

METHOD FOR PLASMA TREATMENT OF GAS EFFLUENTS

The invention relates to technologies for treating gaseous effluents released during the manufacture of semiconductors, in particular during thin-film deposition of materials, or during the plasma cleaning of the deposition reactors, and during the plasma etching of thin films for defining the geometric patterns of the devices.

Methods for etching and cleaning deposition reactors can use perfluorinated (C_2F_6 , and/or $c-C_4F_8$, and/or C_3F_8 , and/or NF_3 and/or CF_4 and/or SF_6) and hydrofluorocarbon (for example CHF_3) gases which, if released into the atmosphere, may contribute significantly to global warming by increasing the greenhouse effect. They are generally not completely consumed in the processes.

One advantageous way for reducing the atmospheric emissions of these gases is to convert them to a plasma in the presence of certain additive gases in order to convert them to chemically reactive species (acidic fluorinated compounds) which can then be easily removed irreversibly by a conventional method such as reactive adsorption on a solid alkaline medium (dry-scrubber) or absorption by a liquid solution in a gas scrubber (wet-scrubber).

It is advantageous to place the plasma downstream of the means for maintaining the rough vacuum in order to avoid interacting with the operation of the process equipment or the pumps. Maximum efficiency in the conditions of total flow and pollutant concentration at the exhaust of the rough vacuum pumps is obtained with high-electron-density plasmas such as microwave plasmas.

In this respect, surface wave microwave plasmas and microwave plasma torches have been used.

The surface wave plasma solution is well adapted to the treatment of effluents for etching

processes, that is, producing gaseous effluents which are not capable of giving rise to the formation of solids in the device.

For treating gaseous effluents from reactor deposition and cleaning processes, the use of a microwave plasma torch burner with waveguide supported axial injection is proposed, as described in the article by M. Moisan et al. "Waveguide based single and multiple nozzle plasma torches: the TIAGO concept", Plasma Sources Sci. Tech., 10, 2001, p. 387-394.

The torch terminates freely in a chamber which confines the gases in order to collect them in the downstream exhaust line. The solid particles are formed in the flame and the plasma plume downstream of the torch nozzle, and therefore do not disturb the operation thereof, provided that they are trapped and entrained at some distance to prevent their indefinite accumulation in the chamber. For this purpose, the standard solution is a gas scrubber installed as close as possible to the outlet of the torch chamber.

The principle of PFC conversion in a microwave plasma consists in dissociating the initial molecules in inelastic collisions caused by the high energy discharge electrons, in order to produce fragments smaller than said initial molecules, atoms and radicals. These fragments react together, are deexcited, recombined and/or rearranged to yield new compounds different from the initial PFCs. More precisely, the objective is to convert the majority of the incoming PFCs to acidic fluorinated compounds such as F_2 , HF , COF_2 , SO_2F_2 , SOF_4 , etc., which, while they are undeniably immediately hazardous gases for life and health, are also highly reactive, and can be removed definitively and irreversibly by a conventional method of neutralization on solid or liquid.

In general, the implementation of the PFC conversion reaction requires the input of an additive gas. This means that if the PFC molecules diluted in

nitrogen are alone in the plasma, dissociation is effective but, once they have exited the discharge zone, the fragments will tend to react together and simply reform the initial molecule.

5 The choice of additive gas is important for the optimization of the PFC destruction methods.

Firstly, this choice can influence the conversion efficiency itself.

10 In fact, the fragments produced by the dissociation of the additive gas in the discharge may have the property of forming stable corrosive fluorinated products more or less easily and rapidly with the PFC dissociation fragments, before the PFCs have had the time to reform when the gas leaves the
15 discharge zone.

Furthermore, the corrosive fluorinated reaction products are different depending on the type of said additive gas. This fact may be exploited to preferably form a particular reaction product rather than another,
20 depending on the post-treatment solution selected to definitively and irreversibly remove said corrosive fluorinated products from the gaseous effluent stream.

This post-treatment solution may be imposed for cost reasons, or other reasons specific to a given
25 user. It is therefore important to be able to adapt optimally to the various situations encountered among the clientele. For example, if it has been decided to operate with a gas scrubber, it is out of the question to use oxygen as an additive gas. This will in fact
30 essentially yield reaction products such as compounds like COF_2 (with fluorocarbons) or SO_2F_2 and SOF_4 (with SF_6) and, in any case, significant quantities of F_2 , of which the reaction with water or an aqueous caustic soda solution can generate OF_2 , an exceptionally toxic
35 gas (legal limit of continuous exposure of workers 50 parts per billion by volume) of which no user will generally tolerate the presence of traces in his premises.

