



**Application of dense plasmas generated at
atmospheric pressure for treating gas effluents**

Technical field and prior art

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The invention relates to the field of the treatment of gases by plasma techniques, and especially the treatment of gases such as perfluorinated gases (PFCs), particularly perfluorocarbon gases, and/or hydro-
10 fluorocarbon gases (HFCs), for the purpose of destroying them.

It relates to a unit or system for treating such gases and to a process for treating these gases.

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One industry particularly concerned by these problems is the semiconductor industry. This is because the manufacture of semiconductors is one of the industrial activities consuming significant tonnages of
20 perfluorinated gases (PFCs) and hydrofluorocarbon gases (HFCs).

These gases are used in plasma etching processes for etching patterns in integrated electronic circuits and
25 in plasma cleaning processes, especially for cleaning the reactors for producing thin-film materials by chemical vapour deposition (CVD).

They are also used in processes for the production or
30 growth or etching or cleaning or treatment of semiconductors or semiconductor or thin-film devices or semiconductor or conducting or dielectric thin films, or substrates, or else in processes for removing photosensitive resins used for microcircuit
35 lithography.

To do this, these PFC and/or HFC gases are dissociated within a cold electrical discharge plasma in a chamber



or reactor, in order to give, in particular atomic fluorine.

5 Atomic fluorine reacts with the atoms at the surface of a material to be treated or to be etched, in order to give volatile compounds which are extracted from the chamber by a vacuum pumping system and sent to the exhaust unit of the system.

10 Perfluorinated or hydrofluorocarbon gases are not in general completely consumed by the aforementioned processes. The amounts discharged by the equipment may exceed 50% of the PFC or HFC inflow.

15 Perfluorinated or hydrofluorocarbon gases are especially characterized by their great chemical stability and by their very high absorption in the infrared. They are therefore suspected of being able to make a significant contribution to the overall heating
20 of the climate by reinforcing the greenhouse effect.

Certain industrialized countries are in principle committed to reducing their emission of greenhouse-effect gases.

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Certain industries consuming these gases have chosen to anticipate the changes in regulations. In particular, the semiconductor industry is in the forefront in adopting voluntary emission reduction policies.

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There are several technological ways of achieving these reductions in emissions.

35 Among the various conceivable solutions, optimization of the current processes seems limited in its possibilities. The use of techniques involving alternative chemistry is inappropriate in most current equipment. As regards the technique of recovering and recycling unconverted PFCs or HFCs, this proves to be

very expensive if the aim is to provide products with a purity sufficient to be able to reuse them in the process.

- 5 There are also techniques for the abatement or destruction of unconverted PFCs or HFCs leaving the reactors.

Among the known abatement techniques, mention may be
10 made of the thermal conversion of PFCs, in a burner or an electric furnace, catalytic oxidation and plasma techniques.

These techniques have a limited efficiency, especially
15 with regard to the most stable molecules such as CF_4 , or do not allow satisfactorily efficient treatment of PFC streams encountered in practice in semiconductor fabrication plants, with flow rates, in the highest cases, typically of the order of a few hundred standard
20 cm^3 per minute.

Documents EP 874 537, EP 847 794 and EP 820 201 describe PFC or HFC gas abatement solutions, but not one gives any practical, in line, implementation,
25 within the context of a semiconductor production unit. Some of the solutions proposed (EP 820 801 and EP 874 537) relate exclusively to the case of carrier gases of the rare-gas type, which can be implemented in a laboratory, but not in such a production unit where
30 the consumption of these rare gases as dilution gases is excluded by manufacturers.

None of the other "plasma" type solutions, known at the present time for treating effluents of processes other
35 than semiconductor fabrication processes, allows satisfactorily efficient treatment of PFCs with high flow rates, such as those encountered in the field of semiconductor fabrication, typically of the order of a few hundred standard cm^3 per minute.

The same problems arise in the case of all the activities involving the techniques used in the semiconductor field, and especially all the techniques using PFC and/or HFC gases.

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Summary of the invention

The invention relates to a system for treating gases with plasma, comprising:

- 10 - a pumping means, the outlet of which is at a pressure substantially equal to atmospheric pressure;
 - means, downstream of the pump, for creating an atmospheric-pressure plasma.

- 15 Such a system proves to be well suited to the treatment of PFC or HFC type gases mixed with a carrier gas at a pressure substantially equal to, or of the order of, atmospheric pressure, in particular in the case of PFCs with concentrations of the order of 0.1% to 1% in a few
20 tens of litres of nitrogen or air per minute.

- Preferably, the plasma is a non-local thermodynamic equilibrium plasma, that is to say a plasma in which at least one region of the discharge is not in local
25 thermodynamic equilibrium.

- A plasma sustained at high frequency, within the MHz or GHz range, for example at a frequency greater than 50 MHz, or of the order of a few hundred MHz or a few
30 GHz, makes it possible to sustain such a non-local thermodynamic equilibrium plasma.

- In order to achieve a high conversion efficiency of the plasma, means for generating a plasma, downstream of
35 the pump, are chosen so as to produce an electron density of at least 10^{12} cm^{-3} , for example between 10^{12} and 10^{15} cm^{-3} or preferably between 10^{13} and 10^{14} cm^{-3} .

Preferably, the pressure drop downstream of the pump is limited to less than 300 mbar.

Now, the use of an atmospheric-pressure plasma,
5 downstream of the pump, may cause in the tube, or in the generally tubular dielectric chamber, within which the discharge is sustained, radial contraction phenomena in the plasma which are deleterious to effective operation of the treatment system according
10 to the invention.

According to one embodiment, a plasma tube having a diameter of between 8 mm and 4 mm, or between 8 mm and 6 mm, is selected so as to maintain a moderate degree
15 of contraction.

