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- (71) **Applicant:** SOLVAY SA [BE/BE]; Rue de Ransbeek, 310, B-1120 Bruxelles (BE).
- (72) **Inventor:** DIANA, Oliviero; Meeuwenlaan, 101, B-1800 Vilvoorde (BE).
- (74) **Agents:** MROSS, Stefan et al.; Solvay S.A., Rue de Ransbeek, 310, B-1120 Bruxelles (BE).
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(54) **Title:** A CHAMBER CLEANING METHOD USING F₂ AND A PROCESS FOR MANUFACTURE OF F₂ FOR THIS METHOD

(57) **Abstract:** Elemental fluorine is often manufactured electrochemically from a solution of KF in hydrogen fluoride and contains varying amounts of HF as impurity. The present invention provides a method for chamber cleaning using F₂ which contains more than 0.1 % by weight and equal to or less than 10 % by weight of HF. Surprisingly, such an F₂ is very well suited for the purpose of chamber cleaning. In a preferred embodiment, the F₂ which contains more than 0.1 % by weight and less than 2.5 % by weight of HF is electrolytically produced, cleaned, delivered and used on site, without any pressurizing treatment. Omitting cleaning steps and process and using process conditions leaving a relatively high HF content in the F₂ allows at the same time to omit pressurizing steps. The advantage is that less cleaning steps.



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A chamber cleaning method using F₂ and a process for manufacture of F₂
for this method

The invention concerns a chamber cleaning method using F₂ with a specific content of HF and a process for manufacture of F₂ for this method.

F₂ (elemental fluorine) is used, i.a., as an etching agent and as a cleaning agent for cleaning of chambers used in the manufacture of semiconductors, micro-electromechanical devices, solar cells, TFTs (thin film transistors). HF was considered as undesirable component in F₂ intended for etching or chamber cleaning. WO 2012/016997 for example provides a purification process for the manufacture of highly pure F₂, useful as etching agent and chamber cleaning agent, with a content of equal to or less than 10 ppm of HF.

F₂ is often manufactured by the electrolysis of hydrogen fluoride (HF) in the presence of molten/dissolved fluoride salts ; especially adducts of HF and KF having a formula of about KF·(1.8 – 2.3)HF are electrolyzed. Often, production of F₂ for chamber cleaning is performed on site, i.e. on the premises of the point of use.

Object of the present invention is to provide a technically and economically advantageous method of chamber cleaning wherein F₂ is used as chamber cleaning agent and a technically and economically advantageous process for providing F₂ suitable for chamber cleaning.

These objects and other objects as apparent from the description and the claims are achieved by the present invention.

Consequently, one aspect of the present invention concerns a method for the cleaning of chambers using elemental fluorine which contains equal to or more than 0.01 % by weight, preferably equal to or more than 0.1 % by weight, of HF, and equal to or less than 10 % by weight, preferably equal to or less than less than 5 % by weight, and more preferably, equal to or less than 2.5 % by weight of HF, and most preferably, equal to or less than 2 % by weight of HF.

It was observed that F₂ which comprises more than 0.1 % by weight of HF is very suitable as agent for chamber cleaning.

More preferably, the content of HF in the F₂ is equal to or greater than 0.5 % by weight. Especially preferably, it is equal to or lower than 2 % by weight. It is especially preferred to apply F₂ with a content of equal to or more

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than 1 % by weight of HF, and a content of equal to or less than 2 % by weight of HF.

The chambers which can be cleaned are preferably those used in the manufacture of semiconductors, micro-electromechanical devices, solar cells, TFTs (thin film transistors). In such chambers, items are treated according to known processes. For example, layers of Si, SiO₂, silicon nitride, silicon oxynitride, metals, metal oxides, carbon-fluorine polymers are formed on the items, e.g. according to plasma enhanced (PECVD) processes, and partially etched away in other treatment steps. During these processes, layers do not only form on the items but also undesired on parts in the chamber, e.g. construction parts, lines, shower heads or the walls. The method of the invention serves to clean the chambers from such undesired deposits.

The technical parameters of chamber cleaning are known to the expert in the art.

The chamber cleaning method of the present invention can be performed thermally or supported by an in-situ plasma and/or by a remote plasma.

While the pressure is very variable, e.g., may be equal to or lower than ambient pressure or greater than ambient pressure, it is preferably lower than ambient pressure for reasons explained below. The temperature during a thermal chamber cleaning is preferably equal to or greater than 400°C. In plasma-supported chamber cleaning, the temperature inside the chamber may often be greater than 100°C.

