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Decomposition of Halide Compounds by Nonequilibrium Discharge

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A narrow-gap silent discharge has been successfully applied to the resolution of halide compounds (CCl_2F_2 and CF_4) diluted in mixed gases of H_2O, O_2, N_2 and Ar with a varied composition at an atmospheric pressure. The optimum composition of the discharge gas is discussed in terms of an effective decomposition energy E_d defined as the energy necessary for e^{-1}-fold reduction of the halide concentration. Efficient decomposition of CF_4 gas is realized with the use of Ar gas as the dilution gas; the minimum value of E_d approaches 760 eV/CF_4-molecule, which must be compared with the value of 18 keV/CF_4 obtained when N_2 is used as the dilution gas.

KEYWORDS: narrow-gap silent discharge, halide compound, decomposition, dilution gas, decomposition energy

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1. Introduction

Halide compounds(CF_4, C_2F_6, SF_6, etc.) are widely used as washing agents for plasma CVD and etching tools, as additives, and for other purposes in semiconductor and liquid crystal factories. Although the amount handled is rather small, they have very high absorption coefficients for infrared radiation and very long life spans in the atmosphere1). Therefore, it has been declared in the Kyoto Protocol to the United Nations Framework Convention on Climate Change, 1997, that their emission by 2010 should be decreased to below 90% of their levels in 1990.

It appears to be rather difficult to find a chemical reaction transforming the halide compounds into matter less harmful to the environment. Another solution might be collecting them for recycling. A hollow thread filter has been developed for this purpose2,3). The purity of the collected halide compounds is about 90%, however, and it seems rather difficult to remove the byproduct, hydrogen fluoride (HF), to attain the 99.9% purity needed for recycled use. A third solution is resolution by combustion heat either without4) or with a catalyst5), or by plasma6).

To decompose the halide compounds efficiently, it is desirable to locate a decomposition device just downstream of the CVD/etching tool, where halide compounds of high purity are available for the formation of a low-pressure plasma. In such a case, however, a slight change in the downstream pressure could cause undesirable effects to the CVD/etching process. Therefore, the decomposing device must be located at the exit of the vacuum pump system, where the halide compound is diluted to a concentration of about 1000 ppm in a dilution gas introduced for the purpose of preventing corrosion and overheating; the flow rate of this gas is about 10 slm at an atmospheric pressure.

Currently, there are a few discharge schemes that generate a plasma under atmospheric pressure: corona discharge, arc discharge, silent discharge and microwave discharge. To dissociate the halide, a nonequilibrium plasma with a relatively small amount of high-energy electrons seems to be preferable to a thermal plasma with a temperature higher than 1000 K, from an energy point of view.

In the present work, a silent discharge7) is applied to the deformation of the halide compounds, Freon12 (CCl_2F_2) and perfluorocarbon (PFC; CF_4), and the efficiency together with the molecular processes involved is discussed.

2. Experimental apparatus

Electrons in the discharge plasma are expected to collide with halide molecules to directly dissociate them to Cl and/or F atoms. If they are diluted in a dilution gas, the discharge energy is also dissipated by the dilution gas molecules to form excited and/or dissociated molecules, which in turn react not only with the halide molecules to decompose them but also with the decomposition products to reproduce the halide molecules. It is necessary to convert them to more stable compounds as soon as possible to minimize the resynthesis of the halide molecules. For the purpose of fixing them to HF, HCl and CO_2, H_2O and O_2 are added to the dilution gas[6)].

The experimental device is shown schematically in Fig.1. The halide compound and a dilution gas, N_2 or Ar, are fed in an electric discharge chamber through a mass-flow controller (MFC). Water vapor necessary for conversion to the stable products is fed either through branching pipes or a bubbler with a moisture meter to have a concentration of up to 5%. The discharge system is essentially the same as that used in ref. (7). As shown in Fig. 1-b, the discharge electrodes consist of a pair of 200-mm-diameter discs facing each other with a spacing of 0.4 or 0.5 mm depending on the thickness of the fan-shaped spacer. The upper electrode is made of ceramics with a Au layer on the outside surface, while the lower electrode with a circular hole in its center is cooled by water.

The halide compounds are supplied from the central aperture. A 300 V-3 kW-10 kHz power supply provides an AC electric field across the gap ranging from 100 to 500 Td for the working gas at 8×10^4 Pa.

An aliquot of the exhaust is extracted at the sampling point (SP) for composition analysis with either a gas chromatograph mass analyzer (GCMS; HP6890GC) or an Fourier transform infrared absorption spectrometer (FTIR; MIDAC-IGA2000). In the former the capillary column used is a 0.32-mm-o.d., 50-m-long and 8-μm-thick film of Al_2O_3 (HP-PLOT). The decomposition efficiencies for Freon12 and PFC are examined as a function of the input power, dilution gas species, H_2O concentration, and other parameters.

The bulk exhaust is fed through a 1.25 g/L solution of calcium hydroxide to collect and neutralize the HCl and HF products before being purged into the atmosphere by an air pump with a capacity of 20 slm.

