

CF₄ Decomposition by Thermal Plasma Processing

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Abstract—Decomposition of CF₄ was investigated by thermal plasma method. Thermal plasma processes applied to environmental problems have the features of high temperature, high activity and rapid decomposition rate, so it can perfectly decompose non-decomposed materials like CF₄ to a high degree. Before the experiment, thermodynamic equilibrium calculations were performed from 300 K to 5,000 K at atmospheric pressure. Based on the thermodynamic equilibrium calculations, the trends in decomposition and recombination of CF₄ were studied. Decomposition was carried out by injecting mixtures of CF₄ bubbled by Ar, with some addition gases, such as H₂ and O₂, at atmospheric pressure. Experiments were performed to determine the effects of additive gas identity, additive gas dilution, input power, etc. on the decomposition of CF₄. Plasma input power has a slight effect on CF₄ decomposition, and the injection of reacting gas through a torch increased CF₄ decomposition. Supply of H₂ and O₂ as addition gases increased the CF₄ decomposition to 99% for experimental conditions tested.

Key words: CF₄, Thermal Plasma, Decomposition

INTRODUCTION

In the semiconductor industry, PFC_s (Perfluoro Compounds) are widely used for plasma etching and plasma cleaning deposition chambers [Kunihiko, 1996]. In 1996 alone, nearly one million tons was used in the world. But, PFC_s are extremely long-lived compounds, having the ability to persist for a long time in the atmosphere. In addition, they are strong infrared absorbers and have been identified as potentially significant contributors to global warming [Rarishankara, 1993; Breitbart, 1997]. Consequently, at the Conference of the Parties (COP3) in Kyoto, Japan, in December 1997, 159 nations participated in a treaty that would include PFC_s in the basket of greenhouse gases (CO₂, NO₂, CH₄, etc.) subject to emission reductions for nations that ratify the treaty. The agreement confirms to reduce its output of greenhouse gases by years 2,008-2,012 to 7% below 1990 levels [Kyoto Protocol, 1997]. If PFC_s are vented without appropriate treatment as at present, they will be clearly restricted by the Kyoto agreement as another source of exhausting greenhouse gas, and have a high probability of impeding the progress of the semiconductor industry.

Recent technology development for emission gas treatment covers inflammable gases and acid gases only, but most PFC_s are exhausted without any treatment. In addition, the method by which PFC_s are separated and recovered from membranes and low temperature cooling devices after pre-treating inflammable semiconductor waste gas through wet or dry process has been announced [Wofford, 1999; Chen, 1998]. Table 1 summarizes current semiconductor waste gas treatment methods and recently-introduced PFC_s treatment methods.

This research is used to decompose CF₄ gas generated in the semiconductor manufacturing process by thermal plasma. The substances produced after decomposition should become harmless through chem-

ical and physical treatment. Since thermal plasma for treating CF₄ gas generates a very high temperature, it is possible to decompose gas phase materials completely regardless of the gas species [Oh and Park, 2000]. Furthermore, if suitable reaction gas is added, the generating gas can be controlled to select the easiest one among conventional after-treatment methods. Additionally, the treatment process can be simple and cost-effective, which can lead to an advantageous position in the world semiconductor industry.

The main issue of this research is the development of a process to convert CF₄ to low molecular weight materials (CO, CO₂, H₂O, HF, etc.) by applying thermal plasma. In this research, we calculated the thermodynamic equilibrium of CF₄ decomposition and conversion into synthesis gas to obtain the quenching temperature which can give the maximum yield of CF₄ decomposition. In optimum experimental conditions, conversion efficiency is over 99%, and CF₄ should not be recombined.

