CF₄ Treatment Using an Elongated Arc Reactor


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Abstract: CF₄ treatment is investigated using an elongated arc. By elongation of arc channel, effective control on the relative ratio between plasma chemistry and thermo chemistry is obtainable. Based on this control concept, optimization of the reactor to produce well distributed high temperature fields within reactor is carried based on the CF₄ removal performance of the reactor. As a result of optimization, above 95% of CF₄ removal with rather low power consumption is obtained. Also, process characteristics for the application of semiconductor fab are further investigated.

Keywords: Perfluorocompounds (PFCs), elongated arc, abatement

1. Introduction

Perfluorocompounds (PFCs) have a higher value of the global warming potential than CO₂. In this reason, they were classified as non-CO₂ greenhouse gases and should be treated properly especially in semiconductor fabs [1]. Although conventional burn-type scrubbers are used on sites, because of unwanted secondary emissions, such as NOx, F₂ and HF, as well as its low removal efficiencies, novel plasma techniques have been considered by many researchers [2~4]. However, non-thermal plasmas, such as DBD and pulsed corona, were not suitable for this purpose because these plasmas have relatively low gas temperature, though these have energetic electrons [5]. On the other hand, considering high temperature plasmas, such as arc torches, high consumption of electricity (say low efficiency) and a low life-time of electrode will be problems to be adopted in a real system.

Motivated by aforementioned problems, we developed an elongated arc reactor to have advantages of the both non-thermal and thermal plasmas. As results, we could achieve over 95% of CF₄ decomposition efficiencies up to 300 slpm of total flow-rate.

Fig. 1 Schematic of the elongated arc reactor and direct photograph of the plume after throat (D) part

2. Experiment
2.1 Elongated arc reactor

The schematic of the elongated arc reactor is shown in Fig.1 together with the photograph of plasma plume ejected from the reactor. As shown in the figure, the reactor consists of an inner conical high voltage electrode and an outer cylinder electrode. Initially an arc will be ignited at the shortest distance between electrodes (A-B), and owing to the convective flow effect it stabilizes at the longest distance (C-D). In this way, an arc channel inside the reactor will have similar characteristics of a gliding arc, so we can expect relatively higher electron temperature than conventional arc and relatively higher gas temperature than a DBD or pulsed corona. Eventually, we can use both an electron induced plasma chemistry and thermo chemistry at the same time properly. Moreover, by controlling the relative portion of plasma chemistry and thermo chemistry, optimization of process is possible. Because the target process or CF₄ decomposition requires environment of 1400°C or above, higher portion of thermal process is preferred.

It is to be noted that since the operating voltage is quite larger and a current is very smaller than an arc torch, the durability of the electrode was significantly improved.

Fig. 2 Schematic of the experimental apparatus

Furthermore, contrary to an arc torch type CF₄ scrubber, which consists of plug-in arc torch operated by separated plasma gas to treated gas stream, the elongated arc reactor operated with treated gas itself by supplying the gas
through the reactor at the top-side position (B) in the Fig. 1. This feature will be very helpful to use a heat from the arc and plasma chemistry efficiently.

2.2 Experimental apparatus

Experimental set-up consisted of a plasma reactor, a power supply, flow controllers, and measurement systems as schematically shown in Fig. 2. As briefly explained previously we constructed axisymmetric type of plasma reactor. A cone-shaped inner electrode, which was connected to high voltage, was placed inside a circular cylinder having 40 mm i.d. which serves as a ground electrode (see Fig. 1 for details). AC power supply, which can provide up to 20 kV in rms value with 5~20 kHz tunable frequency, was used for plasma generation. AC frequency is fixed at 10 kHz, at which methane decomposition rate showed best results in our previous work [5]. The flow rates of gases were controlled by mass flow controllers (Brooks, 5850E-series), and this mixture is supplied tangentially into the top section of the plasma reactor to form a swirling flow field inside the reactor. Right after the ignition at the narrowest gap, the arc is moved downward by gas convection, and follows a spiral trace caused by the swirling motion. Electrical power delivered to the reactor is measured by oscilloscope (Tektronix TDS5054B) with 1000:1 high voltage probe and current probe with amplifier that can measure up to 50 A (Tektronix TCP 303 current probe and TCPA300 amplifier).

