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The atmospheric plasma reactor with water wall to decompose CF4

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Abstract

A new type plasma reactor is proposed to decompose CF4 diluted with N2 gas in atmospheric pressure. The arc plasmas is surrounded with a water wall which acts as a source of water vapor, the solvent of HF, resultant product after decomposition, and conveyer to take away fluorine compound from exhaust gas. Abatement more than 99% is achieved by small size plasmas such as 1 cm in diameter, 25 cm in length and 3.4KW of DC discharge power in such gas as the mixture of 100 sccm of CF4 and 15 slm of N2. Reactors of this type are to be expanded to such a system as Nitrogen flow of 50 slm with 200 sccm of CF4 and 7-8 KW discharge power.

1. Introduction

PFC such as CF4 has great large potential against green house effect and reduction of release of it is strongly required to keep atmospheric environment[1]. At present, PFC in the waste gas after etching of Si wafers is released into atmosphere after only dilution with N2 gas. Then, abatement of PFC in exhaust gas is urgent technical issue for environment protection.

Plasma-assisted abatement is one of promising methods to decompose stable molecules like PFC. It is well known that low pressure plasmas are quite powerful to decompose any kind of compound. However, such a plasma should be placed before final pumping system[2]. Such modification of the production line for ULSI manufacturing is not easily acceptable in industries.

On the other hand, atmospheric pressure plasmas are much easily acceptable in real production lines, because the equipments for abatement can be put after all the pumping system and do not give any influence to the process.

There are two types of atmospheric discharge; one is of low current density like corona and dielectric barrier discharge and another is of high current density like an arc. The both were tested and it was shown that CF4 was decomposed by plasmas and removed from exhaust gas whenever the absorbent of HF is placed as close as possible to the plasma[3]. In this paper it is demonstrated that water wall is the most effective as the absorbent, supplier of water vapor and conveyer of HF away from the abatement system.

2. Reactor structure, experimental setup and results

The plasma reactor has a hot cathode in the gas space and a foil anode in the water falling down along the inside of a tube made of insulator, so that the plasma is surrounded with a water wall acting as the absorber of HF produced in the plasma as the result of decomposition of CF4. Exhaust gas comes in from the cathode side and runs into the arc and goes out with the falling water to the next stage as a separator gas from water. The arc length is adjustable by sliding the ring shaped foil anode along inside of the tube. The cross section of the arc is determined by the diameter of the tube and the thickness of the water wall, the water for which is fed from the outside of the tube and its amount controls the thickness of the water wall.

Fig. 1 shows schematically setup of this study and the structure of the reactor. A typical dimension of the reactor is as follows: inner diameter of the tube is 1.3 cm and the maximum distance between electrodes is 30 cm. The test gas, CF4 diluted with N2, is introduced into the reactor from the cathode side, decomposed in the plasma, exhausted from anode side and sampled to analyze by the GC/mass after separation from the water.

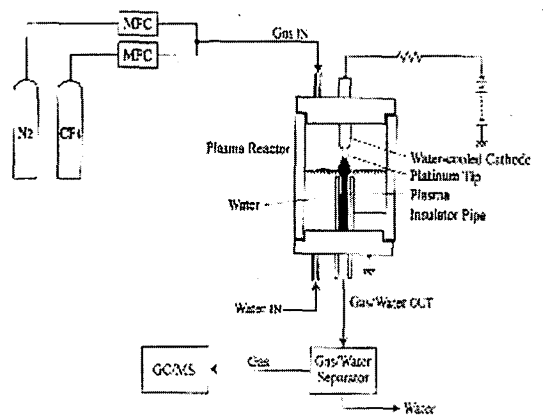

Fig. 1 Schematic draw of the reactor and experimental setup

Experiments are carried out in such a way that N2 gas is only fed and the plasma is ignited initially in order to initialize the experimental system, and then, CF4 is introduced until steady state is established, and finally the plasma is off[4]. Fig.2 shows the calibration of GC/mass spectroscopy. The examples of experimental results are shown in Fig. 3.

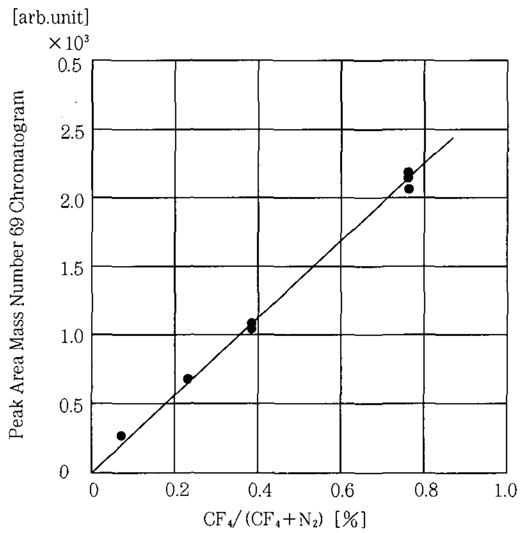

Fig. 2 Calibration of GC/Mass analyzer

In Table 1, results of several run are tabulated. Forming of water thin film surrounding the plasma is the most essential to achieve high performance. Boiling of water close to the cathode decreases abatement efficiency extremely.