Until now, oxygen O_2 has been used as additive gas, generally injected in the form of dry air taken from the compressed air distribution network of the semiconductor plant.

5 This solution corresponds to a technological choice, with a post-treatment solution of the corrosive fluorinated products by reactive adsorption on a solid bed, generally using units designed to preferably trap the products of a dry conversion chemistry using the
10 additive O_2 such as F_2 , COF_2 , SO_2F_2 , SOF_4 .

It is the primary object of the invention to find a novel conversion chemistry for the waste effluents from an industrial process, particularly PFC in microwave atmospheric plasmas.

15 The problem also arises, in the case of PFC effluents, of promoting the formation of HF as corrosive fluorinated by-product, to permit the advantageous use of a solid bed of granules based on soda lime, or of a gas scrubber, as means for
20 irreversibly trapping these by-products, before releasing the effluent stream to the atmosphere.

It is a further object of the invention to improve the conversion yield by the implementation of this alternative chemistry.

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SUMMARY OF THE INVENTION

The invention first relates to a method for plasma treatment of gaseous effluents at substantially
30 atmospheric pressure, comprising

- injecting the effluent to be treated into a plasma source,
- injecting water vapor upstream and/or downstream of the plasma, and optionally into the
35 plasma itself.

The pressure of the effluents is for example between 0.8 bar and 1.3 bar.

The water vapor may be injected in a concentration of between 100 ppm and 5% in a carrier gas which is generally nitrogen.

Its temperature may be between 20°C and 300°C, preferably between 50 and 200°C.

The effluents to be treated may be effluents from semiconductor treatment processes, for example a mixture of perfluorinated and/or hydrofluorocarbon gases and oxygen.

The plasma source is preferably of the surface wave type, more particularly a microwave-excited plasma source.

The invention also relates to a device for plasma treatment of gaseous effluents at substantially atmospheric pressure, comprising plasma generating means and means for injecting water vapor into a mixing zone.

The means for injecting the water vapor may be placed upstream of the plasma formation zone, or be placed downstream of the plasma formation zone.

According to one embodiment, the means for injecting water vapor comprise a vaporizer with temperature regulating means.

The invention serves to implement, in an atmospheric plasma, a PFC wet conversion chemistry which generates practically only HF as fluorinated by-product. Water vapor is added to the plasma other than under its vapor pressure at ambient temperature.

According to another aspect of the invention, at least one chemical compound of which the molecule contains at least one hydrogen atom is injected preferably at the plasma outlet or, at the earliest, in the plasma but close to the outlet of the plasma effluents, in order to essentially generate hydrofluoric acid which then dissolves in the water (or any reducing liquid system), without the necessary use of a "dry" scrubbing system to remove the hydrofluoric acid (in spite of this, the user will sometimes prefer

to use this "dry" system in addition, as a precautionary measure).

According to another aspect of the invention, when products such as WF_6 are present in the reactor, it has been found that the passage of this gas into the plasma accompanied by a partially reducing or hydrogenated element, results in the deposition of W on the walls of the tube, thereby causing it to break almost instantly.

10 In order to solve this problem raised by the use of hydrogenated additives when the first species comprise in particular a fluorinated metal derivative such as WF_6 capable of generating a metal deposit, and when the plasma is produced in a dielectric tube, it is 15 then important to inject at least one hydrogenated element downstream of the plasma, preferably just at the outlet thereof, so that this hydrogenated element reacts as soon as possible with the first species created in the plasma, based on the mixture containing 20 PFCs, and thereby generates second species. (Alternatively, this hydrogenated and/or reducing element could be injected into the plasma itself, in a place such that the PFC or HFC molecules have already been "split" or partially "split", preferably in the 25 zone called the plasma post-discharge zone).

When an element such as WF_6 is present in the reactor offgases, at the inlet of the plasma, this serves to prevent this product from decomposing in the plasma. On the contrary, the first species issuing from 30 WF_6 will then react upon the outlet of the plasma with the reducing species injected downstream, causing the deposition of tungsten metal or other solid tungsten compounds such as oxides or oxyfluorides, on the lines, generally metal, located at the plasma exit, thereby 35 raising no problem for the operation of the plasma system.