3. Results and Discussion

3.1. Decomposition of CCl_2F_2

First, decomposition of Freon12 has been examined to find the optimum concentration for the H_2O additive. The measurements of the CCl_2F_2 concentration were performed as a function of the discharge power for cases of different flow rates of Freon12 ranging from 0.1 to 2 sccm diluted in N_2 or air with a fixed flow rate of 0.5 slm. The results of several runs are summarized in Fig. 2. Here, the concentration of a CCl_2F_2 molecule normalized to that before the application of the discharge treatment is plotted as a function of the normalized energy E_n which is equal to the discharge power divided by the flow rate of CCl_2F_2, which results in an averaged or reduced energy deposited per one CCl_2F_2 molecule. Shown in Fig. 2 are the cases in which the fractional concentrations (%) of [CCl_2F_2, H_2O, O_2, N_2] are (a) [0.019, 0.25, 0, 99.7], (b) [0.095, 0.25, 0, 99.7], (c) [0.38, 0.25, 0, 99.4] and (d) [0.38, 0.25, 20.7, 77.3]. In the last case, dry air was used for the dilution gas, and therefore the difference between the sum of the fractions and 100% is attributed to Ar and other constituents of air.

In the figure, the thin lines connecting the data points are only guides for the eye, while the thick lines are those best fitted to the measured values in cases (a), (b) and (d). The fitting lines show an exponential dependence of the residual amount of CCl_2F_2 molecules on the energy deposited that is proportional to the electron density in the discharge plasma. The exponentially decreasing concentration of the reactant is well explained by the following model.

The molecules in the discharge volume of 12 or 15 cm^3 are refreshed every 36 or 45 ms even at the maximum gas flow rate of 20 slm employed in the present work. Since the transit time is sufficiently longer than the time required for field reversal, 0.05 ms, we can discuss the phenomena in terms of temporally averaged values of the discharge parameters. As the discharge power or the discharge current is increased, the averaged electron density in the ischarge volume, i.e., the number of electrons available for decomposition of the halide molecules, increases.

In the steady state discharge condition, variation in the CCl_2F_2 density n_f is described by the conventional rate equation with only decomposition by electron impact taken into account. Since the gas flow rate is moderate throughout the present experiments, we might assume that there is no density gradient along the radial direction in the absence of discharge. Integrating the rate equation over the discharge volume of the outer radius r, the inner radius R_0 and the gap d, we have, with the help of the Gauss divergence theorem,

$$\frac{n_\mathrm{f}}{n_\mathrm{f0}}F = F - \int_{R_0}^{r} n_\mathrm{e} n_\mathrm{f} \langle \sigma v \rangle 2\pi r\, d\, \mathrm{d}r, \tag{1}$$

where n_e is the electron density, σ is the effective cross section of reactions resulting in decomposition of the CCl_2F_2 molecule, $<\sigma v>$ is the decomposition rate coefficient averaged over the electron velocity distribution function, n_f0 and F (= $2\pi R_0 d n_\mathrm{f0} v_\mathrm{d0}$) are the CCl_2F_2 density and the flow rate (with v_d0 being the drift velocity at the entrance), and $r = R_0$, respectively. By solving a differential equation deduced from eq. (1), we have a solution at the exit, $n_\mathrm{f}(R)$, where

$$n_\mathrm{f}(R) = n_\mathrm{f0} \exp\left\{ -\frac{n_\mathrm{e}\langle \sigma v \rangle}{2R_0\, v_\mathrm{d0}} \left(R^2 - R_0^2 \right) \right\}, \tag{2}$$

which shows its exponential dependence on n_e. In discussing the experimental results, it is convenient to express eq. (2) as a function of the normalized energy E_n that is proportional to n_e. Here we empirically define the characteristic energy as e^{-1}-folding energy, E_d, which is called effective decomposition energy hereafter.

$$n_f(E_n) = n_{f0} \exp\left(-\frac{E_n}{E_d}\right). \tag{3}$$

Since the normalized energy E_n is a product of the effective discharge voltage V and the effective current I divided by the flow rate of the halide compound,

$$E_n = \frac{VI}{F} = \frac{eV\,n_e\,v_e\,A}{2\pi R_0\,d\,v_{d0}\,n_{f0}}. \tag{4}$$

By equating eq. (3) with eq. (2), we have the effective decomposition energy E_d expressed as

$$E_d = \frac{eV\,v_e}{d\langle\sigma v\rangle n_{f0}}, \tag{5}$$

where v_e is the averaged velocity of electrons traveling across the gap~~,~~ and $A = \pi(R^2 - R_0^2)$ is the electrode area. Equation (5) predicts an inversely proportional dependence of E_d on the initial concentration of the halide compound n_{f0}.

Although the C-Cl and C-F bond energies are 3.4 and 5.0 eV, respectively, Fig. 2 shows that a much greater amount of energy is necessary to decompose CCl_2F_2. The energy given to the N_2 dilution gas results in excited molecules, dissociated atoms and ionized molecules/atoms. Most of them eventually return to N_2, resulting in an elevated temperature in the bulk, while some fraction of the products might react with intermediate decomposition products to reproduce CCl_2F_2.