A plasma tube having a length of between 100 mm and 400 mm may furthermore be selected so as to limit the pressure drops downstream of the pump.
20

According to another aspect, the means for generating a plasma comprise a plasma discharge tube, the gas to be treated passing through this tube downwards.

25 This makes it possible to limit the risks of contaminating or blocking the tube with deposited liquids which might result in the coupling of the microwave power into the plasma being disturbed or in an excessively large pressure drop downstream of the
30 pump.

Draining means may therefore be provided in the bottom position of the plasma tube so as to recover the liquid condensates and to remove them from the treatment
35 circuit.

According to yet another aspect, oven-drying or tapping means may be provided in the gas path so as to limit

the deposition of solids or condensation which might increase the pressure drop downstream of the pump.

5 The invention also relates to a reactor unit comprising a reaction chamber, producing at least one PFC or HFC gas, and furthermore including a PFC or HFC treatment system as described above.

10 The reaction chamber is, for example, an item of equipment for the production or growth or etching or cleaning or treatment of semiconductor or thin-film devices or semiconductor or conducting or dielectric thin films or substrates, or else is a reactor for removing photosensitive resins used for microcircuit
15 lithography, or a reactor for depositing thin films during plasma cleaning.

The invention also relates to equipment for producing or growing or etching or cleaning or treating
20 semiconductors or semiconductor or thin-film devices or semiconductor substrates, comprising:

- a reactor for producing or growing or etching or cleaning or treating semiconductors or semiconductor or thin-film devices or semiconductor or conducting or
25 dielectric thin films or substrates, or else a reactor for removing photosensitive resins used for microcircuit lithography, or a reactor for depositing thin films during plasma cleaning;

- first means for pumping out the atmosphere in
30 the reactor;

- a treatment system as described above.

35 The treatment system is preferably located near the reactor. Advantageously, it may be located on a facilities floor of the treatment or production or etching or cleaning unit, or else on a floor of a fabrication or treatment or production or etching or cleaning shop.

The invention also relates to a process for treating gases with plasma, comprising:

- pumping of the gas to be treated, at a pressure substantially equal to atmospheric pressure;
- 5 - treatment of the said gas with an atmospheric-pressure plasma.

The gas to be treated may be premixed with a carrier gas, at substantially atmospheric pressure, for example
10 nitrogen or air, injected using nitrogen or air injection means.

The nitrogen or air has a diluting effect (in the case of dangerous reaction products) and a plasma-generating
15 role.

Advantageously, the plasma treatment takes place in a discharge tube, the process including a prior step of matching the diameter of this tube so as to limit the
20 radial discharge contraction phenomena in this tube.

The process may be applied to a chemical reaction in a reactor, the said reaction producing or emitting at least one waste gas to be treated by the treatment
25 process.

The said reaction may, for example, be a reaction for the production or growth or etching or cleaning or treatment of semiconductors or semiconductor or thin-
30 film devices or semiconductor or conducting or dielectric thin films or substrates, or else a reaction for the removal of photosensitive resins used for microcircuit lithography, or a reaction for the deposition of thin films during plasma cleaning, using
35 PFC and/or HFC gases, the waste gases being in particular PFC and/or HFC gases.

Brief description of the figures

The features and advantages of the invention will become more clearly apparent in the light of the description which follows. This description relates to
5 illustrative examples, given by way of explanation but implying no limitation, with reference to the appended drawings in which:

- Figure 1 shows a diagram of semiconductor
10 production equipment according to the invention;
- Figure 2 shows a diagram of a plasma source; and
- Figures 3 and 4 show schematically semiconductor production plants.

15 Detailed description of embodiments of the invention

The invention will firstly be described within the context of a semiconductor production plant.

20 Such a plant, provided with a treatment system according to the invention, comprises, as illustrated in Figure 1, a production reactor or etching machine 2, a pumping system comprising a high-vacuum pump 4, such as a turbomolecular pump 4, and a roughing pump 6, and
25 means 8 for the abatement of PFC and/or HFC compounds, of the plasma generator type.

In operation, the pump 4 maintains the necessary vacuum in the process chamber and extracts the gases
30 discharged.

The reactor 2 is fed with the gases for treating the semiconductor products, in particular PFC and/or HFC gases. Gas feed means therefore feed the reactor 2, but
35 these are not shown in the figure.

Typically, these gases are introduced into the reactor with a flow rate of the order of about ten, or a few tens, to a few hundred sccm (standard cubic centimetres

per minute), for example between 10 and 200 or 300 sccm.

In general, these gases are not consumed entirely by the semiconductor fabrication or treatment process, this being so up to proportions possibly greater than 50%. It is therefore quite common to have PFC and/or HFC flow rates, downstream of the roughing pump 6, of the order of a few tens to a few hundred sccm, for example between 10 sccm and 100 or 200 sccm.

The means 8 can be used for carrying out a treatment (dissociation or irreversible conversion) of these unconsumed PFC and/or HFC compounds, but they may also produce, thereby, by-products such as F_2 and/or HF and/or SiF_4 and/or WF_6 and/or COF_2 and/or SOF_2 and/or SO_2F_2 and/or NO_2 and/or NOF and/or SO_2 .

These means 8 are means for dissociating the molecules of the incoming gases in the means 8 and for forming reactive compounds, especially fluorinated compounds.

More specifically, the plasma of the means 8 is used to ionize the molecules of the gas subjected to the plasma, by stripping off electrons from the initially neutral gas molecules.

Owing to the action of the discharge, the molecules of the gas to be treated or to be purified, and especially the molecules of the base gas, are dissociated so as to form radicals of smaller size than the initial molecules and, thereafter, as the case may be, individual atoms, the atoms and fragments of molecules of the base gas thus excited giving rise to substantially no chemical reaction.

After passing through the discharge, the atoms or molecules of the base gas are de-excited and recombine respectively, to become intact thereafter.