As a source, particularly gaseous, of the hydrogenated and/or reducing reagent, use can be made

of H_2O , H_2 , CH_4 , NH_3 , alcohols such as methanol, ethanol, etc., glycols, hydrocarbons, hydrides, or any other hydrogenated compounds.

It has in fact been found that the second species thus created contained (using hydrogenated additives) much more hydrofluoric acid HF than when using anhydrous additives, particularly of the oxygen type. Furthermore, when WF_6 (or similar product) is randomly present in the effluents to be treated issuing from the reactors placed upstream of the pumps, the downstream injection (i.e. downstream of the plasma) of hydrogenated products generates a deposit of W (or products derived from W) in the lines located downstream of the plasma, lines which are generally made from stainless steel or plastic, and for which such a deposit, obviously very thin, is absolutely not a drawback.

However, it has been found that if hydrogenated compounds are merely injected exclusively downstream of the plasma, without adding anything to the gaseous effluents upstream, the solution obtained is not fully satisfactory. In fact, the destruction efficiency obtained in this case is lower than what would be obtained, all other things being equal, by introducing the same quantity of hydrogenated additive gas, for example water vapor, upstream of the plasma.

The inventors believe that a significant proportion of the PFCs initially introduced into the plasma is probably reconstituted before their decomposition fragments can react with the hydrogenated compounds introduced downstream. The PFCs thus reconstituted can no longer be dissociated again before leaving the zone where the plasma is present.

In order to solve the two problems mentioned above simultaneously, according to a preferential embodiment, the invention consists in injecting, upstream of the plasma or at the latest therein, preferably gaseous oxygenated compounds not comprising

atoms of hydrogen or other elements liable to react with metal elements such as Al, W, etc. (if they are present in the plasma), while injecting hydrogenated compounds, downstream of the plasma, into the mixture of first gas species generated by the chemical conversion in the plasma, where the temperature of the first gas species issuing from the plasma preferably remains higher than or equal to 150°C, so that these hydrogenated compounds react with the first species.

Without wishing to be bound by any particular theory, the inventors believe that when an anhydrous, particularly oxygenated, additive, for example oxygen or air, is injected upstream of the plasma, said additive will be dissociated and/or excited and its fragments will react very easily with the dissociation fragments of the PFCs and/or HFCs to yield corrosive fluorinated compounds such as F_2 , COF_2 , SO_2F_2 , SOF_4 (the first species). These compounds are very stable at the high temperature of the gas in the microwave plasma and, once formed, there is little possibility of their being dissociated again. In particular, they are not significantly reconverted to PFCs. These anhydrous corrosive fluorinated products like F_2 , COF_2 , SO_2F_2 , SOF_4 are significantly more reactive than PFCs. At the plasma outlet, when the hydrogenated compounds are injected, the temperature is still sufficiently high for them to react more or less completely with the hydrogenated additives to essentially yield HF which is thermodynamically much more stable than the anhydrous corrosive fluorinated compounds. On the other hand, the PFCs which have not been converted by the plasma will not react significantly with these hydrogenated additives at the plasma exit. Thus, the PFC conversion yield is substantially the same as that of the pollution control process using as an additive only the nonhydrogenated compound or compounds, particularly oxygenated, injected upstream of the plasma.

BRIEF DESCRIPTION OF THE DRAWINGS

- Figures 1A and 1B show two alternatives of a device according to the invention,
- 15 - Figure 2 shows the structure of a furnace,
- Figures 3-9 show the measurement results during the implementation of a method according to the invention in various conditions,
- Figure 10 shows an exemplary embodiment 10 avoiding any breakage of the dielectric tube.

DETAILED SUMMARY OF PARTICULAR EMBODIMENTS

An exemplary embodiment of the invention is now 15 described in conjunction with Figures 1A and 1B.

Such a device can be installed at the outlet of an installation for the deposition of thin layers or the treatment of semiconductor materials, for example behind a pump used to transport the gaseous effluents, 20 generally in nitrogen, at substantially atmospheric pressure, of between 0.7 bar or 0.8 bar and 1.3 bar or 1.5 bar. These effluents contain perfluorinated compounds such as C_2F_6 , and/or $c-C_4F_8$, and/or NF_3 and/or CF_4 and/or SF_6 .

25 The plasma source used is of the surface wave type, as described in *M. Moisan and Z. Zakrzewski in Microwave Excited Plasmas*, eds, M. Moisan and J. Pelletier, chap. 5, Elsevier, Amsterdam, 1992.