Comparing case (b) with case (a), we see an improvement in decomposition efficiency when the CCl_2F_2 concentration is increased: the effective decomposition energy E_d is reduced from 410 to 240 eV/CCl_2F_2. Although this is in qualitative agreement with eq. (5), the dependence on n_{f0} is rather moderate. The reason is that the reaction rates of CCl_2F_2 reproduction are appreciable. In case (c), which is at even higher concentrations, however, decomposition does not proceed to over 90%. This is because the reactant H_2O is stoichiometrically insufficient to fully develop the conversion reaction:

$$CCl_2F_2 + 2H_2O \rightarrow 2HCl + 2HF + CO_2. \tag{6}$$

The addition of O_2 in case (d) significantly improved the efficiency, with E_d being further reduced to 150 eV/CCl_2F_2. This implies the importance of fixing the intermediate products of the decomposition reaction to the final ones. The addition of H atoms was still necessary to reach the stoichiometric concentration, which would have further improved the efficiency. However, the addition in the form of H_2O resulted in a decreased efficiency. This could have been due to a short circuiting of the diode. In summary, it should be noted that a deficiency of hydrogen by about 30% does not always result in imperfect decomposition of CCl_2F_2 if the stoichiometric amount of oxygen is supplied.

3.2. Decomposition of CF_4

In examining the decomposition of CF_4, the discharge gap d was enlarged to 0.5 mm so that the applied potential could withstand an even higher humidity. It was confirmed that gap distances ranging from 0.1 mm to 0.5 mm do not influence the decomposition efficiency appreciably. A decrease in the electric field caused by an increase in the gap distance is compensated by an increase in the time of stay in the discharge area.

As in the case of CCl_2F_2, H_2O was added to the CF_4 gas diluted in N_2 or Ar gas to convert the halide to HF through the reaction.

$$CF_4 + 2H_2O \rightarrow 4HF + CO_2. \tag{7}$$

The molar amount of H_2O needed for perfect conversion to HF is stoichiometrically twice that of CF_4. The experimental results show that the most suitable ratio for CF_4 reduction is around 1. This is shown in Fig. 3, where the residual amount of CF_4 is plotted as a function of the H_2O/CF_4 ratio for a variety of N_2 gas flow rates at a fixed flow rate of 15 sccm CF_4 and a fixed discharge power of 1 kW. A possible reason for the decreasing efficiency with increasing H_2O/CF_4 ratio above 1 might be that some of the intermediate products of the CF_4 decomposition process have a large reaction rate with H_2O, leading to a resynthesis of CF_4. This reaction seems to be rather complicated, since the reaction rate constant depends also on the N_2 density, as shown in Fig. 3: the resynthesis reaction rate is an increasing function of N_2 density. At present we have no knowledge of the details of the mechanism.

The decomposition efficiency was examined as functions of the discharge power in a range of 0.3 – 3 kW as well as the N_2 flow rate ranging from 0.15 to 20 slm. The CF_4 concentration was 3.3% in cases of 0.15 – 1.5 slm and 500 ppm for 20 slm, with the fixed ratio of H_2O/CF_4 =1. The results are summarized in Fig. 4, where the normalized density of CF_4 is plotted as a function of the normalized energy E_n, or the reduced energy deposited per one CF_4 molecule. In the cases of low flow rate, the effective decomposition energy E_d ranges from 2.9 – 4.0 keV/CF_4, which are substantially larger values than those for CCl_2F_2

decomposition. This implies that CF_4 decomposition is much more difficult to obtain than CCl_2F_2 decomposition. In the case of the higher flow rate, which is the condition thought necessary for application to practical devices, the efficiency becomes still lower, with E_d being 18 keV/CF_4. The degradation of the effective decomposition energy can be accounted for by the increased energy loss to the dilution gas N_2. Further reduction of the residual amount of CF_4 by two orders of magnitude requires a discharge power reaching 60 kW. Another condition of discharge should therefore be examined.

In view of the large energy loss to the dilution gas and possible reactions of the intermediate products with N_2 molecules and/or their radicals, selection of a monatomic inert gas would be much more effective for the reduction of the discharge power required. The N_2 gas has been replaced by Ar for this purpose. The results are shown in Fig. 5 for the cases in which the flow rates of [Ar, CF_4, H_2O] in slm are [0.3, 0.01, 0.01] and [20, 0.01, 0.01]. As was expected, we found a substantially improved efficiency. The effective decomposition energy E_d decreased to E_d = 760 eV/CF_4. This should be compared with the values for N_2 dilution: E_d = 2.9 keV/CF_4 and 18 keV/CF_4 for the low and high rate of N_2 flow, respectively, with almost the same concentration of CF_4. A modest discharge power of 2.5 kW would reduce the concentration of CF_4 supplied with the flow rate of 10 sccm by two orders of magnitude.

The deduced values of E_d are summarized in Table 1 and plotted in Fig. 6 as a function of the halide concentration for the cases of CCl_2F_2 diluted in N_2, CF_4 in N_2, and CF_4 in Ar. As was discussed earlier, E_d for CCl_2F_2 diluted in N_2 decreases with increasing initial halide density n_{f0} (or concentration in the present case). However, E_d for CF_4 in N_2 does not have a similar dependence on n_{f0} when it is supplied with a fixed concentration of 33,000 ppm in the dilution gas N_2. The anticipated decrease in E_d with increasing n_{f0} seems to be compensated by an increased energy loss to N_2 gas molecules, i.e., molecular ionization, dissociation, vibrational and rotational excitation, etc., in addition to atomic ionization and excitation.

In the case of CF_4 in Ar, on the contrary, we see little change in E_d when the dilution gas flow rate is increased from 0.3 to 20 slm with the same halide density n_{f0}. This means that successive supplies of the flesh Ar do not increase the energy loss to Ar that has atomic energy levels only. It has been demonstrated that Ar dilution is highly efficient for CF_4 decomposition, although CF_4 is rather difficult to decompose compared with CCl_2F_2.