In contrast, the impurities undergo, for example, dissociation and/or irreversible conversion by the formation of new molecular fragments having chemical properties different from those of the initial
5 molecules, which can thereafter be extracted from the gas by a suitable subsequent treatment.

A reactive unit 10 is used to make the compounds resulting from the treatment by the means 8 react with
10 a corresponding reactive element (for example, a solid reactive adsorbent) for the purpose of destroying the said compounds. The gases resulting from the treatment by the means 10 (in fact, the carrier gas laden with PFC and/or HFC type compounds and/or other impurities
15 such as those mentioned above) are then discharged into the ambient air, but without danger, with PFC and/or HFC proportions compatible with environmental protection (typically, less than 1% of the initial concentration) and very low, permitted proportions of
20 harmful impurities, that is to say below the legal exposure limits, typically less than 0.5 ppm or less than 1 ppm.

For safety reasons, the gaseous effluents coming from
25 the reactor or from the production chamber 2 are, downstream or in the exhaust of the roughing pump or the rough-vacuum pumping set, highly diluted in nitrogen (with an additive gas, namely oxygen) or air at substantially atmospheric pressure. The system
30 therefore includes nitrogen (and oxygen) gas or air injection means, not shown in Figure 1. The air, or nitrogen (and oxygen), is injected at the high-pressure stage of the roughing pump.

35 Preferably, dry nitrogen, obtained by cryogenic distillation, is injected as dilution gas. Thus, dilution reduces the problems (explained below) associated with the possible presence of residual moisture, which results in the formation of non-gaseous

products (H_2SO_4 or HNO_3 or SiO_xN_y , or, in the case of tungsten etching, WO_x or WOF_4) or other problems such as the hydrolysis of SiF_4 or WF_6 , which results in depositions right before the decontamination plasma.

5

The fluid flow rate downstream of the roughing pump 6 is imposed by this dilution, the typical flow rates encountered being of the order of a few tens of litres per minute (for example, between 10 and 50 l/min) of
10 nitrogen or air, which flow contains from 0.1% to 1% PFC and/or HFC.

The pressure, downstream of the pump, is of the order of atmospheric pressure, for example between 0.7 bar or
15 0.8 bar and 1.2 bar or 1.3 bar.

The use, at atmospheric pressure, of a carrier gas such as air or nitrogen requires a large amount of energy to ionize the gas by plasma generation means 8 and to
20 sustain the plasma (at least 150 W per centimetre of discharge tube, for example about 200 W per centimetre of discharge tube; according to another example, a power of between 150 and 500 W per cm of tube may be selected).

25

The plasma generated by the means 8 is preferably not in local thermodynamic equilibrium (LTE). This plasma may also be one in which at least one region of the discharge is not in local thermodynamic equilibrium. It
30 is thus possible to use a microwave torch, generally classed in thermal plasmas, but the "envelope" region of which, forming an appreciable volume fraction of the discharge and in which most of the conversion reactions can take place, is substantially not in LTE.

35

Preferably, the discharge or the plasma source is of the type sustained by an HF field in the MHz and GHz range. At these high frequencies, the electrons respond predominantly, or exclusively, to the exciting field,

hence the off-LTE character of these discharges. Controlling the deviation from thermodynamic equilibrium may allow the conversion chemistry to be optimized by controlling the nature of the by-products.

5 Various external operational parameters have an influence on this deviation, for example the choice of dilution gas or the addition in small amounts of certain additive gases, or the excitation frequency. This frequency also has an effect on the electron

10 density of the plasma, which in general increases with it. Plasmas sustained by microwave fields at atmospheric pressure have high densities (from 10^{12} to 10^{15} cm^{-3} at 2.45 GHz, and more specifically from 10^{13} to 10^{14} cm^{-3} in nitrogen or air), which help to achieve a

15 high efficiency in the conversion of PFCs and/or HFCs, including when they are in nitrogen or air.

In practice, the frequency will be chosen from one of the bands centred on 433.92 MHz, 915.00 MHz, 2.45 GHz

20 and 5.80 GHz. The band immediately below 40.68 MHz is already within the radiofrequency range, hence the plasma densities will be too low to obtain a high efficiency.

25 There are several generic families of high-frequency plasma sources that can operate at atmospheric pressure, resulting in ranges of different discharge characteristics and having various advantages or disadvantages, especially as regards their design and

30 manufacturing simplicity, their ease of implementation for the problem posed, and their cost.

Within the context of the envisaged application, the following four types of sources may be used.

35 The first type involves plasmas sustained within resonant cavities. A cavity may be supplied either via a waveguide or via a coaxial line. The spatial extension of the discharge is limited by the size of

the cavity. The plasma electron density cannot significantly exceed the critical density at the frequency in question, unlike in particular surface-wave plasma sources.

5

Also relevant are plasmas sustained within a waveguide, which may in fact be likened to imperfect cavities. Such plasmas also suffer from the abovementioned two limitations, namely size and electron density.

10 Furthermore, the maximum extent of the discharge corresponds to one of the dimensions of the cross section of the waveguide.

Torches represent a third type of high-frequency plasma source able to be used within the context of the present application. The discharge forms a load which, at the end of a length of transmission line (generally a coaxial line), absorbs the HF power. A torch can be supplied with power via a coaxial line or via a waveguide. An increase in the power results both in an increase in the density and the volume of the flame and of the envelope.

25 The fourth type of high-frequency plasma source able to operate at atmospheric pressure consists of the family of surface-wave applicators. Within the context of a surface-wave plasma source, the extent of the plasma column can be increased by simply increasing the incident microwave power, without it being necessary to redesign the field applicator. The density of the plasma in the column exceeds the critical density.

35 More detailed information about these various types of source are given in Chapters 4 and 5 of "Microwave Excited Plasmas", edited by M. Moisan and J. Pelletier, Elsevier, Amsterdam, 1992.