Reference 2 denotes the plasma tube 4, 30 comprising an AlN inner tube 6 and a quartz outer tube 8.

The plasma may be initiated by a high voltage initiator 10.

A gas mixture to be treated, for example a 35 mixture of a PFC and nitrogen, is conveyed into a mixing zone 12.

Water in gaseous form is injected using vaporizer means 14. These means 14 comprise for example

a metering pump 16, which supplies liquid water to an electrothermal vaporization furnace 18.

The water vapor is injected with a flow rate providing a water vapor concentration of between 5 100 ppm and 5% in the gaseous effluents. Thus the conditions do not necessarily remain below the water vapor condensation threshold at ambient temperature (2.3%).

To convert the water in controlled quantity to 10 the gas state, deionized water can be tapped off from a reserve 26 in controlled quantity by the metering pump 16.

An exemplary embodiment of a furnace is shown in Figure 2. This furnace has a FIREWORD (600 W) type 15 cartridge heater 40, a rockwool jacket 32, a coil 34, and a liquid water inlet channel 30.

The water flows in a coil 22 (Figure 1A), comprised in a stainless steel body 24 enveloping the cartridge heater, to be vaporized completely.

20 This cartridge heater may be connected to a temperature controller 24. The latter regulates the water temperature leaving the system using a thermocouple 28 so that it is about 200°C to 300°C, in order to prepare the mixture.

25 The final furnace 18 injects water vapor 20, entrained for example in nitrogen, often used as a carrier gas for the effluents, at a temperature such that, in the concentration considered, recondensation cannot occur before the gas reaches the discharge 30 limit.

The high temperature of the carrier gas also inhibits the deposition of solids (for example silica or tungsten oxide) which could result from the hydrolysis of thin-film etching products in the process 35 chamber, such as SiF_4 or WF_6 .

Such a deposition could cause the obstruction of the plasma inlet.

The quantity of hydrogen provided by this method serves to guarantee a good conversion efficiency; it preferably corresponds at least to the reaction stoichiometry (i.e. enough hydrogen element to form only HF with all the incident fluorine). In practice, depending on the chemical reactivity of the system, the quantity of water necessary to obtain the maximum PFC conversion rate may be higher. It may also depend on the type of PFC concerned.

10 If the water vapor concentration, after injection into the mixture with the gaseous effluents, is lower than or equal to 2%, in any case, no recondensation can occur because the conditions remain below the water vapor condensation threshold at ambient
15 temperature (2.3%).

However, the quantity of PFC emitted may be around several tens of sccm for an etching reactor, to several hundred sccm for a CVD reactor during cleaning, in a nitrogen dilution stream of 20 to 100 slm, depending on the technical specifications of the rough vacuum pump. For example, for 50 sccm of CF_4 , at least
20 100 sccm of H_2O is provided to form HF exclusively. The reaction kinetics must also be taken into account, giving rise to at least 200 sccm of H_2O . For 500 sccm
25 of C_2F_6 , at least 1500 sccm of H_2O are necessary. Hence this gives one or more thousands of ppmv, for example 2000 ppmv, to one or more percent, for example 3% or 5%, of water vapor in the nitrogen or in the mixture of effluents.

30 It should be observed that this would be impossible to obtain an atmospheric pressure and ambient temperature, due to the saturation vapor pressure under these conditions. The water that would be likely to recondense in the system in the form of
35 macroscopic drops or liquid film would not significantly contribute to the conversion reactions. Moreover, the presence of liquid water at this level may be incompatible with satisfactory operation of the

discharge, in particular because the water will absorb the microwaves.

On the contrary, the invention serves to avoid these drawbacks. The injection of water vapor at a temperature of between 20 and 300°C, preferably between 50 and 200°C, serves to create satisfactory conditions for carrying out an effective conversion of the PFCs. A temperature above 100°C will further prevent the hydrolysis of certain products, which could yield solid deposits as explained above.

The mixing zone corresponds to the contact between the initial mixture (or the initial effluent, for example $N_2 + PFC$), of which the flow rate may be about 20 to 100 l/min and on average 50 l/min, with the flow of vaporized water, for example about 1 l/min.

Furthermore, the water in gas form is entrained by the nitrogen into the mixing zone, located near the plasma, which is at a temperature of about 2500K to 7000 K; this eliminates any risk of recondensation, as well as undesirable premature reactions with potential by-products of the etching process.