While any source for F₂ comprising HF as outlined above may be used as chamber cleaning agent in the present invention, preferably F₂ is applied which is produced in one or more electrolytic cells and which is purified as explained further below.

The plant for F₂ manufacture may preferably be located on site of the plant having chambers of which are to be purified. If desired, however, the F₂ may be produced remote from the point of use and be transported from the location of its manufacture to its point of use.

According to a preferred embodiment, the method for chamber cleaning comprises at least two steps :

(I) a step of providing F₂ comprising equal to or more than 0.01 % by weight, preferably equal to or more than 0.1 % by weight, and equal to or less than 10 % by weight, preferably equal to or less than 5 % by weight, and especially preferably, equal to or less than 2.5 % by weight of HF ; and

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(II) a step of chamber cleaning using the F_2 from step 1.

While, as mentioned above, any F_2 with the HF content given above may be use in step (II), preferably, the chamber cleaning step (II) is performed using an F_2 with the HF content as indicated above which HF was manufactured in
5 step (I) in the specific way as described below.

In the following, a preferred embodiment of providing F_2 according to step (I) is described. This preferred embodiment of step (I) as described now is a separate aspect of the present invention.

The preferred embodiment of step (I) concerns a process for the
10 manufacture of F_2 comprising more than 0.1 % by weight and equal to or less than 2.5 % by weight of HF, and this process comprises :

- A) at least one step of electrolytically producing raw F_2 from HF in the presence of KF
- B) at least one step of removing particles entrained in the raw F_2 obtained
15 in step A)
- C) at least one step of filtering any remaining particles out of the F_2 leaving step B)
- and
- D) a step of delivering the F_2 to a buffer tank or a storage tank.

20 The flow of F_2 can be measured, for example, with a flow indicator, for example, a flow indicator operating according the Coriolis type which is very accurate.

Step A) usually is performed by electrolysis of HF in the presence of an electrolyte salt, especially in the presence of KF.

25 Step B) may be performed by contacting the raw F_2 from step B) with liquid HF, e.g. by passing the raw F_2 through liquid HF, in a static scrubber or in a jet scrubber.

The scrubber can be operated in large range of temperatures ; it may be composed of multiple stages ; two or more scrubbers can be arranged in parallel
30 and/or in series ; and each of these scrubbers can be operated at different pressures and/or different temperatures. The temperature of the scrubber or each of the scrubbers, if there are more scrubbers than one, can vary between -200°C and $+20^{\circ}\text{C}$. Preferably, the temperature of the scrubber or each of scrubbers is equal to or higher than -150°C , and more preferably, it is equal to or higher
35 than -82°C . Preferably, the temperature of the scrubber or each of the scrubbers, if there are more scrubbers than one, is equal to or lower than -50°C . A

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preferred temperature range for the scrubber or each of the scrubbers, if more than one scrubbers are in use, is from -150°C to -20°C ; an especially preferred range is from -80°C to -50°C . Depending especially on the number, temperature and the pressure of the scrubber or scrubbers, the amount of HF which is removed from the F_2 , will vary. For example, at a higher pressure, at a lower temperature in the scrubber or scrubbers, and if several scrubbers are assembled in series, the amount of HF removed can be almost completely, such that only a few ppm are left in the treated F_2 . If the temperature is in the upper region of the range given above, at a lower pressure and only one scrubber to be passed, the amount of removed HF is low, and the F_2 after treatment may comprise almost all of the HF entrained. Nevertheless, the advantage of scrubbers, namely to remove solids, still will be achieved.

Step C) may be performed by passing the F_2 withdrawn from step B) through a filter made from suitably resistant material, e.g. made from Monel metal. The pore size may be equal to or smaller than $100\text{ }\mu\text{m}$, preferably equal to or smaller than $20\text{ }\mu\text{m}$. A suitable pore size range is 1 to $20\text{ }\mu\text{m}$. Preferably, the pore size is equal to or greater than $0.001\text{ }\mu\text{m}$. A preferred range is from 0.001 to $20\text{ }\mu\text{m}$.

According to step D), the F_2 withdrawn from step A), step B), step C) may be stored in an optional buffer tank. Preferably, the F_2 is stored in a sufficiently large buffer tank before its delivery to the point of use for the step of chamber cleaning. Alternatively, it is directly delivered according to step (II) to the point of use for chamber cleaning, if desired, through an additional filter.