EXPERIMENTAL

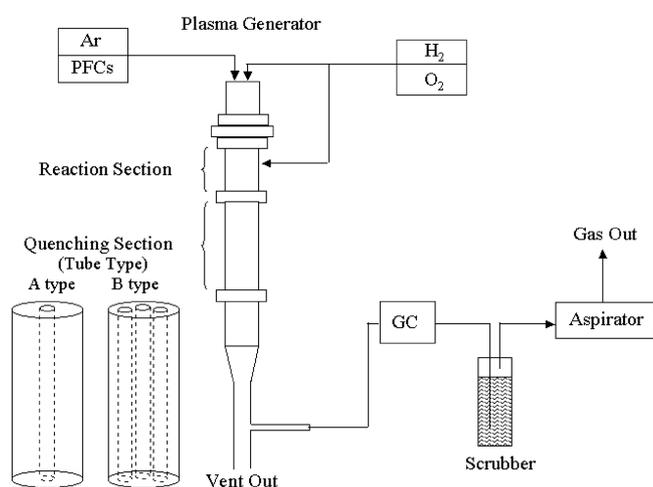
A schematic diagram of experimental apparatus is shown in Fig. 1. The system mainly consisted of a plasma torch, reaction tube, two types of quenching tube (A type and B type), and exhausting part. Plasma was discharged between cathode and anode using Ar gas at atmospheric pressure. The cathode was a tungsten rod of 6 mm diameter and the anode was a copper nozzle of 8 mm inside diameter and 25 mm length. The generated plasma flowed through a reaction tube and then a quenching tube. The reaction tube made up of water-cooled stainless steel was 22 mm of inside diameter and 100 mm long. Since the thermal plasma generator can reach high temperatures to decompose CF₄, the quenching technology to manage the desired quenching temperature is important. The quenching tube was a water-cooled tube and made of copper. Different quenching tube types (A and B type) were applied to investigate CF₄ decomposition efficiency. Reacting gas was mainly injected through the anode nozzle and controlled by flow meter. The final

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Table 1. PFC_s treatment methods

	Treatment method	Merits	Demerits
1	Thermal decomposition	Direct burning: H ₂ , LNG, LPG	- High efficiency - Low operating cost - Big treatment capacity
		Indirect burning: Ceramic heater, Canthal Electric heater	- NO _x generating - Explosion hazard from inflammable gas - PFCs: 80% - Low efficiency
2	Adsorption	Physorption	- Low operating cost
		Catalytic adsorption	- Low efficiency - High operating cost - Small treatment capacity
	Chemisorption	- Low operating cost - Low efficiency	
3	Chemical conversion		- Be limited to SF ₆ , NH ₃ - NO _x generation - High operating cost
4	Recycling		- Low treatment cost - Low separation ability
5	Combination	Thermal decomposition+Chemisorption	- Low operating cost - Low efficiency - Big treatment capacity
6	Plasma decomposition	Non-thermal plasma	- High efficiency - Small treatment capacity

**Fig. 1. Schematic diagram of experimental apparatus.****Table 2. Experimental conditions for CF₄ decomposition**

Plasma input power		6-9 kW (30 V, 200-300 A)
Plasma generating gas		Ar (15 l/min, 25 °C)
Tube	Reacting	I.D.: 22 mm, L.: 10 cm
	Quenching	Two types (A and B) I.D.: 4, 6, 8 mm, L: 53 cm
Flow rate of reacting gas	O ₂	0.15-2 l/min (25 °C)
	H ₂	0.5-4 l/min (25 °C)
	CF ₄	1-4 l/min (25 °C)

products from quenching process were analyzed by gas chromatography (GC, TCD, PORAPAK Q, Supelco). Evacuated gases were passed through the scrubber for neutralization and then vented.

Detailed experimental conditions are given in Table 2. The plasma torch was typically operated from 6 kW to 9 kW input power

with flow rate of 15 l/min of Ar gas. The reactant gas and addition gases were adjusted by the flow meter. The feed rate of CF₄ was controlled from 0.15 l/min to 2 l/min, and the feed rates of addition gases (O₂ and H₂) were controlled from 0.5 l/min to 4 l/min.

In order to compare the decomposition efficiency according to process parameters, the decomposition was defined as follows.

CF₄ decomposition efficiency

$$= \frac{[\text{CF}_4 \text{ before discharge}(\%) - \text{CF}_4 \text{ after discharge}(\%)]}{[\text{CF}_4 \text{ before discharge}(\%)]}$$

RESULTS AND DISCUSSION

1. Thermodynamic Equilibrium Calculations

Equilibrium calculations predict the temperature region in which the required species should appear. Chemical equilibrium compositions were calculated by a software program based on Gibbs free energy minimization-Chemsage [Version 3.2, GTT-Technologies, Germany]. The calculations were performed from 300 K to 5,000 K.

Thermodynamic properties of plasmas are a prerequisite for any plasma modeling work. Compared to calculations for ordinary gases, plasmas impose additional difficulties due to the large number of chemical species at elevated temperatures and the chemical reactions taking place in plasmas. Collision cross-sections required for those calculations suffer from relatively large uncertainties associated with the assumptions which have to be introduced for the interaction potentials. Experimental data, on the other hand, are only available for a number of collision processes. Depending on the temperature, the pressure, and initial mole fractions are solved simultaneously in order to determine the densities of the different species. The method consists of minimizing the Gibbs free energy and it is possible to predict the temperature region in which the required species should appear. Chemical equilibrium compositions were calculated by software program based on Gibbs free energy mini-

mization.