2.3 Test conditions

We choose CF₄ as a target PFCs gas which is hard to remove and tested CF₄ removal performance of the reactor with 0.1 % CF₄ gas. The balance gas was nitrogen and the total flow-rate was varied from 100 to 300 slpm.

To decompose CF₄, we need over 1400 °C environment and hopefully the temperature should be distributed entire volume of the reactor. In the reactor, we can make a very high and distributed temperature field after the region of sudden expansion (beyond spot D), so we can use thermochemistry efficiently. Generation of this high temperature field could depend on the degree of the arc elongation. To optimize the reactor geometry, we checked the effects of various geometrical parameters, such as arc length (say, distance between C-D) and throat (D) size, on the removal efficiency. Additionally, the effect of flow agitation to obtain more distributed reaction zone is estimated.

Noting that water vapor was supplied to stabilize by-products. Doing this we can produce HF instead of F₂, and then HF can be easily captured by wet-scrubbing and C atom can be converted to CO₂.

3. Results and Discussion

3.1 Effects of the reactor length

Plasma characteristics can be altered by changing the length of an arc channel. For example, non-thermal characteristics of plasma can prevail over thermal effects of it in a gliding arc reactor. In this view, we may conceive that the performance of the present elongated arc reactor can be affected by the length of an elongated arc channel. Since the length of an elongated arc is determined geometrically by the distance between C and D (l_CD), Any other geometrical dimensions were fixed, and 0.1 % of CF₄ contained nitrogen stream was treated while 1 cc/min of additive water was being supplied to stabilize the products. To make a proper evaluation, electrical power delivered to the reactors is controlled to have a similar value of 3.4 kW. As you can see in the figure, we compared three different l_CD ( = 114, 164, and 214 mm), and at l_CD = 164 mm most efficient removal of CF₄ can be obtained. This implies that there exists an optimum arc length (say, the reactor length) determined by competing of heat transfer to the gas stream, which will cause thermal reaction, and plasma induced reaction.

Since a normal knife-edge type of a gliding arc reactor has an expanded volume along a gas stream, an overall flow velocity will be reduced for an elongated arc channel, which means deteriorated heat transfer to the gas stream from a high temperature arc channel [6]. On the contrary, because the present reactor does not have an expanded volume in the region of the elongated arc, robust heat transfer can be possible to the gas stream. Using this elongated arc we can expect a thermal reaction as well as a non-thermal effect (plasma chemistry). However, for further increase of the arc channel, the arc channel may be cooled down beyond the critical level of CF₄ removal thermo-chemistry, while the portion of an electron induced plasma chemistry is increased. This decreased portion of thermal reaction will be responsible for the low decomposition efficiency of the longest l_CD.

![Fig. 3 CF₄ decomposition results according to the reactor geometry or elongated arc length](image)

3.2 Effects of the throat size

Another geometrical parameter which can affect to the removal efficiency should be the throat size (the diameter of D part in Fig. 1, Dₐ). Beyond the throat, an after-plasma-plume can be observed (see Fig. 1). In the after-plasma-plume region, the most of the thermal reaction can occur. Since Dₐ alters flow velocity of ejecting out plume, it might affect the recirculation feature near the...
throat so to the temperature field. In this reason we need to check the possibility of existing optimum size of the throat.

In Fig. 4, we show the comparison results for three different $D_{th} = 14$, 16, and 18 mm. As you can see, $D_{th}$ does not affect to the efficiency significantly demonstrating a little deteriorate efficiency at $D_{th} = 18$ mm. Decreased ejecting velocity by increased $D_{th}$ may has a negative effects on the formation of reaction preferable temperature field at the after-plasma-plume region.

3.3 Role of the expansion reaction chamber

As discussed previously, we can make a fine tune of the reactor by varying the reactor length and the plume ejecting throat size. Since the effects of high temperature thermal reaction is major route of CF$_4$ removal compared to plasma chemistry, the role of the expansion reaction chamber which corresponds to after-plasma plume region is very important. In this reason we tested several different geometries as shown in Fig. 5. Tested geometrical conditions are listed in the figure, and the expansion reaction chamber type C (100 mm i.d. and 300 mm in length) shows the best result among the tested conditions demonstrating around 10 % superior decomposition efficiency.