Before reaching this mixing zone, the water, which is initially provided to the unit in liquid form, undergoes a vaporization process implemented using a furnace as explained above.

The water vapor is mixed with the initial effluent mixture preferably at a level as close as possible to the plasma, in order to avoid, in the case of the treatment of real process effluents, the premature interaction of certain products of the process with the water vapor.

According to a first embodiment (Figure 1A), the outlet of the vaporizer 14 is located very close to the plasma 4.

In consequence, upstream of the plasma, the water is injected vertically and perpendicular to the arrival of the mixture to be treated, which is PCF-nitrogen here.

Another procedure (Figure 1B) is to inject the water vapor, this time downstream of the plasma and as close as possible to the limit thereof.

5 In Figure 1B, only the furnace 18 has been shown, but it is in fact accompanied by all the elements 16, 19, 24, 26, 28 described above in conjunction with the configuration in Figure 1A.

At the outlet of the actual discharge zone, by definition, there are no charged particles, ions and
10 electrons. However, this does not mean that the neutral species are all in a final stable form, nor in their fundamental energy state. The atmospheric microwave plasma is not very far from thermodynamic equilibrium and the temperature of the heavy particles there (as
15 opposed to that of the electrons) is typically 2500 to 7000K on the central axis.

Due to the generally high velocity of the gases (small characteristic diameter of the plasma due to the radial contraction), the gas may remain very hot along
20 a certain distance before the reformation of the PFC molecules from their dissociation fragments becomes very probable.

Moreover, metastable high energy states may also exist for certain species, of which the
25 progressive deexcitation may also play a role in the reaction kinetics in the near post-discharge.

The injection of water vapor in this near post-discharge, as in Figure 1B, can therefore also serve to convert the PFCs to HF with good efficiency.

30 In the case of the surface wave tube, the water vapor is injected from the downstream fluid fitting, hence after the downstream end of the ceramic discharge tube 6 and consequently a few cm from the downstream limit of the discharge.

35 Downstream of the plasma, the injection therefore takes place horizontally and perpendicular to the gas leaving the plasma.

To demonstrate the formation of HF and the improved PFC conversion yield by the implementation of a method according to the invention, tests can be conducted with, respectively, the following PFCs: SF₆ and CF₄. These, in a manner known per se, particularly for CF₄, are the most difficult to destroy of the PFC family.

Experimental tests were first performed with O₂; to destroy PFCs, the following mixture was used: PFC + N + O₂, where N was a carrier gas and O₂ the additive gas allowing the formation of stable corrosive fluorinated by-products subsequently treated by reactive adsorption on a solid bed (for example a commercial system from CS Clean Systems).

The PFC concentration may, for example, vary from 1000 ppm to 1% in a total flow rate of about 50 l/min.

The quantity of oxygen is generally 1.5 times higher than that of the PFC to have an optimal destruction rate and nitrogen is present in sufficient quantity, always being the majority component in the real gaseous effluents which, for safety reasons, are systematically diluted in a large stream of nitrogen before they leave the rough vacuum pump.

These three gases are mixed using a gas distribution panel containing a loop to ensure a homogeneous and stable mixture. It reaches the plasma surfaguide source 4 via an insulating alumina fitting, which is one of the elements of the fluid connections of the discharge tube.

In the alternative chemical process according to the invention, this mixture is modified by adding H₂O in the gas phase instead of (or with) O₂.

The gas does not enter the same mixing process: PFC, nitrogen and oxygen, but rather PFC + nitrogen for one part, the water vapor being introduced for the other part independently at another location, as observed above in conjunction with Figures 1A and 1B.

It is possible to observe and compare the formation of HF and by-products produced by the destruction of the PFCs, and also the conversion yield, in the two configurations explained above, upstream and downstream of the plasma.

Tests

To demonstrate the formation of HF and the improved conversion yield by the implementation of the method according to the invention, destructive tests were carried out with SF₆ (1000 ppm and 5000 ppm) and CF₄ (5000 ppm).

The experimental conditions were as follows:

- Microwave generator: power between 4 and 6 kW at a frequency of 2.45 GHz.

- Aluminum nitride tube: length $l = 350$ mm, inside diameter $I_a = 8$ mm, outside diameter $I_D = 12$ mm.

- Total throughput: $Q_{total} = 50$ l/min.

- $P = 4000$ W for SF₆ and $P = 4500$ W for CF₄.