Another preferred embodiment of step (I) concerns a process for the manufacture of F_2 comprising equal to or more than 2 % by weight and equal to or less than 10 % by weight of HF, preferably equal to or more than 4 % by weight and equal to or less than 8 % by weight of HF and this process comprises :

- A) at least one step of electrolytically producing raw F_2 from HF in the presence of KF
- B) at least one step of removing particles entrained in the raw F_2 obtained in step A) and
- C) at least one step of filtering remaining particles out of the F_2 leaving step B).

Step A) and C) are usually performed as described above. Step B) in this embodiment is usually a mechanical separation of particles, e.g. by means of a settling box.

This embodiment is particularly advantageous in that it is possible to produce F₂ gas suitable for use according to the method according to the invention without purification steps requiring cooling of the gas or washing of the gas with HF.

5 In the process according to the invention, it may be useful to have available two or three filtering devices for filtering the F₂ stream which can suitably be operated in alternating mode. This allows to ensure continuous operation of the F₂ manufacture. A particularly suitable filtering device comprises a first filter having relatively wider pore size (e.g. from 5-50 µm) and a second filter having
10 relatively narrower pore size (e.g. from 0.001 to 0.005 µm). In this case the F₂ gas to be purified from particles is first passed through the first filter and thereafter through the second filter.

It has also been found that it is particularly advantageous to clean the filters used in the present invention with liquid HF, thereby removing from the filter
15 particles filtered off. The cleaning operation is generally carried out when the filter is not in use to remove particles from the F₂ stream. The cleaning HF recovered from this step can suitably be fed to a step of electrolytically producing F₂. In that case the cleaning HF is suitably fed to the electrolytic step in liquid form.

20 In a particular aspect, when the F₂ manufacturing plant comprises a plurality of cells, the F₂ gas streams may be combined and filtered through a single filtering device (and optional additional filtering devices for operation in alternating mode).

Figure 1 shows a schematic representation of an illustrative plant suitable
25 for providing F₂ for use in the processes and methods according to the invention. The invention also concerns the said plant for F₂ manufacture. Raw F₂ is produced in electrolytic cells and supplied through line (1) to a filtering device having a plurality of filter sets (two shown in the figure) composed of a first filter having relatively wider pore size (5) and a second filter having relatively
30 narrower pore size (6). The filter sets can be operated in alternating mode by shutting or opening valves (7) placed in the respective lines. F₂ purified from particles and containing HF as described above is supplied through line (4) to a point of use, in particular for chamber cleaning, possibly after passing through a buffer tank. When appropriate, liquid HF is supplied through line (2) controlled
35 by a valve (7) to the filter set to clean the filters (5) and (6). HF recovered from

the cleaning of filters (5) and (6) can be withdrawn through line (3) controlled by a valve (7) and fed to the electrolytic cell for F₂ manufacture.

There are two particular alternatives to perform the process of F₂ manufacture and the method of chamber cleaning of the invention.

5 According to a first alternative, F₂ is provided which comprises HF in the concentration as indicated above, namely more than 0.1 % by weight and less than 2.5 % by weight of HF or in preferred concentrations as given above ; said F₂ is subjected to a pressurizing treatment, e.g. in a compressor or a pump, and thus, it is delivered to the point of use at a pressure greater than in the
10 electrolytic cell, i.e. usually it is delivered with a pressure of greater than 1 bar (abs). Often, in this first alternative, it is delivered at a pressure which is equal to or greater than 2 bar (abs) and equal to or lower than 10 bar (abs.). The advantage of this alternative is, for example, that smaller storage tanks may be utilized ; the disadvantage is that pumps or compressors must be provided which
15 always impart additional risks of escaping F₂ or machine failure. Additionally, being at relatively high pressure, F₂ might escape from the lines and apparatus and thus, might pose a safety risk. Thus, this alternative is not the preferred one.

 According to the second alternative which is the preferred one, the F₂ is delivered from its generation to the point of use without being subjected to any
20 pressurizing treatment.

 The expert is aware that F₂ and H₂, when getting into contact, may react in the form of heavy explosions. Thus, the F₂ compartments in an electrolytic cell are separated by so-called "shirts" from the H₂ compartments.

 To avoid any risk of contact between F₂ and H₂, it is preferred that the
25 pressure in the electrolytic cell both on the F₂ and H₂ side does not oscillate over a too high range ; often, it is preferred to keep the cell pressure within ± 0.01 to ± 0.05 bar of a preset value. The pressure in the cell may be from 1 bar (abs) to 2 bar (abs) and even higher, up to 6 bar (abs). But to be on a safe side in view of the control of pressure oscillation which is easier at lower pressures, often, a
30 pressure in the electrolytic cell in the range of from 1 to 1.1 bar (abs) is preferred.