It is interesting to note that E_d for the two cases of N_2 dilution have the same functional dependence on the concentration, and E_d for CF_4 in N_2 is extrapolated to 860 eV/CF_4 at 100% concentration. This value is very close to the E_d =760 - 800 eV/CF_4 value found in the case of the Ar dilution. This implies that the deterioration of the effective decomposition energy is solely due to energy losses to molecules, and that E_d =760 - 800 eV/CF_4 would be close to the minimum value to decompose CF_4 in all cases of possible selection of the dilution gas.

Finally, the effect of gas temperature on the decomposition process is discussed. It is estimated that a thermal plasma with a temperature exceeding 2300 K would have been needed to decompose CF_4 if it had not been for electron impact dissociation and ionization. Since the electrodes are cooled with water in the present experiments, the rise in gas temperature is considered to be modest. A heat transfer calculation shows that N_2 and Ar gas temperature remains at about 340 K and 380 K, respectively, under 1 kW operation with the electrodes cooled by water. Therefore, the difference in the effective decomposition energy for CF_4 between the dilution gases is not significantly explained by the temperature difference.

4. Conclusion

The narrow-gap silent discharge has been successfully applied to the decomposition of halide compounds diluted in N_2 and/or Ar at atmospheric pressure with H_2O and/or O_2 added as fixers to the final products, HF, HCl and CO_2. The effective decomposition energy E_d has been defined as the energy necessary for the e^{-1}-fold reduction of the halide concentration. It has been found that the observed minimum values of E_d are 150 eV/CCl_2F_2-molecule diluted in N_2 gas and 760 eV/CF_4 in Ar.

The most important issue with attaining high decomposition efficiency is the removal of the intermediate products so that they can be fixed to stable molecules, HF, HCl and CO_2. The addition of H and O atoms in the form of H_2 and O_2, which are less stable than H_2O, would further improve the efficiency and has the additional merit of having no possibility for condensation and consequent breakdown. The use of a pulsed power supply[8)] might also improve the efficiency.

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Figure captions

Fig.1. Schematic of experimental apparatus for discharge decomposition of Freon12 and CF_4. In the latter case, the GCMS is replaced by a FTIR equipment. The discharge is operated at a pressure of 8×10^4 Pa.

Fig.2. Decomposition of CCl_2F_2 in dilution gases with a flow rate of 0.5 slm. The normalized concentration of CCl_2F_2 is plotted as a function of the normalized energy, *i.e.*, the discharge power divided by the CCl_2F_2 flow rate. The fractional concentrations of [CCl_2F_2, H_2O, O_2, N_2] are (a) [0.019, 0.25, 0, 99.7] (%), (b) [0.095, 0.25, 0, 99.7] (%), (c) [0.38, 0.25, 0, 99.4] (%) and (d) [0.38, 0.25, 20.7, 77.3] (%).

Fig.3. Optimum concentration of H_2O. The normalized density of CF_4 is plotted as a function of the H_2O/CF_4 ratio in the dilution gas of N_2 with a flow rate ranging from 0.2 to 10 slm. The CF_4 flow rate and the discharge power are fixed to 15 sccm and 1 kW, respectively.

Fig.4. Decomposition of CF_4 diluted in N_2. The normalized concentration of CF_4 is plotted as a function of the normalized energy, *i.e.*, the discharge power divided by the CF_4 flow rate. The respective flow rates of [N_2, CF_4, H_2O] in slm are (a) [0.15, 5×10^{-3}, 5×10^{-3}], (b) [0.3, 1×10^{-2}, 1×10^{-2}], (c) [0.6, 2×10^{-2}, 2×10^{-2}], (d) [1.5, 5×10^{-2}, 5×10^{-2}] and (e) [20, 1×10^{-2}, 1×10^{-2}].

Fig.5. Decomposition of CF_4 diluted in Ar. The normalized concentration of CF_4 is plotted as a function of the normalized energy. The flow rates of [Ar, CF_4, H_2O] in slm are (a) [0.3, 1×10^{-2}, 1×10^{-2}] and (b) [20, 1×10^{-2}, 1×10^{-2}].

Fig.6. Effective decomposition energy E_d for CCl_2F_2 diluted in N_2, CF_4 in N_2, and CF_4 in Ar.