For flow rates of the order of a few tens of litres per minute of nitrogen or air carrier gas (with PFCs and/or

HFCs at a concentration of between 0.1% and 1% or a few %), it is quite possible to achieve degrees of conversion greater than 95% with an atmospheric-pressure HF plasma source.

5

Whatever the plasma source used (apart from torches), it employs a generally tubular chamber within which the discharge is sustained or a dielectric tube within which the discharge is generated. For example, it may
10 be a tube of the type described in document EP 1 014 761. A tube or tubular chamber having a length of between 100 and 400 mm, for example around 300 mm, and an internal diameter of between 4 and 8 mm, avoids introducing excessively large pressure drops downstream
15 of the pump, that is to say which would be incompatible with the roughing pump 6. This is because the roughing pump can in general operate only with, downstream, a pressure drop of at most 300 mbar, too large a pressure drop, of around 400 mbar, causing in general the
20 roughing pump to stop, which situation, in an application in a semiconductor production line, is difficult to accept.

Despite selecting a suitable length of tube, another
25 problem is that of the formation of solid and/or liquid deposits in the gas circuit located downstream of the roughing pump. Such deposition may occur and in turn give rise to pressure drops and/or corrosion liable to substantially impair the operation of the production
30 unit and result in it being shut down. This is the case, for example, in regions where cooling is carried out, especially downstream of the plasma.

Moreover, in atmospheric-pressure HF discharges, and
35 within the range of flow rates usually imposed by the pump 6 (a few tens of litres of carrier gas per minute), a radial contraction phenomenon may occur - the electron density decreases from the axis towards the periphery of the tube and the molecules of the gas

flowing at the periphery encounter fewer active species over their path than those flowing close to the axis of the tube. In certain cases, the discharge may no longer fill the entire cross section and one then witnesses
5 the appearance of several plasma filaments moving in an erratic manner, so that the conversion yield drops suddenly.

The degree of contraction depends on several factors,
10 in particular the diameter of the tube, the nature of the dilution gas, the impurities and adjuvant gases, the velocity of the flux, the thermal conductivity of the wall of the tube and the excitation frequency. In general, all other things being equal, the degree of
15 contraction decreases when the internal diameter of the discharge chamber is reduced or the frequency is decreased. However, the diameter of the tube cannot be reduced arbitrarily since, on the one hand, the thermal stress on the wall would increase correspondingly and,
20 on the other hand, the pressure drop across the plasma decontamination reactor 8 might become prohibitive depending on the total flow rate (for example in the case of several roughing pumps being connected together).

25

Now, as already explained above, an excessive pressure drop results in the roughing pump 6, and hence the entire production unit, stopping.

30 The internal diameter of the tube may be selected to be between 8 mm and 4 mm in order to reduce the contraction and obtain a high degree of conversion, while not imposing an excessive pressure drop on the roughing pump 6. By operating within the most
35 favourable conditions, the length of the discharge allowing a given degree of conversion to be obtained is reduced.

It is therefore preferable, before operating the plant, to select the internal diameter of the tube so that the contraction phenomenon is less pronounced. The use of variable diameter tubes allows the efficiency of the
5 process to be varied.

Another way of increasing the path length of the PFC molecules in the discharge is to alter the way the gas stream flows, for example by generating a vortex so as
10 to make the path of the particles curvilinear rather than linear.

Preferably, the tube will have a thickness of around 1 mm or between 1 and 1.5 mm.

15 The tube is therefore thin. In operation, the temperature of its external face is all the higher. However, it has been found (from trials lasting several hundred hours of operation) that this does not
20 prejudice the thermal stability of the cooling fluid: this fluid does not undergo any appreciable degradation, even over a very long time.

Furthermore, a tube having a thickness of close to 1 mm
25 allows optical measurements to be carried out in order to monitor the proper operation of the plasma source, and especially to monitor the length of the column. A plasma in air or nitrogen can be optically monitored through a tube having a thickness of 1 mm, or between
30 1 mm and 1.5 mm, something which is much more difficult through a tube having a thickness of 2 mm.

Depending on the type of source chosen, these general principles may be applied in various ways and may help
35 to a greater or lesser extent in optimizing the conversion efficiency.

In a resonant cavity, the plasma density cannot greatly exceed the critical density, at least if one is

confined to true cavity modes. This is because if the power is increased, surface-wave modes may appear, corresponding to standing waves if the cavity remains closed by conducting walls at its ends, travelling waves otherwise. In the case of a surface mode, the density is always greater than the critical density. For a closed cavity, the extent of the discharge along the tube is limited by the size of the cavity. The length of the latter is therefore chosen, by construction, so as to provide a sufficient plasma volume to obtain the desired conversion yield.

The same type of consideration applies to a discharge in a waveguide. In this case, one dimension of the cross section of the waveguide determines the maximum length of discharge, unless, for a sufficient power and depending on the configuration of the waveguide, the wave propagates outside the latter, which then becomes a surface-wave applicator. The dimensions of the waveguide will furthermore satisfy the conditions for the existence of the guided propagation mode at the frequency in question.

The case of a torch is substantially different, both the inner cone and the envelope of the plasma flame emerging in a chamber whose dimensions are generally quite large compared with those of the nozzle, so as not to disturb the regularity of the flow and the symmetry of the flame. This chamber is used to collect the stream of gas laden with by-products, so as to direct it towards the post-treatment means located downstream. The details of the shape of the nozzle (the number and dimensions of the orifices and the position in the cross section) play a role in controlling the path of the species in the flame. It may also be pointed out that the flow in the chamber may be optimized for the same purpose.

Finally, in the case of a surface-wave plasma, the extent of the discharge is not limited by the size of the conducting structure of the field applicator, which consequently does not need to be matched according to
5 the desired performance. The length of the discharge in the tube may be increased to the desired value by increasing the incident HF power delivered by the generator.