 The F₂ is especially preferably generated in the electrolytic cell at a pressure of approximately 1.05 ± 0.02 bar (abs) and forwarded, via several steps to the point of use as chamber cleaning agent, having a pressure below
35 1 bar (abs), preferably having a pressure in the range from equal to or greater than 0.2 bar (abs) to equal to or lower than 0.55 bar (abs).

The second alternative will now be explained in detail. According to this preferred embodiment, the F_2 is not pressurized from step A) through step B), step C), including the delivery to the point of use in step D). If a buffer tank is applied, the F_2 is not pressurized in the buffer tank, too. This means that the driving force passing the F_2 from step A) to the final point of use is the pressure of approximately 1 to 1.1 bar (abs) in the electrolytic cell compartment in which the raw F_2 is generated.

In the preferred embodiment of the inventive process of F_2 manufacture which will now be described, the production, purification, the optional storage, and the delivery of F_2 containing more than 0.1 % by weight and less than 2.5 % by weight of HF to the point of use are well matched to each other such that at the point of use, F_2 is provided to the chamber or chambers to be cleaned with a pressure which is lower than ambient pressure. Preferably in this preferred embodiment, the content of HF in the F_2 is preferably equal to or greater than 0.5 % by weight. Preferably, it is equal to or lower than 2 % by weight ; and the pressure of the F_2 in the line to the chamber or chambers to be cleaned, i.e. at the point of use, preferably is 0.2 to 0.55 bar (abs).

Especially preferably, the pressure of the F_2 at the point of use is from equal to or greater than 0.2 to equal to or lower than 0.55 bar (abs.), and the concentration of HF is from equal to or greater than 0.5 % by weight to equal to or lower than 2 % by weight, and more preferably, from equal to or greater than 1 % by weight to equal to or lower than 2 % by weight.

As will be described below, a preferred embodiment of the invention provides F_2 in step A) by electrolytic generation from a molten electrolyte salt having the formula $KF \cdot (1.8 - 2.3)HF$, passing the raw F_2 in step B) through a static scrubber to contact it with liquid HF, passing the F_2 then in step C) through a filter to remove remaining solids, and, in step D), storing the F_2 in a buffer tank and passing the F_2 from the buffer tank to the point of use as chamber cleaning gas. If desired, the F_2 can be passed to the point of use via a flow indicator, e.g. a flow indicator operating according to the Coriolis type.

To give an impression of the trend of the pressure in the different steps from electrolytic generation of F_2 to the delivery of the point of use for chamber cleaning, the estimated minimal and maximal pressure drop in each step is given in the following table 1. It has to be noted that in the following description, a method is further explained wherein the pressure in the electrolytic cell is 1.05 bar (abs) because this is the preferred embodiment. The absolute pressure

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(but essentially not the pressure drop) may also be higher if the cell is operated at a higher pressure of the F₂ compartment.

Table 1 : Pressure drop in intermediate steps from F₂ generation to the point of use

Part	Pressure Drop	
	Minimal [mbar]	Maximal [mbar]
Static HF scrubber	40	80
Filter for solids	25	150
Flow indicator	5	50
All piping	20	50
In total	90	330

5 If, optionally, a solid trap for HF, especially a NaF tower, is provided, the minimum pressure drop for such an HF trap is estimated to be 10 mbar, the maximum pressure drop is estimated to be 150 mbar. Thus, in this case, the total pressure drop would be (90 + 10 =) 100 mbar as minimum, and (330 + 150 =) 480 mbar as maximum.

10 Under the assumption that the F₂ is generated in the electrolytic cell compartment having a pressure of 1.05 bar (abs), and under the assumption that it is desired to deliver the F₂ after its treatment with a pressure of from equal to or greater than 0.2 bar (abs) to equal to or lower than 0.55 bar (abs), and under the assumption that – in the absence of an NaF tower – the minimum pressure
15 drop is 90 mbar, and the maximum pressure drop is 330 mbar, then the F₂ pressure must be reduced using control valves

- from 0.95 bar (abs) to 0.2 bar to 0.55 bar if a minimum pressure drop is observed, or
- from 0.72 bar (abs) to 0.2 bar to 0.55 bar if a maximum pressure drop is
20 observed.