3.4 Improvement of expansion reaction chamber

The present reactor use swirling motion to generate rotating elongated arc. However, the tangential velocity component may soon be diminished passing through the reactor. In such a case, the flow-field right after the throat will be like a simple axial jet, so there may exist a significant temperature gradient inside the expansion reaction chamber. Consequently, possible local low temperature zone can cause reduction of overall performance. To solve this un-preferable temperature field, we employed spiral groove at the throat so that a swirling motion can be boosted at the moment of plume ejection.

To validate the effects of newly designed throat geometry, numerical calculations using FLUENT were conducted. Only the expansion reaction chamber was considered as a calculation domain, and inlet conditions are fixed at $V = 43.3$ m/s, $T = 300$K, and $P = 1$ atm with heating at throat with 750 kW condition.

![Fig. 6(a)](image)

(a) Comparison of temperature magnitude contour with and without flow control

![Fig. 6(b)](image)

(b) Pathline of velocity in each cases

![Fig. 7](image)

Fig. 6 Flow pattern change by throat embedded groove

![Fig. 7](image)

Fig. 7 The effect of flow control by throat embedded groove resulting in elevated decomposition rate of about 10%

Fig. 6(a) shows the comparison results of temperature fields. As shown in the figure, without the spiral groove, outer part of near the throat exit has low temperature feature. However, with the spiral groove, this high local temperature gradient was improved and show much better distributed temperature field. Moreover, as can be seen in Fig. 6(b), streak line can reach the outer part of the expansion chamber because of the spiral groove driven
swirling motion. Also, we tested the decomposition efficiency with this spiral groove, and plot the result in Fig. 7 together with the result without the groove. As shown in the figure, we can achieve 10% increase of removal efficiency, and it can be an evidence for that the most removal reaction might occur inside the expansion reaction chamber.

3.5 Evaluation for application possibility

In real semiconductor manufacturing fab, PFCs emission occurs irregularly with much amount of nitrogen dilution. Since the corresponding total flow rate with N₂ dilution for each vacuum chamber can reach around 100 slpm, PFCs scrubbing system must cover 100 slpm at least.

First, to be a real fab applicable PFCs scrubbing system, we tested several different flowrates Q = 100, 200, and 300 slpm. As results, we can get over 95% of removal efficiency for each flow-rate depending on delivered electrical power. To check a running cost of the reactor, we plot the required electrical powers with which 95% of CF₄ reduction in Fig. 8. As can be seen, specific power to treat unit volume of CF₄ containing gas is decreased for increasing flow-rate.

Second, we tested the variation of decomposition efficiency with time, since conventional arc discharge shows short life-time of electrodes. Fig. 9 shows the removal efficiency as time elapsed. For 1 hour, there is no significant change in efficiency, and the electrode showed no significant change in weight as well as bare-eye inspection for 50 hours irregular operation.

Last, we check the response capacity of the variation of CF₄ concentration up to 1%. As shown in Fig. 10, there is little difference in decomposition efficiency. If a plasma chemistry was dominant mechanism to remove CF₄, then the removal efficiency should have shown concentration dependence. Since a plasma chemistry means a collisional reaction with electrons and chemically active species, it might show concentration dependence. In this reason, we can say again that a high temperature thermal reaction is the dominant mechanism for CF₄ removal.

4. Conclusions

We developed the elongated arc reactor and applied to PFCs removal successfully. The main mechanism for CF₄ removal was thermal reaction rather than a plasma induced chemistry, and to achieve energy efficient system flow-geometrical features were the key point. As results, we could remove CF₄ in nitrogen with over 95% decomposition efficiency, and maximum testing total flow-rate was 300 slpm with 1% of CF₄ (max.) concentration. These features are all better than conventional arc torch methods, and we expect that PFCs scrubbing plasma system can be possible combining with well-known wet scrubbing technique.

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References