10 The gas circuit of all of the treatment means of the system in Figure 1 comprises, starting from the roughing pump 6, the line 7 conveying the effluents into the reactive plasma module 8, then the line 9 linking the plasma to the by-product post-treatment
15 device 10 and finally the line 12 for venting into the atmosphere the detoxified gases which can be discharged without any danger. To these may be added various fluid management components (by-pass valves and purging and isolating utilities for maintenance) and safety sensors
20 (flow-fault and overpressure alarms), these not being shown in Figure 1. The circuit components are chosen to be compatible with the products with which they are in contact for reliable operation.

25 Oven-drying or trapping systems may furthermore be present.

This is because the effluents extracted by the roughing pump 6, and returned to atmosphere pressure, do not all
30 necessarily remain in gaseous form. The problems are generally aggravated by the presence of any residual moisture (a few hundreds of ppmv) in the dilution gas. For example, an SF_6 etching process may produce solid sulphur, H_2SO_4 and HNO_3 , etc. Certain effluents may
35 condense or be deposited in solid form, thus running a risk of increasing the pressure drop downstream of the pump 6. As a result, there is a risk, already mentioned above, of the roughing pump 6, and with it the entire production unit, stopping.

Moreover, the diameter of the tubular plasma chamber, given the radial contraction phenomenon already mentioned above, may not in general exceed about ten mm. For a total flow rate of the order of a few tens of
5 slm (imposed by the roughing pump 6), the velocity of the gas stream is such that the heat exchange (radial heat diffusion) is too slow for most of the thermal energy generated in the plasma to be carried away by the fluid for cooling the chamber. As a result of the
10 microwave power needed to sustain a sufficiently dense plasma in nitrogen or air being very high, a considerable enthalpy is transported downstream of the discharge chamber. In this region, the gas is rapidly cooled by cooling means, for example by means of a
15 water heat exchanger structure, in order to prevent the line from being destroyed. By doing this, a preferred region for the condensation of residues, corrosion and/or blockage of the said line is thus created, and hence, again, there is a risk of increasing the
20 pressure drop downstream of the pump 6.

Under these conditions, according to one embodiment of the invention, unlike in all the current existing plasma plants, the decontamination reactor 8 is
25 prevented from being operated with an ascending stream, with the exchanger at the top of the reactor.

Furthermore, in the case of an ascending stream, solid and liquid residues may return to the plasma chamber
30 simply under gravity, and impair its operation. It has been observed, for example in the case of SF_6 etching, that sulphuric acid, a viscous liquid with a low vapour pressure, wetting the internal wall of the tube, precludes any re-ignition of the plasma because of its
35 poor dielectric properties. The tube must then be rinsed and dried, all the more awkward because of its geometry.

It is therefore preferable, for these reasons, to reverse the direction of flow of the gas stream and to make it flow downwards. Optionally, draining means may be provided in the bottom position of the tube, for example an exchanger-collector structure allowing the liquid residues to drain to the bottom point.

Figure 2 shows treatment means 8 according to the invention, comprising a microwave generator 14, a waveguide 18 and a discharge tube 26. The latter is placed in a sleeve 20, made of a conductive material and as described, for example in document EP - 820 801.

This surfatron-guide is furthermore provided with means 24, 52 for adjusting the axial position of the waveguide plunger 46 and of the tuning plunger 48 coaxial with the discharge tube. This second plunger forms a quarter-wave trap. It is fixed to a sliding disc 50, for example made of Teflon. The means 24, 52 are in fact rods that can be manually actuated for the purpose of adjusting the impedance of the system.

In Figure 2, the gas is shown flowing downwards, in accordance with what was explained above. The reference number 22 furthermore denotes draining means in the bottom position of the tube 16, for draining the liquid residues to the bottom point.

The length of the lines may influence the nature of the products which actually reach the post-treatment system 10. It may be indicated, in the case of a system with a solid reactive adsorbent, to locate the said system as close as possible to the plasma outlet, so that it treats only gaseous products for which it is specifically designed.

The specifications of the post-treatment system 10 are preferably chosen in order to take account of the generation of by-products (corrosive fluorinated gases

such as HF, F₂, COF₂, SOF₂, etc., nitrogen oxides, etc.) by the process and the PFC conversion plasma. Making use of the departure from thermodynamic equilibrium does not provide absolute flexibility for controlling
5 the respective concentrations of these by-products.

Furthermore, certain features of the post-treatment device 10 may be imposed *a priori*, for example in the case of already existing plants or established
10 decontamination methods at the user's premises.

In general, cooling means (not shown in Figure 1) are provided for the plasma source (especially for the discharge chamber and the gas outlet) and the
15 electromagnetic energy supplies. Apart from the thermal power to be extracted, certain temperature ranges may be imposed, for example in order to prevent condensation upon stopping. The architecture of the cooling circuits is therefore preferably tailored so as
20 to be able to use, as refrigeration sources, the standard cold-water networks in the plant.

The incident HF power is an operational parameter both of the electromagnetic energy circuit and the plasma
25 source. In order for the source to operate under proper energy efficiency conditions (effective transmission of the power into the plasma), it is sought to minimize the power reflected by the generator and the heating losses in the field applicator structure.

30 Depending on the design of the plasma source, external adjustment means, such as short-circuiting plungers 46 (Figure 2) which can move at the end of the waveguide or tuning screws, can be used so as to ensure correct
35 impedance tuning.

Impedance tuning may be relatively insensitive to the operating conditions (equipment start/stop, multi-step process, drift and fluctuations). The systems based on

cavities are, for example, "sharper" than surface-wave systems and it may be indicated to provide automatic tuning means slaved to the reflected power measurement. The reflected power is also, in general, a parameter
5 characterizing the proper operation of the plasma source, malfunctions generally being associated with an appreciable increase in the reflected power.