Of course, the actual pressure drop depends on the apparatus used, on the temperature, gas flow and other parameters. Thus, the values given above are only to help the expert to better understand the invention.

In the following, this preferred embodiment is explained in further detail.
25 Preferred embodiments of step A) :

In step A), F₂ is produced electrolytically. Often, salt compositions of the approximate formula KF·(1.8 – 2.3)HF are applied. Such compositions have a melting point, depending on the composition, around 80°C or above. Usually, an electrolyzer contains several electrolytic cells. Each cell often contains a
30 multitude of anodes. Often, the cell vessel containing the molten salt serves as

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cathode, or separate electrodes. Fresh HF is supplied continuously or batch wise to the cell to replenish electrolyzed HF.

HF is electrolyzed to form F_2 and H_2 which are collected in separate cell compartments. H_2 may be dumped. The raw F_2 formed contains up to 10 % by weight of HF, and possibly even more ; the raw F_2 further contains entrained particles which are essentially constituted of solidified electrolyte salt.

In step A), the raw F_2 is withdrawn from the respective cell compartment having a pressure of equal to or greater than 1 bar (abs). Usually, the pressure of the raw F_2 in the F_2 compartments is approximately 1.05 ± 0.05 bar (abs).

Preferred embodiments of step B) :

In step B), the raw F_2 is subjected to a purification treatment to separate all or a major part of solid impurities from the raw F_2 . Preferably, the solid-removing treatment comprises at least one step of contacting the raw F_2 with cooled liquid HF in a static scrubber.

The liquid HF with which the raw F_2 is contacted has a low temperature and consequently a low vapor pressure. The temperature of the liquid HF during its purifying contact with the fluorine is equal to or higher than the melting point of the HF at the respective pressure in the static scrubber. Preferably, it is equal to or higher than -83°C , more preferably, it is equal to or higher than -82°C . It is preferably equal to or lower than -60°C . The temperature of the liquid HF is preferably in the range between -60°C and -82°C . The HF can be cooled by cooling machines which provide a suitably cooled liquid to heat exchangers to keep the HF at the desired low temperature. In a preferred embodiment, the liquid HF in the scrubber is indirectly cooled by means of liquid N_2 which, when passing from the liquid to the gaseous state, provides the desired cooling effect.

The F_2 can be contacted with technical grade liquid HF. If desired, purified liquid HF can be applied.

Methods to purify HF, mainly to remove phosphorous compounds, sulfur compounds, arsenic compounds, metals, hydrocarbons and water are well known. See for example US patent 5,362,469 and US patent 5,585,085. According to US patent 5,362,469, water, arsenic compounds, boron compounds, phosphorous compounds and sulfur compounds as well as carbon compounds and metal compounds are removed from HF by contacting liquefied hydrogen fluoride with lithium fluoride and elemental fluorine. The HF is then distilled to provide pure HF. According to US patent 5,585,085, water and hydrocarbons

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are removed from HF by contacting it with elemental fluorine and subsequent distillation.

The raw F₂ from step A) may preferably be contacted with a purified liquid HF which is essentially free of at least phosphorous compounds, sulfur
5 compounds and arsenic compounds. HF can be purified according to the process of US patent 5,362,469 and then has a content of water of less than 1 ppm.

Often, it is sufficient to perform step B) only once to achieve a desired degree of solids removal. But if desired, the contact between F₂ and liquid HF can be repeated once, or even more often.

10 The raw F₂ is supplied to the static scrubber to be contacted with liquid HF under the pressure it has in the electrolytic cell compartment. No pump or compressor is used to raise the pressure of the raw F₂ withdrawn from the electrolytic cell compartment. Due to the marginal pressure loss in the line from the electrolytic cell compartment to the scrubber, the raw F₂ enters the scrubber
15 with a pressure corresponding to the pressure in the electrolytic cell, i.e. 1.05 ± 0.02 bar (abs).

Due to the low temperature of the liquid HF during its contact with fluorine, the vapor pressure of HF is very low. Thus, not only the content of entrained solids is reduced, but also entrained HF is removed. The F₂ after the
20 contact with liquid HF contains more than 0.1 % by weight and less than 2.5 % by weight.

The liquid HF which is used in the purification step is preferably circulated or reused, optionally after regeneration, e.g. by a step of distillation, to remove any solids washed out from the raw fluorine as described above. The advantage
25 is that any water initially present in the HF reacts with F₂ to form HF and OF₂ ; after some time, the water is consumed, and the fluorine to be purified will not be consumed by water in a side reaction, and the fluorine will not take up any OF₂ anymore because it is no longer formed.