Fig. 2 shows thermodynamic equilibrium composition in CF_4 (1 mole) direct decomposition as a function of temperature at atmospheric pressure. CF_4 was very stable at high temperature up to 3,000 K. As the temperature increased, CF_4 started to be dissoci-

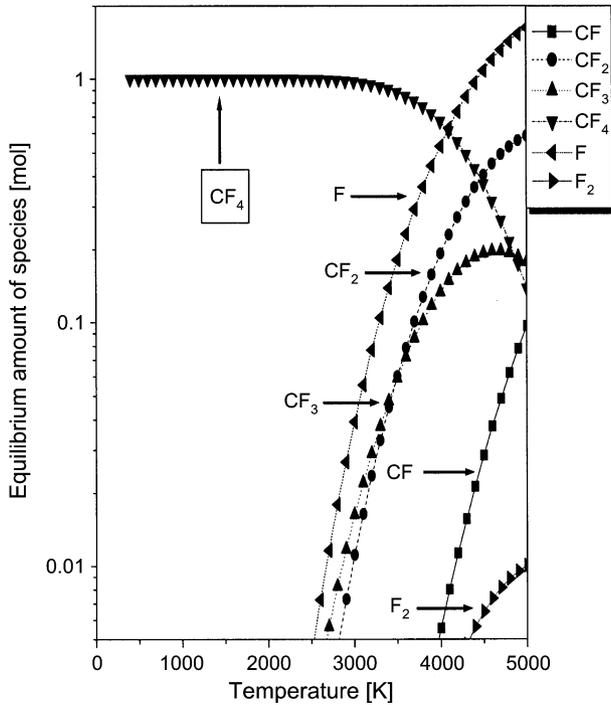


Fig. 2. Thermodynamic equilibrium composition of 1 mole CF_4 .

ated slightly above 3,000 K and decomposed rapidly at the temperature over 4,000 K. The intermediate species of CF_4 such as CF_3 , CF_2 , CF , F and F_2 were shown as a result of CF_4 dissociation. From these calculations, it was found that CF_4 needs very high temperature above 3,000 K to be decomposed.

Fig. 3 shows the thermodynamic equilibrium composition for a mixture of 1 mole CF_4 and 1 mole O_2 . CF_4 started to be dissociated at 2,000 K, and decomposed rapidly above 3,000 K. Compared to CF_4 direct decomposition, the decomposition temperature decreased. From 2,000 K, CF_4 was rapidly reacted with O_2 and by-products such as CO , CO_2 , COF , and COF_2 were produced. The carbon issuing from CF_4 decomposition was completely recovered into CO and CO_2 . Small amount of CO and CO_2 reacted with fluorine to form COF , COF_2 . These calculations indicate that the reaction between CF_4 and O_2 would make the decomposition of CF_4 more easily.

Fig. 4 shows the thermodynamic equilibrium composition for a mixture of 1 mole CF_4 and 1 mole H_2 . From very low temperature, HF was formed due to the dissociation of H_2 and the following reaction with CF_4 . In addition to the main by-product (HF), solid state carbon was shown from the low temperature region. The dissociation and re-association of CF_4 and H_2 were very effective for CF_4 decomposition.

Fig. 5 shows the equilibrium amounts of species in the system of $CF_4/O_2/H_2=1/2/4$ at atmospheric pressure. Both O_2 and H_2 were added to confirm if the production of H_2O could cause the equilibrium to be shifted toward the decomposition of CF_4 . CF_4 started to be decomposed from low temperature, and HF was formed by the re-association between CF_4 and H_2 . As expected, some by-products like HF , $H_2O(g)$, CO_2 , CO were shown from low temperature. But, in this calculation, solid state carbon was not found. This equilibrium calculation indicated that the addition of H_2 & O_2 should