However, this is not systematic and other physical
10 parameters may be used to ensure proper operating safety, such as certain signatures characteristic of plasma (extent, luminosity, etc.), which may be diagnosed by optical sensors, or abnormal thermal variations in the plasma source. The latter is
15 furthermore provided with suitable initiation means. This is because a nitrogen or air plasma cannot be spontaneously initiated at atmospheric pressure when the HF power is established.

20 In practice, there may be constraints associated with integration and operation in a semiconductor fabrication unit. However, as a general rule, the proposed structure according to the invention may be consistent with the methods of operating the process
25 machines in this field and with the general practices of semiconductor manufacturers, for example in the case of intermittent operation only during the process phases, with suitable stop/start procedures and a unit for interfacing the controllers with the pump and with
30 the deposition/etching equipment.

It is also compatible with taking up a small amount of floor space, often imposed by the structures of semiconductor production units because of the scarcity
35 and the cost of floor space in semiconductor fabrication plant facilities floors.

As illustrated in Figures 3 and 4, various arrangements may be chosen.

The treatment unit 8 may be located a few metres (for example, less than 5 m) from the machine or reactor 2 or from the roughing pump 6, on the facilities floor 60 in the production unit, as in Figure 3. The reactor 2 itself is located in the fabrication shop 62.

In the case of Figure 4, the treatment unit may be more compact and integrated, with the vacuum pump 6, and as close as possible to the equipment 2, on the floor of the fabrication shop 62.

One particular illustrative example will now be given. It relates to a surface-wave system for an $\text{SF}_6/\text{C}_4\text{F}_8$ etching reactor.

15

1. Microwave circuit and field applicator.

The chosen excitation frequency was 2.45 GHz. Transfer of microwave power sufficient for the application (several kW) is possible, at this frequency, using a waveguide, generally to the WR 340 standard, having a cross section of reasonable size. The field applicators may be of the surfatron-guide or surfaguide type, the latter providing greater simplicity. A surfaguide allows excellent impedance tuning merely by adjusting the position of the movable short-circuiting plunger closing off the waveguide at its end, without having to use a three-screw matcher.

30 The microwave circuit therefore comprises:

- a microwave generator (switched-mode power supply and magnetron head) with adjustable power up to a maximum power of 6 kW;
- a circulator with a water charge suitable for dissipating all of the reflected power, so that none of it is returned to the magnetron;
- means for measuring the incident power and the reflected power;

- the surfaguide field applicator, together with the dielectric discharge tube, constituting the plasma source;

- finally, a movable short-circuiting plunger, operated by hand or motor-driven, at the end of the waveguide, for impedance tuning.

2. Gas circuit.

10 This is basically made of a material resistant to the fluorinated corrosive products, i.e. a polymer of the PVDF or PFA type, except for the active parts of the plasma source 8 and the components where there is considerable heat generation, such as the immediately downstream line element contiguous with the discharge tube, which remain made of metallic or ceramic materials.

On the exhaust side of the rough-vacuum pump 6, a system of by-pass valves (a three-way valve or three two-way valves, depending on the commercial availability of suitable components) makes it possible to avoid the treatment system via the gas stream in the event of an operating incident or during maintenance phases. These valves are mechanically or electrically interfaced so as to prevent any inopportune closure of the exhaust, which would cause the pressure to rise and the pump to stop. The plasma decontamination unit 8 itself includes means for detecting any excess pressure drops in the stream of gas to be treated.

The discharge tube is a double-walled tube, the cooling being provided by the circulation between these two walls of a dielectric fluid by means of a hydraulic gear pump. This fluid is in turn cooled continuously by heat exchange with the cold mains water delivered to the facilities of the semiconductor fabrication unit. The central tube, in contact with the plasma, is made of a suitable ceramic material, which is a good

dielectric, refractory and resistant to thermal stresses and also to chemical attack by the corrosive fluorinated species.

5 On leaving the discharge tube, the gas may be at a high temperature since the atmospheric-pressure microwave plasma, although in general not being in thermal equilibrium, is not a "cold" plasma similar to low-pressure discharges. The gas is therefore cooled, by a
10 water heat exchanger, before being sent into the downstream line. This cooling may cause, locally, the condensation of liquid or solid products which it is desirable to be able to collect suitably, in order not to risk the plant being blocked. For this reason, as
15 already explained above, the operation is carried out with a descending stream, with the exchanger located in a low position. A suitable tap-off makes it possible, when necessary, to drain the collector at regular intervals.

20 The device 10 for neutralizing the corrosive fluorinated gases is preferably installed a short distance downstream of the plasma. It is a cartridge with a solid reactive adsorbent, preferably designed to
25 fix molecular fluorine, which will be the main by-product if the etching or cleaning process does not use water or hydrogen. The bed also retains, in a lesser amount, the etching products such as SiF_4 or WF_6 , and other dissociation products from the process plasma or
30 the decontamination plasma, such as COF_2 , SOF_2 , etc.

The gas circuit includes a number of manually operated or motor-driven valves, making it possible to isolate, purge and flush the various parts of the system with an
35 inert gas.

3. Cooling fluids circuit.

The water delivered to the facilities of the semiconductor fabrication plant is used to cool the
5 switched-mode power supply and the magnetron head of the generator, the dielectric fluid for cooling the discharge tube and the gas on the output side of the plasma tube. To extract the heat from the dielectric fluid, water from the actual cold mains is used, in a
10 closed circuit (about 5°C) in a plate exchanger. On the other hand, in the case of the generator, it is not desirable to risk condensation phenomena that could cause short-circuits. It will therefore be preferable to use the "town" water at about 20°C, which will
15 circulate in succession in the switched-mode power supply and the magnetron head, and then in the exchanger-collector remote from the plasma. In practice, this "town" water will also come from a closed circuit and its temperature is preferably
20 regulated centrally if a large number of machines have been installed.

