A Plasma Scrubber as Exhaust Gas POU Abatement System

B. Glocker *, B. Aburass*, C.C. Cheng[+], N.H. Guo[+]
PlasmaAir AG*, Germany, Zyra Research inc.[+] Taiwan

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1. Introduction

Green house effect and global warming are the critical issues in this new era. The influence is not only the environment, but also the economic and national safety. The majority gas, PFCs and SF_6, the GHG(Green House Gas) defined in Kyoto Protocol are generated gas out from the semiconductor and optical electronics dry etching procedure accumulated and mixed with CVD gas for chamber clean. The special PFCs gases from the tools such as SF_6, CF_4, C_2F_6, C_3F_8, CHF_3 and NF_3 have to be treated before emission.

A plasma scrubber system was developed and tested as Point of Use abatement system for the treatment of PFC loaded gases coming from a production line from semiconductor industry. The system consists of an arc heated water steam plasma unit followed a combustion chamber and a quench-scrubber-system.

For chemical destrucion of PFC material, a water plasma is favorable because both, the oxygen and the hydrogen, which is necessary to produce the desired products after the high temperature zone- CO, CO_2, HF and HCl- are supplied by the heat carrier itself. Therefore a new plasma torch system using water as plasma gas was developed and tested under the specification to achieve a long lifetime of the electrodes.

The system was developed and tested under industrial condition at a process line in semiconductor industry. It was demonstrated, that, with this process a reduction of PFC in the exhaust gas of > 99.9 % can be achieved.

2. The Plasma Process

For destruction of fluorinated compounds such as PFCs/HFCs (SF_6, CF_4, C_2F_6, C_3F_8, CHF_3 and NF_3, etc) a special plasma source is needed. Plasma generators for noble gases and gases like nitrogen are well known and often used because of little erosion and a long lifetime for the electrodes.

The cracking process is a high-temperature pyrolysis process. The strong chemical bond between C and F or Cl (halogen) will be broken, reacted with oxygen and hydrogen and produces hydrogen fluoride and hydrogen chloride as stable compounds. Especially for the CF_4 which has the most stable and strong C-F bond, it needs more than 1600 °C for pyrolysis process. In the mean time, the oxygen and hydrogen have to be provided to react with F. Otherwise it return to stable CF_4 again. It Therefore, we need to supply O and H free radical at the same time while cracking PFCs/HFCs to increase the destruction efficiency. It is not helpful to use standard plasma technologies for the destruction of PFCs. The problem was solved by developing a special high-temperature pyrolysis process using steam plasma in which the PFCs/HFC molecules are cracked by heat and O and H radicals into smaller units, in order to obtain hydrofluoric acid and hydrochloric acid for recovery as valuable chemicals. Therefore the water plasma is generated in an arc heated plasma torch. The PFC containing gas is injected into the reactive plasma in a mixing chamber. To ensure a full reaction, the mixture is fed through a high temperatur reaction chamber.

3. The Plasma Torch

Conventionaly used arc heated plasma torches work with argon as a plasma gas. For some applications Nitrogen is used. For the here described PFC reduction process an oyidiziend plasma gas is required to assure the chemical reaction process. The main problem using oxidizing gases is the short life time of the electrodes. This limts the operation time of the system. Building a exhaust gas cleaning system, a continous operating system that operates several 100 hours is required. Therefore, a new plasma torch was developed. The focus on the development was to achieve a lifetime of min. 500 hours using water steam as plasma gas.

The power level was fixed between 5 and 20 kW. This is the level that is required to treat typical exhaust gas streams containing PFC coming from production processes or from processes in semiconductor industry.

The newly developed plasma generator is of linear design with the cathode in the center and with a water-cooled anode. To avoid, that oxidizing gases can come into contact with the hot cathode, the cathode is shielded by a small Argon flow. The Anode is made of a special resistant material. The steam flow is injected between the cathode tip and

the Anode. In this way the arc burns in the steam and forms the high temperature water plasma that is coming out as a plume out of the torch. Due to the special design, operation times of more than 500 hours up to 1000 hours can be realized. After these operation hours the electrodes have to be changed.
The characteristic of this torch has been investigated intensively with steam as main plasma gas and Argon as protection gas in a power range from 5-32 kW. The torch itself can be operated up to 50 kW.
Parallel to the torch the complete equipment necessary to operate the torch was developed. A special evaporator, cooling cycle and the power supply were developed and optimized for long continuous operation.
Table 1 shows a typical operation point of the torch. The current voltage characteristics at constant mass flows show the typical arc heated plasma source characteristics. Under normal operation conditions the Argon flow can be selected between 5 % up to 50 % of the steam flow without effect on the cathodes erosion.

Opera-tion point	Current A	Voltage V	Steam flow kg/h	Argon flow mg/s
1	100	182	1,5	25
2	60	185	1,2	25

Table 1 Typical Operation Point of the torch

It was developed and qualified in the power range between 5 and 20 kW. The life time of the system in continous operation is currently proven 800 hours before electrodes have to be changed.
The same torch can be operated without changes with several other plasma gases. It was continously tested with water steam, air, pure oxygen and nitrogen. Instead of the Argon, hydrogen can be used to protect the cathode from erosion.