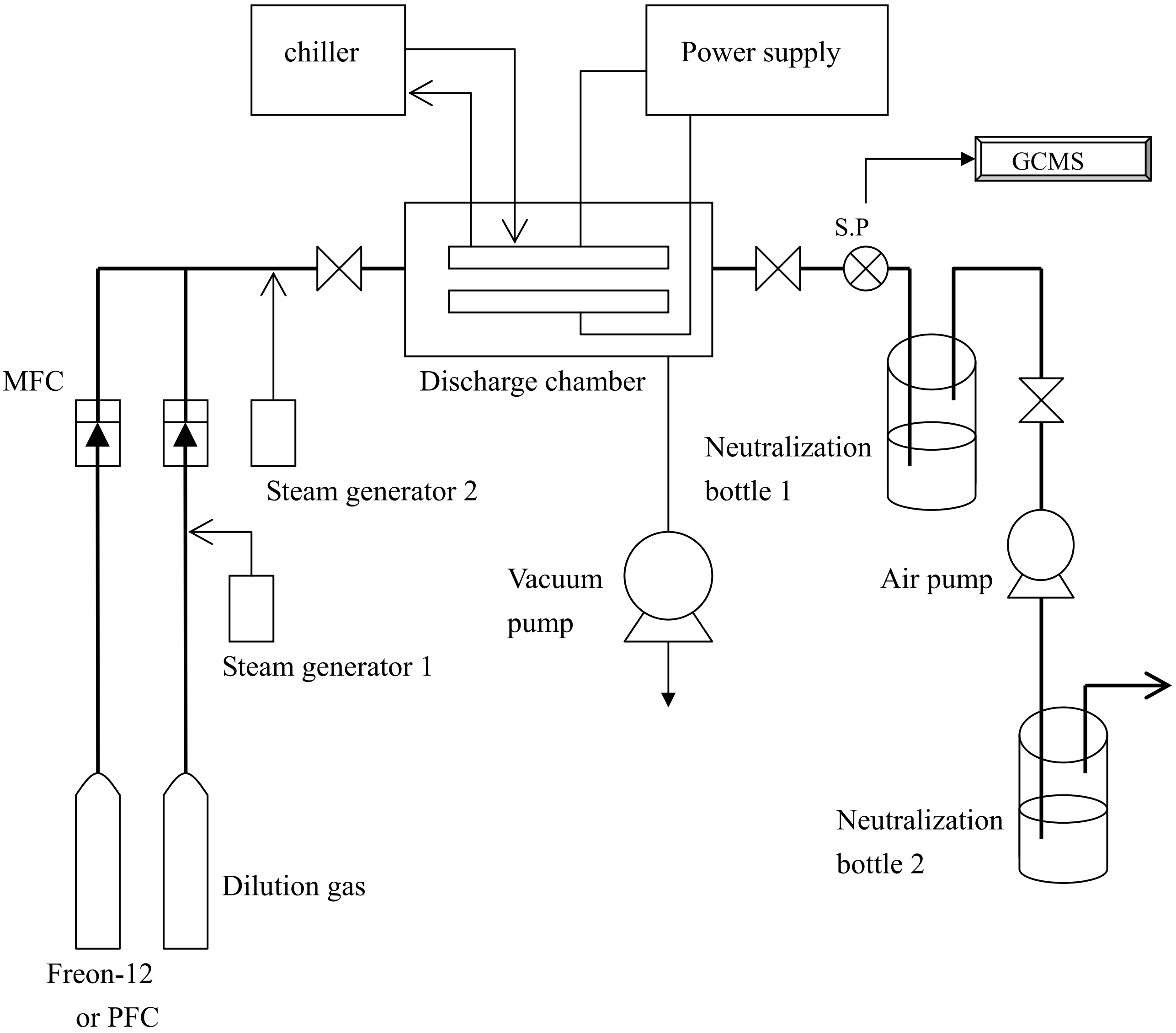

chiller
Power supply
GCMS
S.P
MFC
Discharge chamber
Neutralization bottle 1
Steam generator 2
Vacuum pump
Air pump
Steam generator 1
Neutralization bottle 2
Dilution gas
Freon-12 or PFC

Fig. 1-a

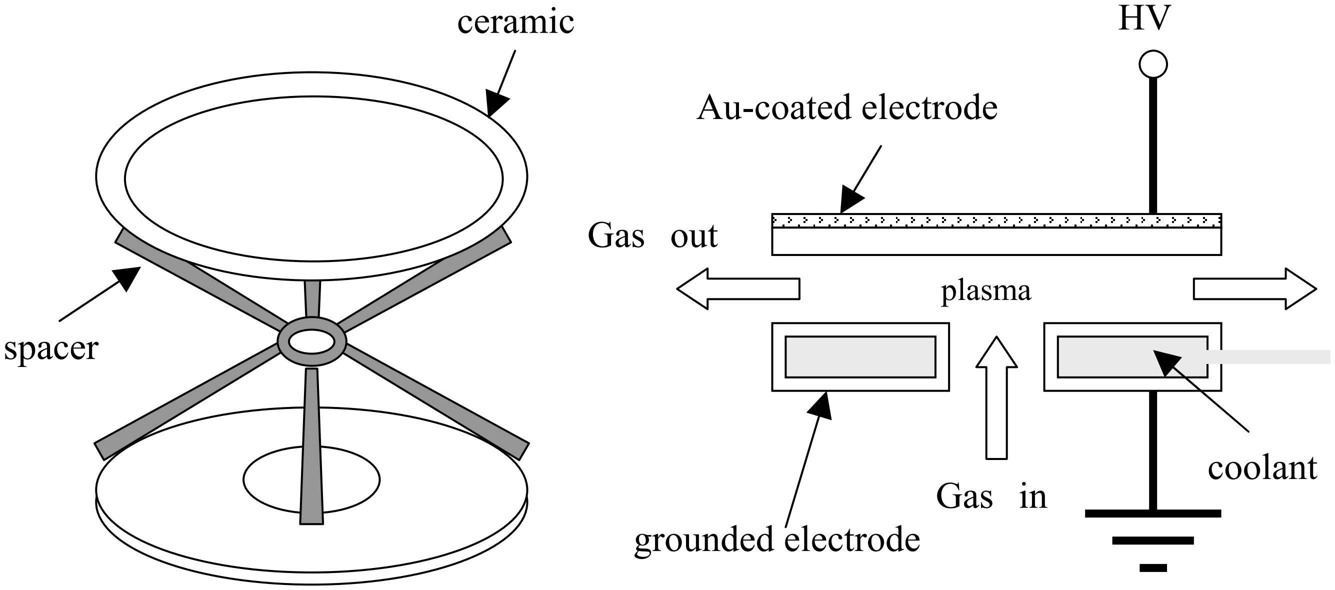

ceramic
spacer
HV
Au-coated electrode
Gas out
plasma
coolant
Gas in
grounded electrode