4. Example of the process and performance.

25 A plasma decontamination system, according to the invention, was installed as shown in the diagram in Figure 1 downstream of an ALCATEL 601E plasma etching machine 2. The chemistry for etching single-crystal silicon used, in sequence, the gases SF_6 and C_4F_8 (14"-
30 3", for example) with respective flow rates of 170 sccm and 75 sccm.

In practice, after passing through the vacuum pumps 4, 6 and the output line, the gases entered the plasma
35 decontamination unit 8 with a concentration averaged over time. With the concentrations indicated above, the SF_6 entered the unit 8 with a concentration of 90 sccm, accompanied by C_4F_8 with a concentration of 24 sccm.

The system 10 for neutralizing the fluorinated acid gases was a commercially available cartridge of the CleanSorb™ brand. The stream of gaseous effluents was analysed at various points in the system by quadrupole
5 mass spectrometry.

The ALCATEL etching process used the PFC gases SF₆ and C₄F₈. The exhaust from the roughing pump 6 was diluted with dry air (approximately 100-150 ppm residual H₂O)
10 at 30 slm. The SF₆ and C₄F₈ concentrations were measured downstream of the etching chamber 2 (high-density ICP source). The degrees of destruction in the decontamination plasma were calculated as the ratio of the concentration on leaving the said plasma to the
15 concentration on entering the said plasma, i.e. without including the prior dissociation by the etching process itself.

The output from the decontamination plasma 8 contained, apart from the residual concentrations of the two PFCs,
20 the following by-products: SiF₄, F₂, COF₂, SOF₂, NO₂, SO₂, NOF and, possibly, HF because of the residual moisture in the dilution air. After passing over the neutralization cartridge 10, none of these pollutants
25 dangerous to the air was present in the gas stream with a concentration greater than the average or limiting exposure value.

The degree of abatement of C₄F₈ was almost 100%, the residual concentration being less than the detection
30 noise level. The degrees of abatement of SF₆ are given in Table I for various conditions. It may be clearly seen that the degree of abatement increases with the incident microwave power, that is to say with the extent of the plasma region. It may also be seen that
35 the destruction efficiency, all other things being equal, increases when the diameter of the tube decreases. Furthermore, the direction in which the gas stream flows - ascending or descending - has little

effect on the destruction efficiency, but makes it possible to avoid certain risks already mentioned above.

- 5 Similar results were obtained with higher flow rates of SF_6 (up to 300 sccm) and with greater dilutions (up to 70 slm), and for other PFCs, such as C_3F_8 , NF_3 , C_2F_6 , CF_4 , CHF_3 , etc.
- 10 In Table I, the "process inlet" denotes the inlet of the reactor 2 and the "detox inlet" denotes the inlet of the treatment device 8.

Table I

15

Tube Ø (mm)	SF_6 flow rate, process inlet (slm)	SF_6 flow rate, detox inlet (slm)	Dilution gas		Additive O_2 (slm)	Degree of destruction			
			Air (slm)	N_2 (slm)		$P_{\min}$ (kW)	%	$P_{\max}$ (kW)	%
10 ⁽¹⁾	-	170	-	20	1	3	70	3	70
	170	75	30	-	-	3	70	3	70
8 ⁽¹⁾	-	170	-	20	1	3	97	3.5	98
	170	75	30	-	-	2.5	94	3.5	97
6 ⁽¹⁾	-	170	-	20	1	1.6	95	2.5	99
10 ⁽²⁾	-	300	30	-	0.45	3.5	77	3.5	77
8 ⁽³⁾	-	200	20	-	0.3	3.5	97	3.5	97
10 ⁽³⁾	-	200	20	-	0.3	3.5	81	3.5	81
12 ⁽²⁾	-	200	20	-	0.3	3.5	67	3.5	67
(1) Measurement on alpha-test with off/on etching process (2) Laboratory measurement with ascending stream (3) Laboratory measurement with descending stream									

The invention has been described within the context of a chamber 2 for the production or etching of semiconductor components.

It applies in the same way, and with the same advantages, to the case of a chamber or reactor 2 for the production or growth or etching or cleaning or treatment of semiconductors or semiconductor or thin-
5 film devices or semiconductor or conducting or dielectric thin films or substrates, for example silicon substrates during the fabrication of microcomponents or microoptic devices.

It also applies, again with the same advantages as described above, in the case of a reactor for removing photosensitive resins used for microcircuit lithography, or else in the case of a reactor for
5 depositing thin films during plasma cleaning.

CLAIMS

1. System for treating gases with plasma, comprising:
 - a pumping means (6), the outlet of which is at a pressure substantially equal to atmospheric pressure;
 - means (8), downstream of the pump, for creating an atmospheric-pressure plasma.
2. System according to Claim 1, the means (8) for generating a plasma comprising means (14) for producing a high-frequency discharge.
3. System according to Claim 2, the discharge being produced at a frequency within a band centred on 433.92 MHz or 915 MHz or 2.45 GHz or 5.80 GHz.
4. System according to one of Claims 1 to 3, the means (8) for generating a plasma comprising a resonant cavity.
5. System according to one of Claims 1 to 3, the means (8) for generating a plasma comprising means for sustaining a plasma within a waveguide.
6. System according to one of Claims 1 to 3, the means (8) for generating a plasma comprising a torch.
7. System according to one of Claims 1 to 3, the means (8) for generating a plasma comprising a surface-wave applicator.
8. System according to one of the preceding claims, the means (8) for generating a plasma allowing a plasma to be produced with an electron density of at least 10^{12} cm^{-3} or between 10^{12} cm^{-3} and 10^{15} cm^{-3} or between 10^{13} cm^{-3} and 10^{14} cm^{-3} .
9. System according to one of the preceding claims, the means (8) for generating a plasma comprising a plasma

discharge tube having a length of between 100 mm and 400 mm.