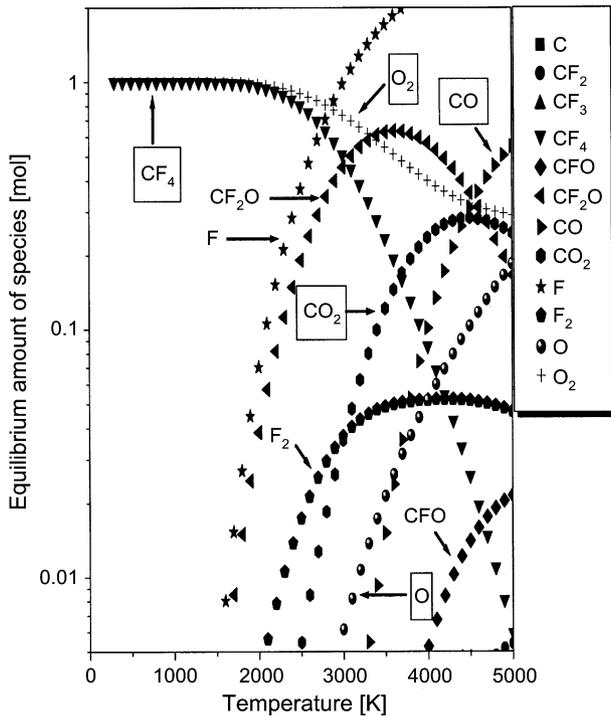


Fig. 3. Thermodynamic equilibrium composition of a mixture of 1 mole CF_4 and 1 mole O_2 .

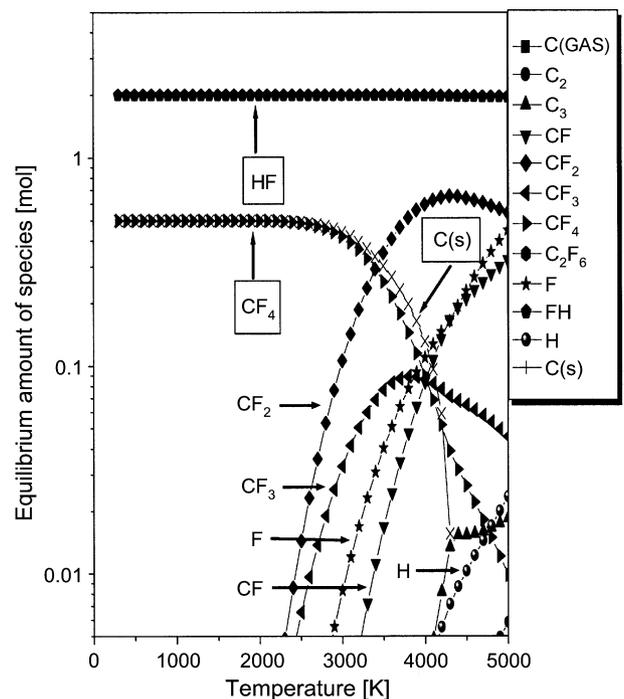


Fig. 4. Thermodynamic equilibrium composition of a mixture of 1 mole CF_4 and 1 mole H_2 .

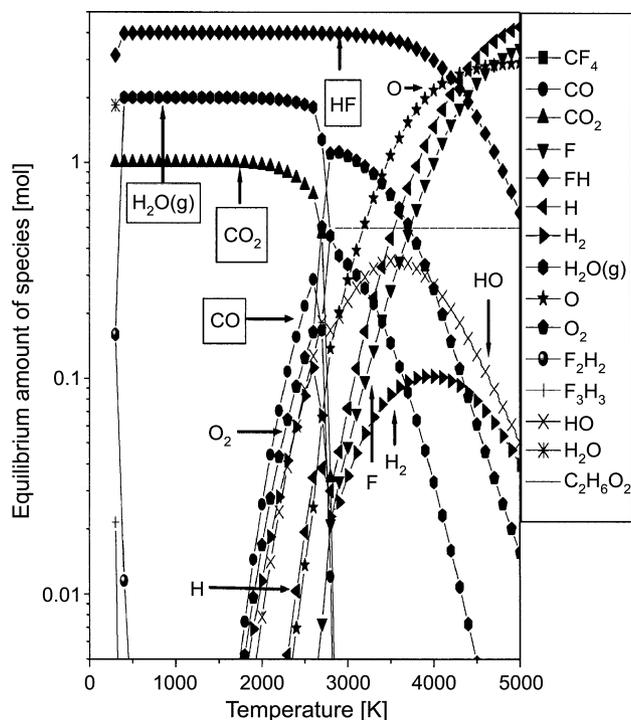


Fig. 5. Thermodynamic equilibrium composition of a mixture of 1 mole CF₄, 2 mole O₂, and 4 mole H₂.