Fig. 1-b

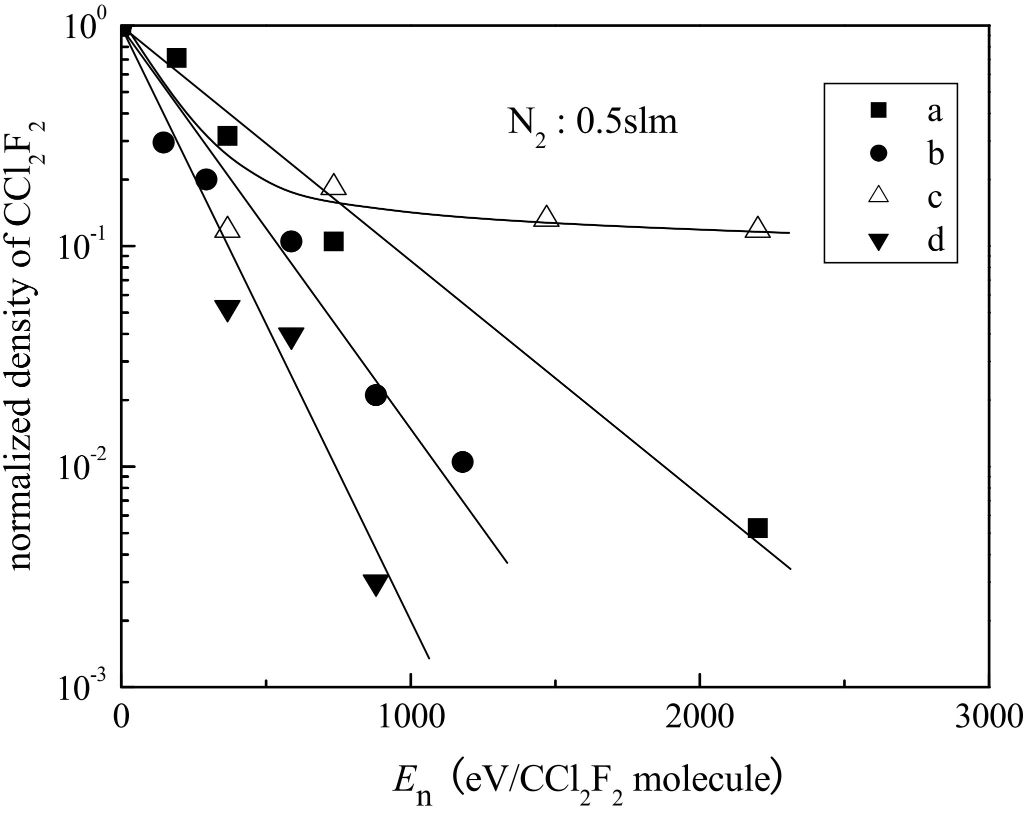
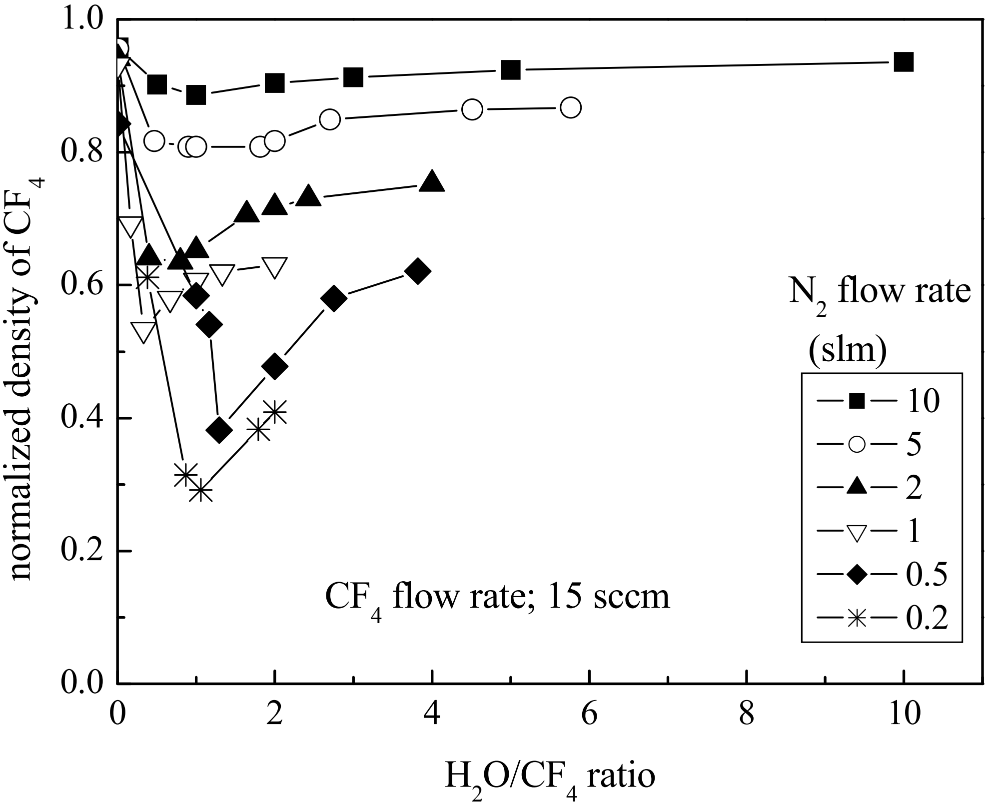