10. System according to one of the preceding claims,
5 the means (8) for generating a plasma comprising a plasma discharge tube having an internal diameter of between 8 mm and 4 mm.

11. System according to one of the preceding claims,
10 the means (8) for generating a plasma comprising a plasma discharge tube (26) and means for generating a vortex in the tube.

12. System according to one of the preceding claims,
15 the means (8) for generating a plasma comprising a plasma discharge tube (26), the gas to be treated passing through this tube downwards.

13. System according to the preceding claim, draining
20 means (22) being placed in the bottom position of the plasma tube (26).

14. System according to one of the preceding claims,
comprising a reactive unit (10) for making the
25 compounds resulting from the plasma treatment (8) react for the purpose of destroying them.

15. Reactor unit comprising a reaction chamber (2),
producing at least one perfluorinated (PFC) or
30 hydrofluorocarbon (HFC) gas, and furthermore including a system for treating a perfluorinated gas (PFC) or a hydrofluorocarbon gas (HFC) according to one of Claims 1 to 14.

35 16. Unit according to Claim 15, the reaction chamber (2) forming part of equipment for the production or growth or etching or cleaning or treatment of semiconductor or thin-film devices or semiconductor or conducting or dielectric thin films or substrates, or

else being a reactor for removing photosensitive resins used for microcircuit lithography, or a reactor for depositing thin films during plasma cleaning.

- 5 17. Equipment for producing or growing or etching or cleaning or treating semiconductors or semiconductor or thin-film devices or semiconductor substrates, comprising:
- 10 - a reactor (2) for producing or growing or etching or cleaning or treating semiconductors or semiconductor or thin-film devices or semiconductor or conducting or dielectric thin films or substrates, or else a reactor for removing photosensitive resins used for microcircuit lithography, or a reactor for
- 15 depositing thin films during plasma cleaning;
- first means (4) for pumping out the atmosphere in the reactor;
- a treatment system according to one of Claims 1 to 14.
- 20
18. Equipment according to Claim 17, the treatment system being located less than 5 metres from the reactor (2).
- 25 19. Equipment according to Claim 17 or 18, the treatment system being located on a facilities floor (60) of the production or growth or etching or cleaning or treatment unit.
- 30 20. Equipment according to Claim 17 or 18, the treatment system being located on a floor of a production or growth or etching or cleaning or treatment shop (62).
- 35 21. Process for treating a gas, containing impurities, with plasma, comprising:
- pumping of the gas to be treated, in order to bring the gas to a pressure substantially equal to atmospheric pressure;

- treatment of the said gas with an atmospheric-pressure plasma.

22. Process according to Claim 21, the gas to be
5 treated containing a carrier gas, at substantially
atmospheric pressure, with which the impurities are
mixed.

23. Process according to Claim 22, the carrier gas
10 being nitrogen or air.

24. Process according to one of Claims 21 to 23, the
gas having, after pumping, a flow rate of between 10
and 50 l/min.

15 25. Process according to one of Claims 21 to 24, the
impurities comprising a perfluorinated gas (PFC) and/or
a hydrofluorocarbon gas (HFC).

20 26. Process according to one of Claims 21 to 25, the
gas to be treated containing SF_6 and/or C_4F_8 .

27. Process according to one of Claims 21 to 26, the
plasma being generated in a discharge tube (26) through
25 which the gases to be treated flow downwards.

28. Process according to one of Claims 21 to 27, the
gases to be treated having, after pumping, a flow rate
of between 10 sccm and 200 sccm.

30 29. Process according to one of Claims 21 to 28, the
plasma treatment having taken place in a discharge
tube, the said process including a prior step of
matching the diameter of this tube so as to limit the
35 phenomena of radial discharge contraction in this tube.

30. Process for producing a chemical reaction in a
reactor, the said reaction producing or emitting at
least one waste gas, and then comprising a treatment of

this waste gas by a treatment process according to one of Claims 21 to 29.

31. Process according to Claim 30, the reaction being a
5 reaction for the production or growth or etching or
cleaning or treatment of semiconductors or
semiconductor or thin-film devices or semiconductor or
conducting or dielectric thin films or substrates, or
else being a reaction for removing photosensitive
10 resins used for microcircuit lithography, or a reaction
for depositing thin films during plasma cleaning, by
means of perfluorinated (PFC) and/or hydrofluorocarbon
(HFC) gases, the waste gases containing or being
perfluorinated (PFC) and/or hydrofluorocarbon (HFC)
15 gases.

32. Process for the production or growth or etching or
cleaning or treatment of semiconductors or
semiconductor or thin-film devices or semiconductor or
20 conducting or dielectric thin films or substrates, or
for the removal of photosensitive resins used for
microcircuit lithography, or for plasma cleaning,
comprising:

- a step of reaction of the semiconductors or thin
25 films or substrates, or of removal of resins or of
plasma cleaning, with a perfluorinated (PFC) and/or
hydrofluorocarbon (HFC) gas, in a reactor;

- pumping out the atmosphere from the reactor (2);
- treatment of the gas of the atmosphere in the
30 reactor with a plasma using a process according to one
of Claims 21 to 29.

33. Process according to Claim 32, the perfluorinated
(PFC) and/or hydrofluorocarbon (HFC) gas entering the
35 reactor with a flow rate of between 10 sccm and
300 sccm.

34. Process according to one of Claims 21 to 33, the
treatment of the gas by the plasma comprising the

dissociation of the impurities in the gas in order to form reactive compounds.

- 5 35. Process according to Claim 34, comprising a reaction of the reactive compounds formed with a reactive element for the purpose of removing them from the gas to be purified.