resent experiment with those of the model simulation.

First, our experiment [8] is briefly reviewed. Decomposition experiment using argon gas under satu-

rated water vapor conditions was conducted at a total pressure of 130 kPa and an initial $CF_4$ concentration of 1000 ppm. The e-beam pulse duration was 80 ns and the input energy density in the irradiated volume per pulse was 25 mJ/cm$^3$ which is estimated from the pressure-jump method. Therefore, an error is approximately ±10% considering radiation loss. [8] And an error of the concentration of $CF_4$ is less than 10 ppm. The interval between shots was 5.3 s and the total shot number of the e-beam irradiation was 2671. The total gas volume was 58 L and the gas volume irradiated by the e-beam was approximately 10 L. The gas was circulated through a water reservoir at a gas flow rate of 5 L/min; thus, the gas flow between shots was 0.44 L. Therefore, the gas remained in the irradiated volume for 23 shots. The products are removed by gas circulation through a water reservoir with calcium hydroxide.

Second, the kinetic model simulation condition for the experiment is shown. The total gas density, which corresponds to a total pressure of 130 kPa at 293 K, was $[Ar] + [CF_4] + [H_2O] = 3.2 \times 10^{19}$ cm$^{-3}$, where [X] is the number density of X, $[CF_4] = 3.2 \times 10^{16}$ cm$^{-3}$. The $H_2O$ concentration of saturated water vapor depends strongly on the gas temperature. The saturated vapor pressures are 2.3 kPa at 293 K, corresponding to $H_2O$ concentrations of 1.8%, namely, $[H_2O] = 5.8 \times 10^{17}$ cm$^{-3}$. We assumed that the input e-beam had a square pulse with a pulse duration of 80 ns and an input energy density per pulse of 25 mJ/cm$^3$. To model the gas circulation, we removed the gases, except for $CF_4$ and $H_2O$, after 23 shots of irradiation. The density of $CF_4$ was maintained and the density of $H_2O$ was restored to the initial density. We assumed a 1-ms interval between pulses to save computational time, because the reactions terminate within 0.1 ms when $H_2O$ is used as the additive gas [12].

Figure 1 shows the experimental and simulated removal efficiencies of $CF_4$. The experimentally obtained removal efficiency values are denoted by closed circles and its error is approximately ±10%. The solid line shows the simulation results. The removal efficiencies obtained by the simulation agree reasonably well with those obtained experimentally. It shows that main decomposition of $CF_4$ in the experiment can be explained by reactions with the ions and metastable atoms of argon.

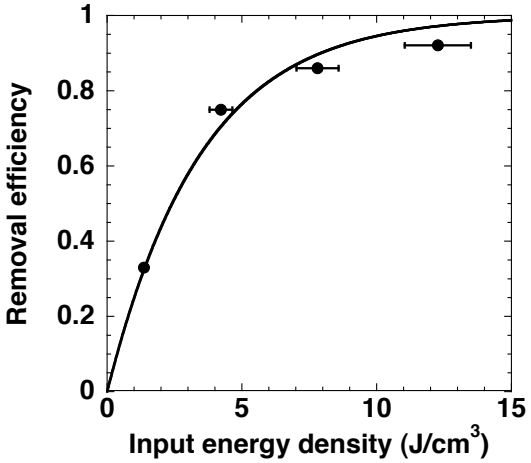


Fig. 1 Removal efficiency as a function of input energy density. Lines represent the simulation results. Closed circles show the experimental data and an error of input energy is approximately ±10%.

## 3. Conclusion

A kinetic model of $CF_4$ decomposition in an argon gas using e-beam was proposed. We verified the model by comparison of the removal efficiencies of $CF_4$ with the recent experiment [8].

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