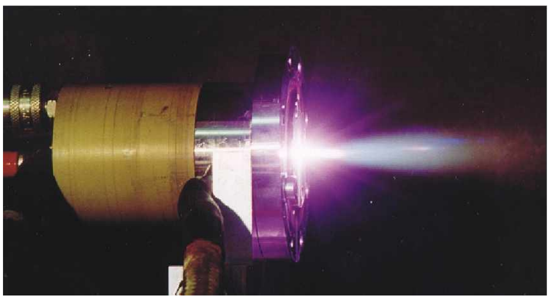
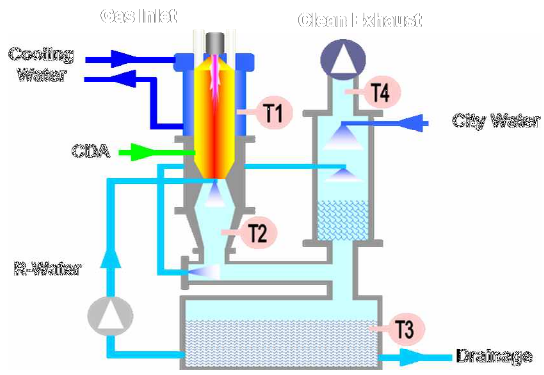


Fig 1: Steam plasma torch in operation

4. The Plasma Scrubber System

Plasma cracking is a non-incineration thermal process using temperatures more than 2000°C by cracking high stability materials like fluorinated compounds into smaller molecules.
The process gas is mixed into a steam plasma jet. Through the high temperatures and the available radical the PFC is cracked and reacts with the oxygen and the hydrogen coming from the water plasma to CO_2 and HF. The exhaust gases from the high temperature reactors are cooled and cleaned in a specially developed quench and water scrubber stage.
In the first stage, the gas stream is quenched down by a injected water stream. In parallel to the quench effect one gets a first cleaning of the gas stream from the acid components. Temperature of the stream can be cooled to 40 °C after quenching.
After the first stage, additional cleaning stages are followed by using recycling water for gases scrubbering. For achieving the required clean gas concentration, the last fine cleaning stage is done with clean city water.



The management of the water flow inside the scrubber is optimized to maintain lowest water consumption with best clean gas values.

Fig 2:Scheme of the Plasma scrubber

Fig 3: Test Equlpment

5. Field Tests Results

With a prototype the PFC decomposition was investigated under industrial condition. It was positioned in the exhaust gas line of a production process in semiconductor industry in Singapore. For the first qualification test a typical production in semiconductor industry was investigated. With a FT-IR system the concentration of the green house gases were tested and recorded. The results are shown in table 2-4. It can be seen that the Destruction Removal Efficiency (DRE) was very high compared to conventional used systems even for the thermal and chemical very restistant substances.

Site Operation Test #1:

- Process: Etch (Equip: Lam Research)
- POU Abatement System: ZRI-XP-20
- Site Operation
  7 Chambers Etch treated in 2 set of XP-20
  Operation: 1-Operation, 1-Standby
- Operation Condition:
  Total Gas Flow into Scrubber: 288.5 SLM
  Plasma Power Level: 16 KW
  Steam flow: 1m^3/hr (over heated)
  Argon flow: 0.7 L/min

Gas	Conc. (PPMv)			DRE%
	Recipe	Inlet	Outlet	
SF_6	2488	1674	3.28	99.74%
C_2F_6	2494	1294	1.81	99.80%
CF_4		416	4.89	98.35%
HF		210	0.16	99.90%
HCl		324	0.01	99.99%

* CF_4 is C_2F_6 byproduct

Table 2: Destruction Removal Efficiency Test #1

In a next test the destruction efficency for another process with different exhaust gas contribution was investigated.

Site Operation Test #2:

- Process: PECVD (Equip: Novellus-C1)
- POU Abatement System: ZRI-XP-20
- Site Operation:
  4 CVD Chambers to 2 set of XP-20
  Operation: 1-Operation, 1-Standby
- Operation Condition
  Total Gas Flow: 185 SLM
  Plasma Power Level: 12 KW
  Steam: 0.8 m^3/hr
  Argon: 0.6 L/min
  CDA: 30 SLM

Gas	Conc. (PPMv)			DRE%
	Recipe	Inlet	Outlet	
SiH_4	1725	766	ND	>99%
C_3F_8	6132	820	0.9	99.88%
CF_4		824	1.5	99.89%
NH_3	27717		ND	>99%
HF			ND	>99%
COF_2		1548	1.86	99%

* CF_4 is C_2F_6 byproduct

Table 3: Destruction Removal Efficiency Test #2

Even in this case the destruction efficency was very high.

Fig 5 Foto of the industrial system (two units)

In a third test the destruction efficency in the case

that CF_4 was the main pollutant was invertsigated.

Site Operation Test #3:

- Process: Etch (Equip: Lam Research)
- POU Abatement System: ZRI-XP-20
- Site Operation
  6 Chambers Etch treated in 1 set of XP-20
  Operation: 1-Operation, 1-Standby
- Operation Condition:
  Total Gas Flow: 242 SLM
  Plasma Power Level: 18 KW
  Steam Flow: 1m^3/hr
  Argon Flow: 1.2 L/min

Gas	Conc. (PPMv)			DRE%
	Recipe	Inlet	Outlet	
CF_4	745	713	35.5	95.02%
CHF_3	331	236	ND	99.99%
COF_2		280	4	96.26%
HF		96	1	98.57%

Table 4: Destruction Removal Efficiency Test #3

Summery

A steam plasma system for as exhaust gas POU abatements system was develped and tested under industrial condition. A very high destruction efficiency of the system was demonstrated under typical operation conditions. The continous operation time of the system before some mantanance was deemed was extended up to more than 800 hours. These systems are sucessfully operated in semiconductor industry for more than 3 years until now. It will help to reduce the green house gases coming out from semiconductor industry. The system can be used in chemical industry either to clean gasstreams containing PFC gases up to high concentration.

The POU Abatement systems installed and tested in Singapore job site help client to reduce specified PFC emission much more than 10% from 1995 level by the end of 2010 mentioned by Kyoto Protocol. This would be a great achievement for the green house reducing.