10^0
10^{-1}
10^{-2}
10^{-3}
0
1000
2000
3000
normalized density of CCl_2F_2
E_n (eV/CCl_2F_2 molecule)
N_2 : 0.5slm
■ a
● b
△ c
▼ d

Fig. 2



normalized density of CF_4
H_2O/CF_4 ratio
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
N_2 flow rate
(slm)
—■— 10
—○— 5
—▲— 2
—▽— 1
—◆— 0.5
—✳— 0.2
CF_4 flow rate; 15 sccm

fig. 3

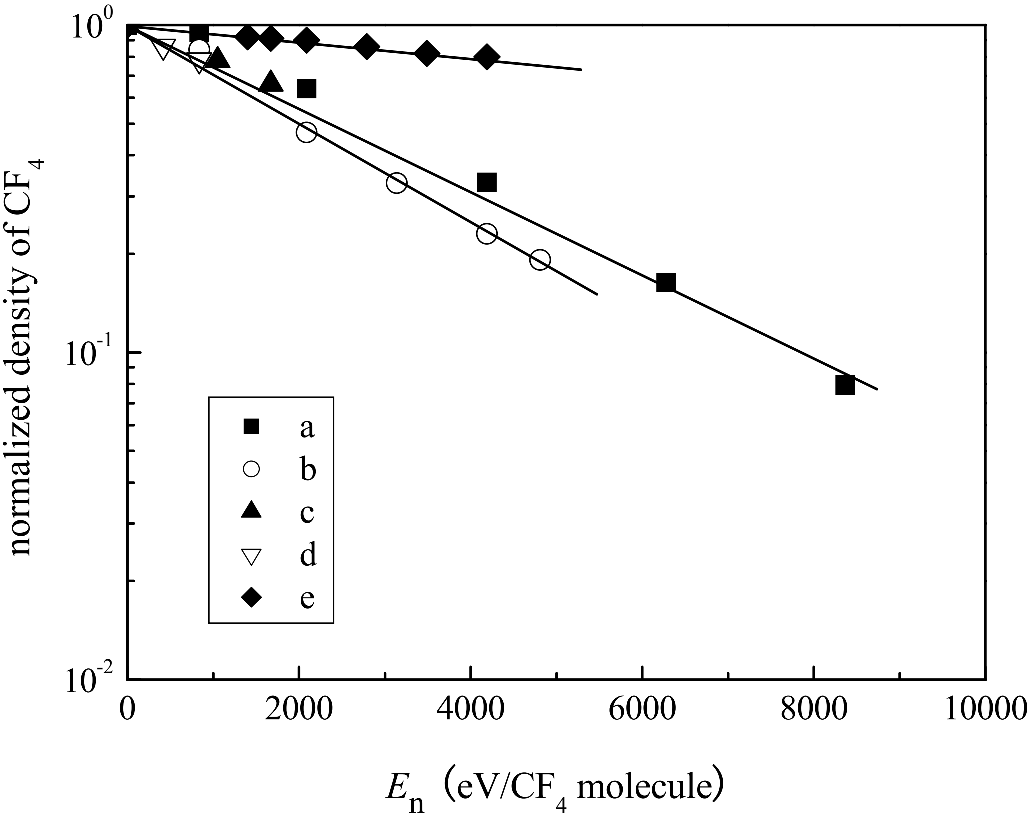

normalized density of CF$_4$
10^0
10^{-1}
10^{-2}
0
2000
4000
6000
8000
10000
E_n (eV/CF$_4$ molecule)
■ a
○ b
▲ c
▽ d
◆ e