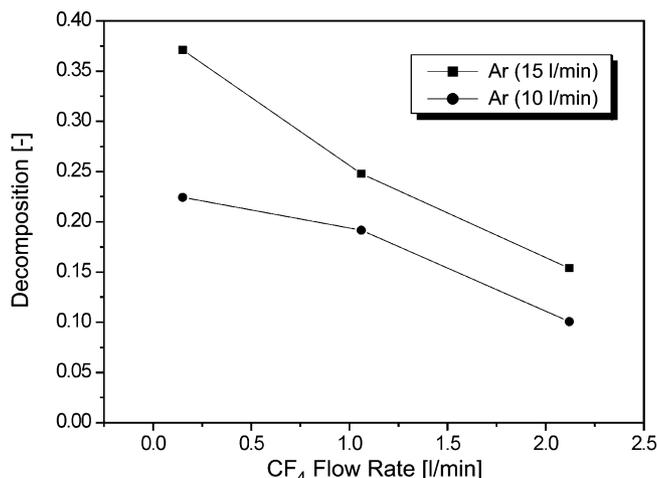


Fig. 6. Direct decomposition of CF₄ [Power: 6 kW].

be very effective for decomposing CF₄.

2. Physical Decomposition

Fig. 6 is a plot of CF₄ decomposition as a function of the flow rate of CF₄ and argon dilution rates. Decomposition efficiencies were varied between 0.15 and 0.37 at 6 kW. It is shown that the CF₄ decomposition was more effective at lower CF₄ flow rate, since lower flow rate can keep plasma temperature high. When CF₄ was decomposed without any additive reaction gas, the CF₄ decomposition efficiency was increased up to 0.37. Without addition gas, CF₄ fragments tended to recombine with the downstream of the discharge and higher decomposition could not be accomplished. Argon dilution in the reacting stream appeared to have little effect on the decomposition, and 15 l/min argon resulted in higher decomposition

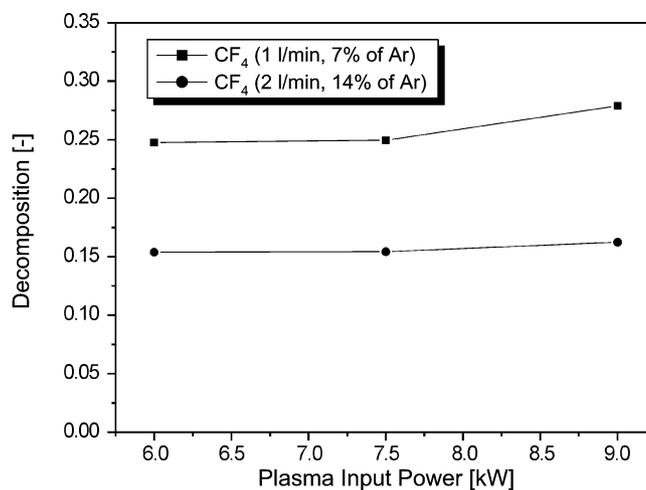


Fig. 7. The effect of input power in the decomposition of CF₄ [Ar (15 l/min), Power (30 V, 200-300 A)].

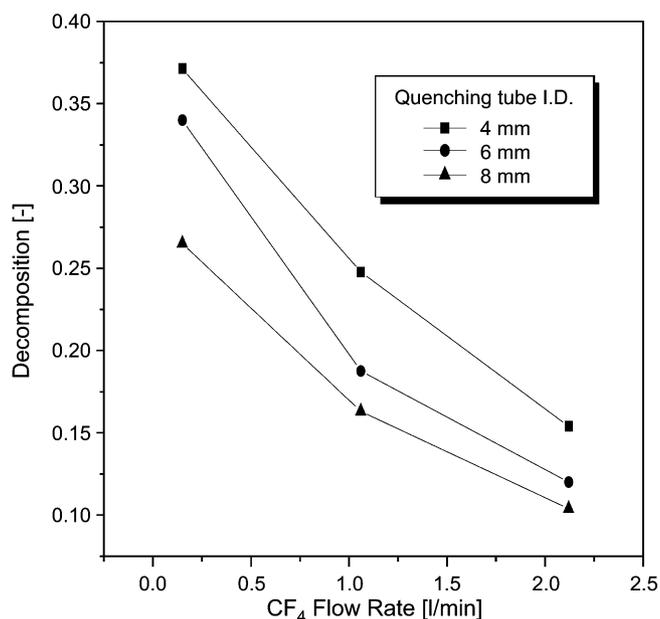


Fig. 8. The effect of quenching I.D. in the decomposition of CF₄ [Ar (15 l/min, Power (6 kW))].

efficiency than 10 l/min. This result indicated that at 15 l/min argon, the plasma flame was more stable and effective for CF₄ decomposition.