In order to identify the by-products produced by the destruction of PFCs by microwave plasma, a Fourier transform infrared spectroscopy (FTIR) analysis was carried out after treatment by the plasma, using an FTIR spectrometer ("Thermo Nicolet Avatar 360"), in the following conditions:

- Cell length $l = 10$ cm.

- ZnSe windows.

- Sampling conditions: atmospheric pressure and ambient temperature.

- Flow sampled for analysis = 3 l/min.

All the experimental conditions being defined, the results of the tests with gas injection upstream of the plasma are presented, first with the destruction of the SF₆ and then with that of the CF₄.

For each molecule, the spectrum of the by-products produced by the plasma destruction was obtained and the PFC conversion yield was determined:

- with O₂ and without H₂O,

- with H₂O and without O₂,
- with H₂O and with O₂.

This method serves to clearly observe the influence and role of each of these molecules in the PFC destruction process.

Case of the destruction of SF₆

In the case of the injection of O₂ upstream of the plasma, the following conditions were used:

- 10 - SF₆ : concentration 1000 ppm,
- nitrogen flow rate : = 49.5 l/min,
- SF₆ flow rate : = 0.05 l/min,
- oxygen flow rate : = 0.075 l/min.

As shown in Figure 3 (results of the IR analysis) the by-products produced by the destruction of SF₆ with O₂ (without H₂O) are as follows: HF, SO₂F₂, SOF₄.

Water was then added in the following conditions:

- 20 - SF₆ : concentration 1000 ppm,
- nitrogen flow rate : = 49.9 l/min,
- SF₆ flow rate : = 0.05 l/min,
- oxygen flow rate : = 0.075 l/min,
- water flow rate : = 0.4 l/min.

25 The results of the IR analysis are shown in Figure 4.

The incorporation of H₂O, with or without O₂, yields the same by-products: HF, SO₂. However, the quantity of HF is higher with the addition of H₂O, and the corrosive compounds such as SO₂F₂, SOF₄ have disappeared and are replaced by SO₂.

The post-treatment of these products raises no problem on a scrubber or a soda lime cartridge.

It is also possible to take the prior precaution of selecting the line materials to avoid the formation of sulfuric acid in the upstream circuit and in a wet atmosphere, especially if a large excess of water is introduced.

Although F_2 has not been quantified, by analogy with similar cases, it is presumed that it has practically disappeared as SO_2F_2 and SOF_4 . Thus, there is no risk of generating OF_2 during a post-treatment on
5 a scrubber.

In conclusion, for the H_2O addition tests performed upstream of the plasma, significant advantages can effectively be observed, that is:

- the corrosive fluorinated by-products which
10 would be incompatible with neutralization post-treatment on a "wet scrubber" or on soda lime, have effectively disappeared, and are essentially replaced by HF ;

- in addition, from the conversion yield
15 standpoint, the destruction rate is significantly improved.

Figures 5 and 6 respectively show the influence of O_2 and H_2O on the destruction of SF_6 as a function of the gas flow rate (water vapor) added.

20 Figure 5 shows, as a function of the added gas flow rate, the SF_6 destruction rate at 1000 ppm and at 4 kW.

Curve 5-I represents the case of the addition of O_2 alone without water, curve 5-II that of the
25 addition of H_2O alone without O_2 , and curve 5-III that of the addition of H_2O with O_2 , the latter being added at a flow rate of 0.075 l/min.

These curves show that the destruction rate (DRE, in %) is higher in the case of curve 5-II, which
30 is that of the addition of H_2O alone without O_2 . The rate increases from 70% in the present situation (O_2) to 88% with H_2O .

At 1000 ppm, H_2O by itself is found to improve the DRE by 18%. On the contrary, the introduction, or
35 not, of O_2 , has barely any effect on the destruction rate.

Figure 6 shows, as a function of the added gas flow rate, the destruction rate, in %, of SF_6 at 5000 ppm and at 4 kW.

Curve 6-I represents the case of the addition of O_2 alone without water, curve 6-II that of the addition of H_2O alone without O_2 , and curve 6-III that of the addition of H_2O with O_2 , the latter being added at a flow rate of 0.25 l/min.

At 5000 ppm, the water is found to have a lesser effect of the destruction of SF_6 ; the rate only rises from 70% to 80%. On the contrary, the influence of oxygen (O_2) is the same. The influence of water vapor depends on the SF_6 concentration in the mixture, with was not the case for the conversion chemistry with oxygen.