According to Table 1, the higher abatement is expected even in the case of larger flow rate of N2

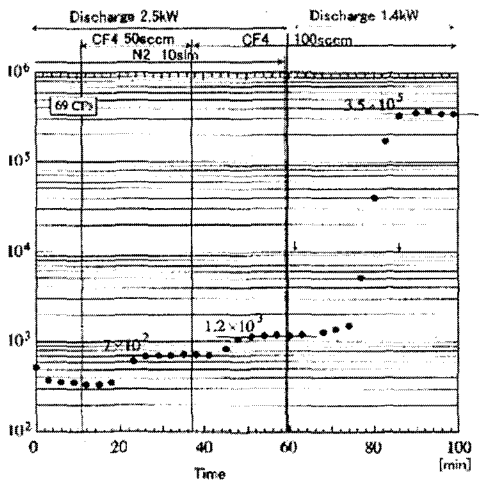

Fig. 3 Change of peak area of mass number 69 (CF3) during experiment corresponding to change of operation condition

when the longer arc length is used. Except for the cathode, all of the material forming the reactor are working in low temperature range below the boiling point of water, so that, the life time of the reactor will be limited only by the hot cathode. The Pt cathode is the most reliable substance against CF4 plasmas because stable operation over 20 hours as the total is achieved without any change or maintenance about cathode.

Some types of dielectric barrier discharges were tried and 40% abatement was obtained. However, no result was obtained which exceeds the water wall type.

3. Discussion

As shown in Table 1, this reactor has ability enough to be applicable to real semiconductor manufacturing. For cleaning of chambers used in CVD process, however, much more capacity to total gas flow may be required. In order to extrapolate performance of this reactor, electrical properties of the arc are formulated on the basis of measured values obtained by changing arc length, discharge current, gas flow of N2. Arc resistance is almost linear function of arc length and both the electrode voltage drop and the increment of the resistance per unit arc length are function of the discharge current.

The numerical analysis gives the experimental equation for arc resistance of this reactor as follows.

$$R=5.48\times\exp(-1.94\times I)+0.08\times L/I^{1.1} \quad (1)$$

Then, arc voltage and electric power consumed in the arc are respectively

$$V=RI=5.48\times I\times\exp(-1.94\times I)+0.08\times L\times I^{-0.1} \quad (2)$$

$$P=RI^2=5.48\times I^2\times\exp(-1.94\times I)+0.08\times L\times I^{0.9} \quad (3)$$

On the other hand, decomposition of CF4 should obey the equation of continuity. The flow velocity of gas is almost equal to the flow velocity of N2 and to be constant in the tube, then,

$$\frac{dn}{dx}=-nn_e\nu_e\sigma/\nu=-\frac{nj\sigma}{e\nu}=-\frac{In\sigma}{eQ} \quad (4)$$

where $I=jS$, $Q=S\nu$, $j=en_e\nu_e$, σ is the decomposition cross section. of CF4.

By integration of (4), the following is obtained

$$\frac{I\sigma L}{eQ}=-\ln\left(\frac{n}{n_0}\right)=\alpha \quad (5)$$

where $\alpha=4.6$ for 99% decomposition and $\alpha=6.9$ for 99.9% decomposition respectively.

The value of σ is unknown and is calculated with the experimental data and obtained as

$$\sigma=2.44\times10^{-14} \quad (6)$$

With this value of σ, equation (5) changes as

$$\frac{IL}{Q} \geq 1.8, \qquad (7)$$

where L is expressed in cm and Q does in slm..

With Use of these equations, reactors of larger capacity can be estimated as follow:
in the case of $Q=50$ slm and $I=1.2$, $L=75$ cm, $V=6.5$KV $P=7.8$KW, and for $Q=50$ slm $I=2.0$ amp, $L=45$ cm $V=3.6$ KV $P=7.2$KW.

These values are all realistic and promising to practical application in industries.

3. Conclusion

A new type of plasma reactor, the arc plasma with water wall, is proved most efficient to abate CF4 in practical level in industries. More than 99 % of CF4 of 100 sccm diluted with N2 of 15 slm is decomposed by discharge power of 2.9 KW and more than 98% of CF4 of 100 sccm diluted with N2 of 20 slm is decomposed by discharge power of 3.8 KW. Fluorine may change into HF and dissolve in water without any catalyst.

Furthermore, extrapolation on the basis of experiments tell us more large capacity reactors is possible.

Acknowledgement

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Table 1. Results of Experimental Run

CF4 (sccm)	N2 (slm)	Arc Length (cm)	Voltage (V)	Current (I)	Power (KW)	Abatement (%)
3	3	7			1	>99
3	3	13			1.5	100
3	4	13			1.5	>99
3	5	13			1.5	>98
3	10	25			2.9	100
50	10	21			2.5	>99
100	10	21			2.5	>99
100	–	4			1.4	>98
100	15	15	2.2	1.2	2.64	97
100	15	20	2.4	1.2	2.88	99
100	15	25	2.8	1.2	3.36	>99
100	15	30	3.1	1.2	3.72	>99
100	20	25	2.8	1.2	3.36	>97
100	20	30	3.1	1.2	3.72	>98