Fig. 7 shows the effect of power on the CF₄ decomposition. The plasma input power from 6 kW to 9 kW had a negligible effect on the decomposition. As shown in Fig. 6, increased input power did not have a significant influence on the decomposition. When the amount of CF₄ was varied from 1 l/min to 2 l/min, the trend between decomposition efficiency and input power was almost similar.

Fig. 8 presents the effect of different quenching tube inner diameter on the CF₄ decomposition. When the quenching tube inner diameter was increased from 4 mm to 8 mm, the decomposition was decreased due to quenching rate. Effective quenching can prevent CF₄ recombination and help sufficient decomposition. At 4 mm I.D. quenching tube, the CF₄ decomposition efficiency was most effective.

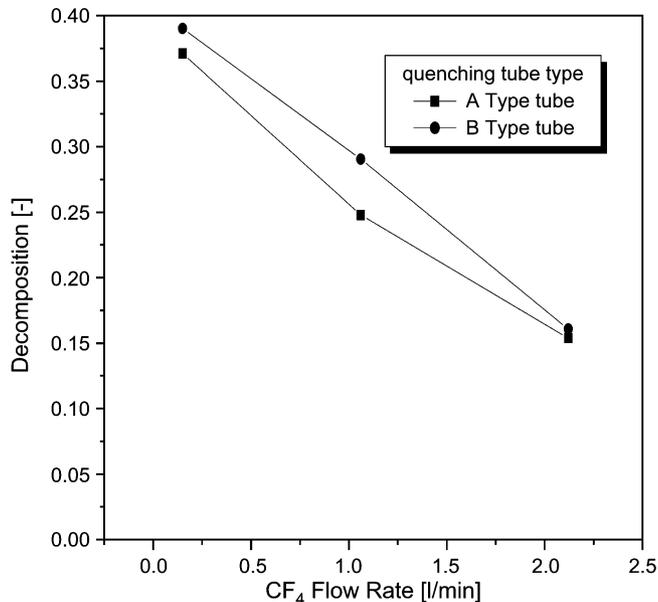


Fig. 9. The effect of quenching tube type in the decomposition of CF₄ [Power: 6 kW].

tive. Because the small quenching tube I.D. resulted in high heat transfer rate, the decomposition increased with decreasing quenching tube I.D.

In Fig. 9, the CF₄ decomposition is shown at different quenching tube types with the flow rate of CF₄ from 0.15 l/min to 2 l/min. The schematic drawing of each tube type is shown in Fig. 1.

The decomposition efficiency at the type B of quenching tube was higher than the type A. As B type tube led to more effective quenching rate, it could prevent the recombination among CF₄ fragments.

3. Chemical Decomposition

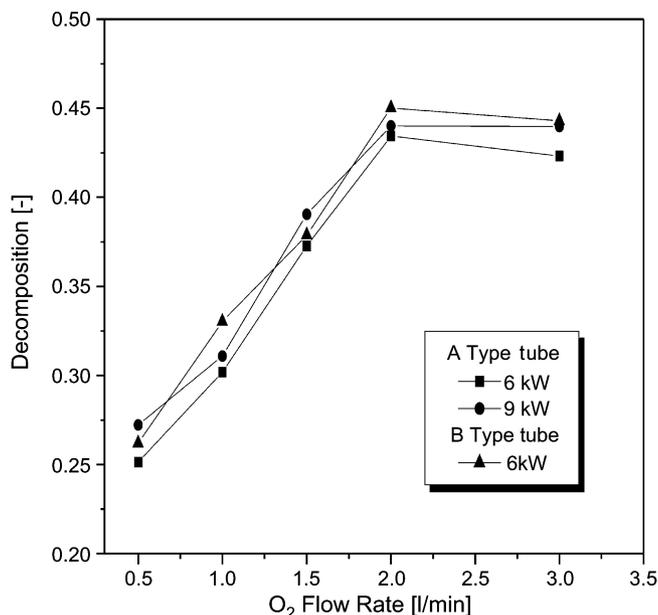


Fig. 10. The effect of added O₂ in the decomposition of CF₄ [Ar (15 l/min, CF₄ (1 l/min))].