Case of the destruction of CF_4

In the case of CF_4 , O_2 was first injected upstream of the plasma, and the following experimental conditions were used:

- CF_4 : concentration 5000 ppm,
- power : 4000 W,
- total throughput : = 50 l/min,
- oxygen flow rate : = 0.375 l/min.

As shown in Figure 7 (results of the IR analysis), the by-products produced by the destruction of CF_4 with O_2 (without H_2O) are as follows: HF, COF_2 , CO_2 , FNO, FNO_2 .

Water was then added in the following conditions:

- CF_4 : concentration 5000 ppm,
- total throughput : = 50 l/min,
- H_2O flow rate : = 0.6 l/min,
- power : = 4000 W.

The results of the IR analysis are shown in Figure 8.

The incorporation of H_2O with or without O_2 yields the same by-products: HF, CO and NO. However,

the quantity of HF is higher with the addition of H_2O , and the products such as COF_2 , CO_2 , FNO , FNO_2 have disappeared and are replaced by CO and NO.

Figure 9 shows, as a function of the added gas flow rate, the destruction rate of CF_4 at 5000 ppm and at 4.5 kW.

Curve 9-I represents the case of the addition of O_2 alone without water, curve 9-II that of the addition of H_2O alone without O_2 , and curve 9-III that of the addition of H_2O with O_2 , the latter being added at a rate of 0.2 l/min.

At 5000 ppm, the addition of H_2O , into the mixture $CF_4 + N_2$, has a lesser influence than with SF_6 ; the destruction rate is raised from 56% to 64%. However, in the case of CF_4 , the influence of H_2O is identical at 1000 ppmv and 5000 ppmv.

Water injection downstream of the plasma

In the course of tests, it was found that the destruction efficiency was lower than in the previous case, unless, obviously, oxygen had already been added in excess upstream.

This is explained by the fact that the SF_6 or CF_4 dissociation fragments have had the time, upon leaving the plasma column, to react significantly together to reform the initial PFC molecule, before being able to contact the water vapor and react with it to form stable corrosive fluorinated by-products. The conversion rate is not zero, because the gas is still very hot at this level, the temperature being about 700 to 1700 K (hence the presence of the heat exchanger downstream). However, this temperature is lower than in the plasma column (much higher than 2000 K) and furthermore, the populations of more highly excited states outside equilibrium, which play a role in the dissociation efficiency, have substantially decreased.

The invention, regardless of its embodiment, allows the use of a solid bed of granules based on soda

lime, or of a gas scrubber, as a means for irreversibly trapping the by-products of the plasma reaction, before releasing the effluent stream to the atmosphere.

5 The semiconductor manufacture reactors (not shown in Figure 10) which operate under vacuum, are connected to pumps of which Figure 10 (which will now be described) only shows the rough vacuum pumps 1 which deliver an effluent at atmospheric pressure at the outlet 2.

10 A plurality of pumps 1 connected to various reactors are connected in parallel, in order simultaneously to treat the effluents issuing from reactors which may execute different steps of the process (deposition, etching, reactor cleaning, etc.).

15 A first particle filter 4 is provided before introduction via 5 of these gases into the plasma system 6 (which may be any plasma system for the destruction of effluents, particularly a system as described in US-A-5 965 786).

20 At the outlet of the plasma system 6, heat exchanger means 9 are placed to cool the gases treated, with, in the lower part of these means 9, means 16 for recovering any liquids condensed in these means 9 or any solids formed upstream or in the means 9.

25 After passing through the valve 10 which serves to isolate the plasma from (its discharge line) downstream if necessary, the low temperature gases pass through the line 11 to reach an additional trap 13 (optional, depending on the method) optionally to
30 condense waste products or to trap any solids which are removed at 15, while the remaining gaseous effluents flow via the line 12 into the dry or wet trapping means 14 for gaseous products, means known per se to a person skilled in the art.

35 According to the invention, elements other than oxidizing elements are injected at the points A (7) upstream of the plasma 6 and/or B downstream of the plasma 6, while at least one oxidizing element is

optionally (but not necessarily) injected into the plasma means 6, as explained above.

If the effluents in the line 5 do not contain a gaseous compound, for example WF_6 , of a metal liable, by passage through the plasma, to generate a metal deposit on the walls of the chamber where the plasma is generated, any hydrogenated and/or reducing gaseous product can be injected upstream of the plasma, including products containing both oxygen and hydrogen, without the risk of a metal deposit in the plasma generating means 6. The injection of exclusively hydrogenated and/or reducing reagent issuing from the plasma may be maintained, reduced or eliminated.