fig. 4

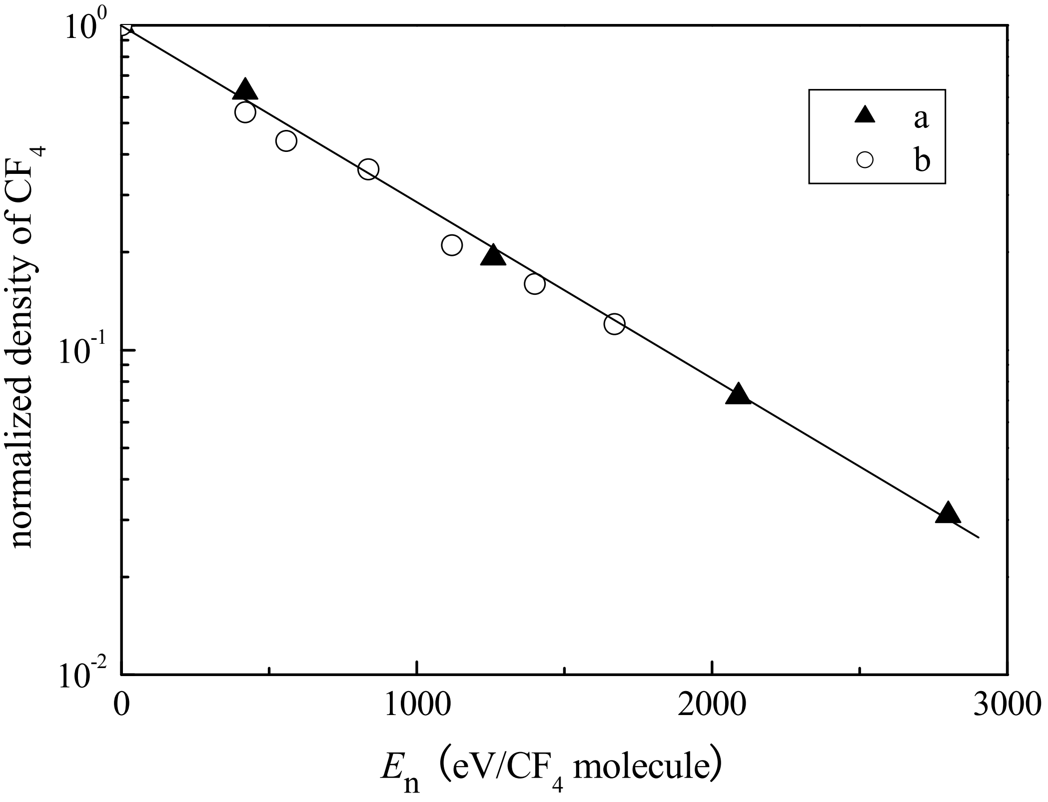

10^0
10^{-1}
10^{-2}
0
1000
2000
3000
normalized density of CF_4
E_n (eV/CF_4 molecule)
▲ a
○ b

fig. 5

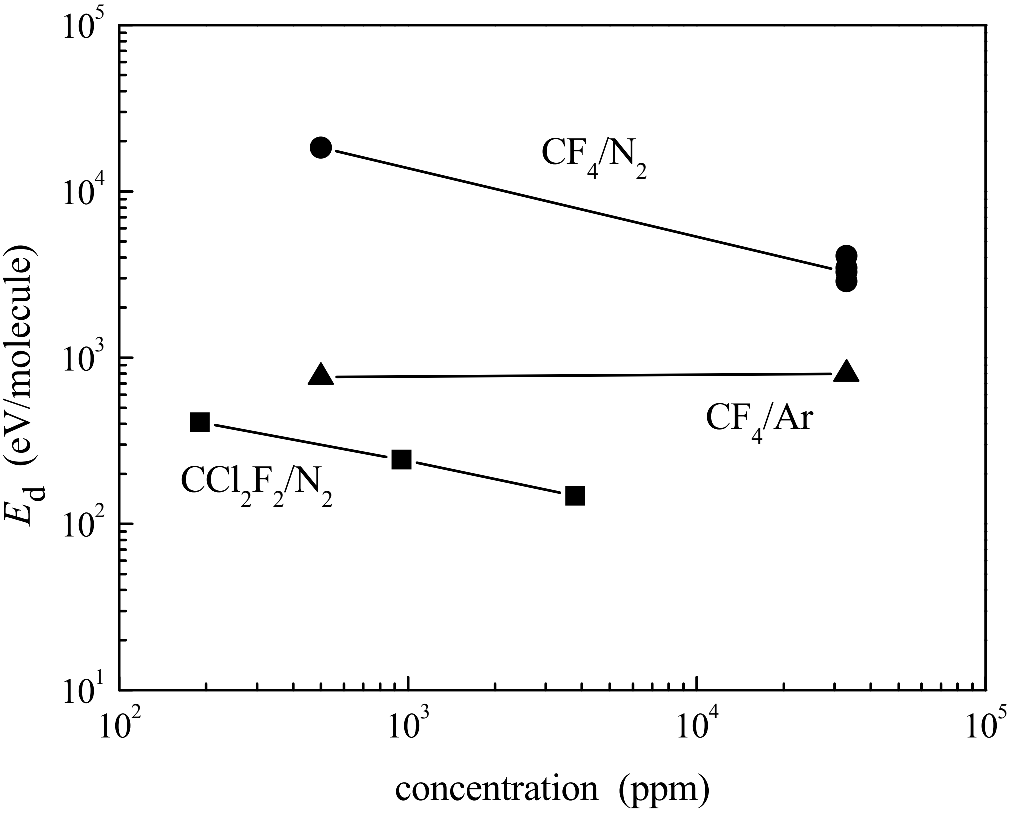

10^5
10^4
10^3
10^2
10^1
E_d (eV/molecule)
CF_4/N_2
CF_4/Ar
CCl_2F_2/N_2
10^2
10^3
10^4
10^5
concentration (ppm)

fig. 6

Table 1. Effective decomposition energy E_d for CCl_2F_2 diluted in N_2, CF_4 in N_2, and CF_4 in Ar.

Dilution gas (slm)		O_2 (slm)	H_2O (sccm)	Halide compound			E_d (eV)
					(sccm)	(ppm)	
N_2	0.5	0	1.3	CCl_2F_2	0.095	190	410
	0.5	0	1.3		0.48	950	240
	0.4	0.1	1.0		1.9	3800	150
N_2	0.15	0	5	CF_4	5	33000	3500
	0.3	0	10		10	33000	2900
	0.6	0	20		20	33000	4100
	1.5	0	50		50	33000	3300
	20	0	10		10	500	18000
Ar	0.3	0	10	CF_4	10	33000	800
	20	0	10		10	500	760