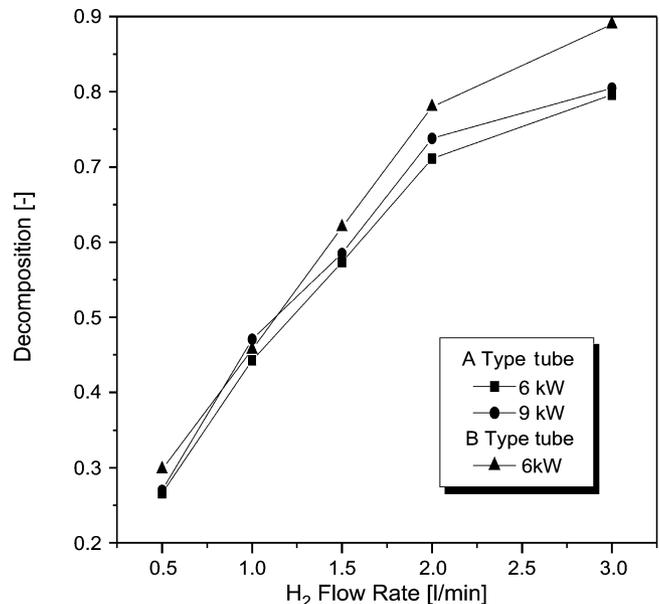


Fig. 11. The effect of added H₂ in the decomposition of CF₄ [Ar (15 l/min, CF₄ (1 l/min))].

Oxygen gas was inserted with a flow rate from 0.5 l/min to 3 l/min in the process stream. In Fig. 10, the decomposition of CF₄ is plotted as a function of the O₂ addition. The CF₄ decomposition efficiency increased from 0.25 without O₂ to 0.43 with 2 l/min O₂ at 1 l/min CF₄ and 6 kW. When the flow rate of O₂ increased, CF₄ decomposition increased, and the decomposition efficiency was maximized at 2 l/min. As expected from thermodynamic equilibrium calculations, the carbon from CF₄ decomposition reacted with O₂ and recombined to produce by-products such as CO and CO₂. It could prevent re-formation by forming those stable by-products. In this experiment, the CF₄ flow rate was maintained at 1 l/min, and the two types of quenching tube were tested.

Fig. 11 shows the effect of H₂ addition on CF₄ decomposition. 1 l/min of CF₄ was introduced to the decomposition process under varying the flow rate of H₂ from 0.5 l/min to 3 l/min. The CF₄ decomposition efficiency increased with the flow rate of H₂ gas. With the addition of 3 l/min of H₂ to 1 l/min of CF₄, the decomposition efficiency reached approximately 0.9 at B type quenching tube. The added H₂ during discharge reduce CF₄ fragments such as F and CF_x species to recombine with H, and decomposition by-product was primarily HF. The ability of H as F elimination source was sufficiently effective for decomposition. Although the H₂ addition had a surprisingly powerful ability to decompose CF₄, it could not be an effective method for decomposition because the solid state carbon which affects the process performance was appearing from the effluent stream.

Fig. 12 and Fig. 13 show the decomposition of CF₄ with the flow rate of addition gases (O₂ and H₂). CF₄ was decomposed with high efficiency when these two gases were added simultaneously. In all experiments, the CF₄ flow rate was kept to 1 l/min. Experiments were conducted to find the optimum flow rate of the addition gases (O₂ and H₂) on the CF₄ decomposition. In Fig. 12, the flow rate of O₂ varied from 0.5 l/min to 3 l/min, while the other addition gas, H₂, was kept to 1 l/min. The O₂ and H₂ gases based decomposition