If, on the contrary, the effluents contain at least one gaseous compound of at least one metal (for example WF_6), at least one anhydrous oxygenated element (oxygen, air, nitrogen) is exclusively injected upstream of the plasma, into the effluent to be treated, while at least one hydrogenated and/or reducing additive product is injected preferably downstream of the plasma (or at the earliest into the plasma or into the post-discharge zone) into the mixture of first species created. (In case of uncertainty concerning this injection, it is preferable to use this second solution).

In this case, at least one reducing additive can be injected downstream of the plasma, such as H_2O , H_2 , CH_4 , NH_3 , alcohols such as methanol, ethanol, a glycol, a hydrocarbon, a hydride and/or a hydrogenated element.

Downstream of the plasma at point B (8), before cooling, oxidizing additives may optionally be added (if necessary).

CLAIMS

1. A method for plasma treatment of gaseous effluents at substantially atmospheric pressure,
5 comprising

- injecting the effluent to be treated into a plasma source,

- injecting water vapor upstream and/or downstream of the plasma.

10

2. The method as claimed in claim 1, in which the pressure of the effluents is between 0.8 bar and 1.3 bar.

15 3. The method as claimed in either of claims 1 and 2, in which the water vapor is injected in a concentration of between 100 ppm and 5%.

4. The method as claimed in one of claims 1 to 3,
20 in which the water vapor is injected at a temperature of between 20 and 300°C.

5. The method as claimed in one of claims 1 to 4, in which the effluents to be treated are effluents from
25 semiconductor treatment processes.

6. The method as claimed in one of claims 1 to 5, in which the effluents to be treated are a mixture of perfluorinated and/or hydrofluorocarbon gases and
30 nitrogen.

7. The method as claimed in one of claims 1 to 6, in which the plasma source is of the surface wave type.

35 8. A device for plasma treatment of gaseous effluents at substantially atmospheric pressure, comprising plasma torch means (4, 6, 8, 10) and means

(14, 16, 18, 24, 26) for injecting water vapor into a mixing zone (12, 21),

9. The device as claimed in claim 8, in which the
5 means for injecting the water vapor are placed upstream of the plasma formation zone.

10. The device as claimed in claim 8, in which the means for injecting the water vapor are placed
10 downstream of the plasma formation zone.

11. The device as claimed in one of claims 7 to 10, in which the plasma generating means comprise a surface wave source.

15

12. The device as claimed in one of claims 7 to 11, in which the means for injecting water vapor comprise a vaporizer with temperature regulating means (24, 28).

20 13. The device as claimed in one of claims 7 to 12, further comprising means for irreversibly trapping the plasma reaction products, for example a solid bed of granules based on soda lime, or a gas scrubber.

25 14. The method as claimed in one of claims 1 to 6, in which the effluents issuing from a reactor are destroyed, said effluents being transported through at least one pump and to plasma means capable of destroying at least some of the bonds in the PFC or HFC
30 type molecules between the fluorine and the other elements of these molecules of the PFC or HFC types, in order to generate first species which are then converted to second gaseous, liquid or solid species before interaction of these second species with dry or
35 wet stripping means, method in which at least one hydrogenated and/or reducing reagent is injected downstream of the plasma, but upstream of the stripping means, in order to react with the first species created

and to form the second species, of which at least some of these second species may be removed by wet stripping means such as a water scrubber, the water vapor injection step upstream and/or in front of and/or
5 downstream of the plasma optionally being eliminated.

15. The method as claimed in claim 14, characterized in that the injection of at least one hydrogenated and/or reducing reagent takes place at the
10 earliest in the plasma or in the post-discharge zone thereof.

16. The method for destroying effluents as claimed in either of claims 14 and 15, characterized in that
15 the hydrogenated and/or reducing reagent is selected from H_2O , NH_3 , CH_4 , and/or alcohols.

17. The method as claimed in one of claims 14 to 16, characterized in that at least one oxygenated
20 compound is injected upstream of the plasma.

18. The method as claimed in claim 17, in which the effluents do not comprise elements capable, by passage into the plasma, of generating a metal deposit on the
25 walls of the chamber in which the plasma is generated, characterized in that the oxygenated compound injected upstream may also contain hydrogen atoms, while the injection of the hydrogenated and/or reducing reagent may be maintained, reduced or even eliminated.