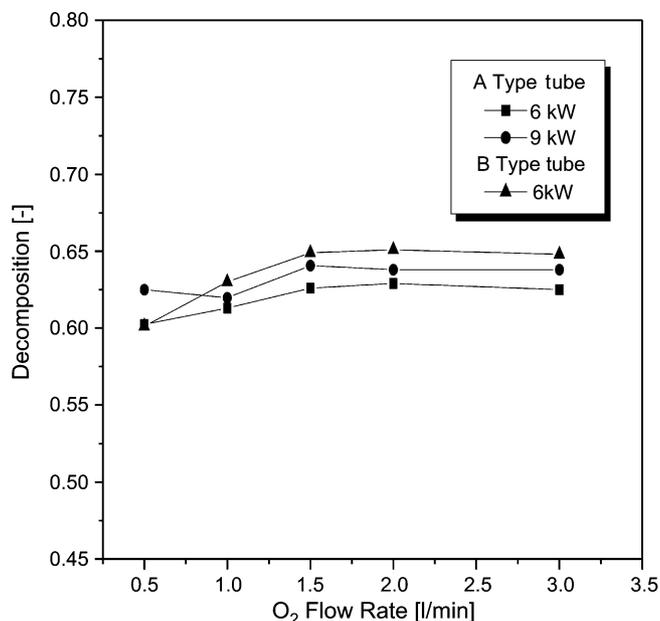


Fig. 12. The effect of added O₂ and H₂ in the decomposition of CF₄ (1) [Ar (15 l/min), CF₄ (1 l/min), H₂ (1 l/min)].

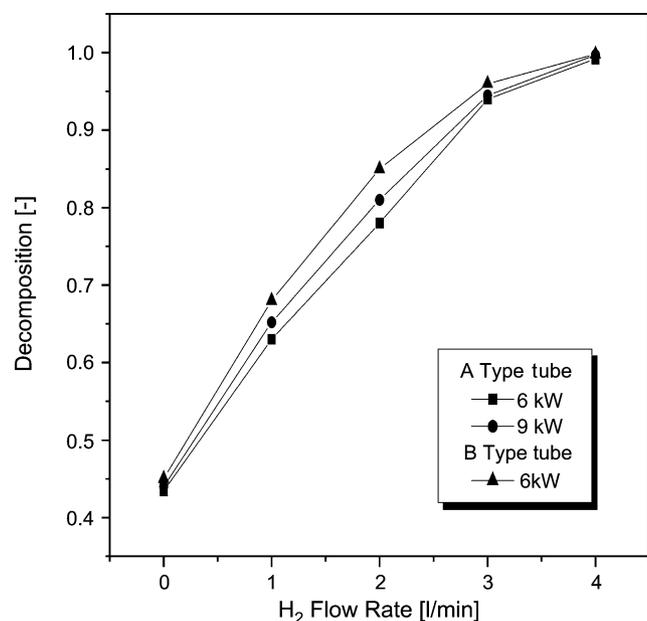


Fig. 13. The effect of added O₂ and H₂ in the decomposition of CF₄ (2) [Ar (15 l/min), CF₄ (1 l/min), O₂ (2 l/min)].

required a lower flow rate of O₂ to reach the same decomposition efficiency compared to O₂ addition only. At the same condition (2 l/min of O₂), the decomposition efficiency increased from 0.43 without H₂ to 0.63 with 1 l/min H₂. Fig. 12 shows the CF₄ decomposition when the H₂ addition was varied from 1 l/min to 4 l/min. In this case, using O₂ and H₂ as decomposition additives, CF₄ decomposition was greater than 0.95. From these results, the optimum flow rate of addition gases was CF₄/O₂/H₂=1/2/4. And, the solid state carbon shown in H₂ addition was not generated from this decomposition process.

CONCLUSION

Based on thermodynamic equilibrium calculations, experiments were conducted to find the optimum conditions of CF₄ decomposition according to parameters such as flow rate, input power, quenching tube, addition gases, etc. From the results, the following conclusions were made:

1. CF₄ decomposition was inversely proportional to the flow rate of CF₄, and, at 15 l/min Ar, decomposition was more effective than 10 l/min Ar.
2. Plasma input power had a little effect on CF₄ decomposition, but did not increase sufficiently.
3. The 4 mm tube had maximum decomposition efficiency and B type quenching tube led to more effective quenching ability for decomposition.
4. CF₄ was efficiently decomposed by using O₂ or H₂ as an addition gas. When H₂ was added, the CF₄ decomposition efficiency was increased significantly up to 0.9. But, during discharge, solid state carbon as a by-product appeared from the stream.
5. Using O₂ and H₂ as addition gases, CF₄ decomposition was greater than 0.95. And the solid state carbon shown in H₂ addition disappeared in the fluent stream. The optimum flow rate ratio of reacting gases was CF₄ : O₂ : H₂=1 : 2 : 4.

In this study, addition gas identity and flow rate strongly influenced the CF₄ decomposition. Overall, thermal plasma decomposition is a technically viable and effective method for abating CF₄ from several processes in the semiconductor industry.

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