The F₂ which leaves the static scrubber has a pressure which is, as a rule of
30 thumb, approximately 40 to 80 mbar lower than upon entering the static scrubber. The HF content depends from several conditions, e.g. from the initial HF concentration, from the temperature of the liquid HF and from the contact time. The conditions of contact between the liquid HF and the F₂ are selected such that the HF content is in the range given above, and notably, in the
35 preferred ranges.

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Preferred embodiments of step C) :

The F₂ withdrawn from step B) is then treated in step C). Once again, no pump or compressor is used to raise the pressure of the F₂ withdrawn from step B) and forwarded to step C). For solids removal, the F₂ is passed in step C)
5 through one or more particle filters with small pores to remove any residual solids content. The filter or filters may comprise pores in the range of 0.01 to 20 µm. Pore size denotes the pore diameter. Particle filters with a pore size greater than 20 µm could be applied but may not be effective enough. The particle filters serve to remove any solid particles before the contact with
10 liquid HF, or to remove solids still entrained after the purifying treatment of the present invention ; the particle filters may be constructed from materials resistant to F₂, especially from steel or Monel metal.

The temperature in the filter should advantageously be lower than the melting point of the solids (which is usually somewhat above 80°C). Preferably,
15 the temperature in the filter is equal to or lower than 50°C. Especially preferably, step C) is performed at ambient pressure.

The F₂ leaving the filter in step C) has a pressure which is approximately 10 to 150 mbar lower than upon entering the filter.

F₂ having passed steps B) and C) is suitably pure to be used as cleaning
20 agent for chambers used for CVD-enhanced deposition of matter on items. It is especially suitable for cleaning of chambers which have been used for deposition and/or etching of layers, like CVD chambers, used in the manufacture of semiconductors, micro-electromechanical devices, solar cells, TFTs (thin film transistors).

Preferred embodiments of step D) :

The F₂ leaving step C) is subjected to step D). In step D), it is delivered to the point of use, i.e. a chamber or a plurality of chambers to be cleaned. No pressurization is performed, thus it is not passed through a pump or a
compressor.

Preferably, in step D), the F₂ leaving step C) is stored in a storage tank. In the storage tank, it is preferably stored at the pressure with which it is withdrawn from step C). If desired, a control valve may be applied to reduce the F₂ pressure in the buffer tank. In the buffer tank, the F₂ pressure preferably is in a range from equal to or greater than 0.2 bar (abs) to 0.8 bar (abs). In view of this
30 relatively low pressure, the buffer tank or tanks may require a large internal volume. For example, one or more buffer tanks having an internal volume from
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10 to 50 m³ are preferred. Using two or more buffer tanks, e.g. 4 buffer tanks, having an internal volume of 25 m³ provides sufficient capacity to provide a reliable F₂ delivery.

Preferably, the chamber cleaning method of the invention is performed
5 such that step A) is performed in an electrolyzer, step B) is performed in a static scrubber, step C) is performed using a metallic filter, step D) is performed in a buffer tank or storage tank, and the F₂ leaving step D) is delivered to at least one chamber and used in the chamber in a chamber cleaning step (II), wherein the electrolyzer, the static scrubber, the metallic filter, the buffer tank or storage tank
10 and the at least one chamber are operably connected.

Preferably, the pressure of the F₂ in each of the steps B) to D) and in step (II) is lower than the pressure of F₂ in the preceding step. Preferably, the F₂ pressure in step A) is equal to or lower than 1.1 bar (abs), preferably equal to or lower than 1.05 ± 0.02 bar (abs), and preferably, the F₂ is delivered to the
15 chamber in step (II) at a pressure from equal to or greater than 0.2 bar (abs) to equal to or lower than 0.55 bar (abs).

Another aspect, as mentioned above, concerns process for the manufacture of F₂ which contains more than 0.1 % by weight and less than 2.5 % by weight of HF, comprising a step (I) comprising the following steps :

- 20 A) at least one step of electrolytically producing raw F₂ from HF in the presence of KF
B) at least one step of removing particles entrained in the raw F₂ obtained in step A)
C) at least one step of filtering any remaining particles out of the F₂ leaving
25 step B)
and
D) a step of delivering the F₂ to a buffer tank or a storage tank.

From this buffer tank or storage tank, it can be delivered according step (II) to the chamber to be cleaned.

30 A preferred process for the manufacture of F₂ which contains more than 0.1 % by weight and less than 2.5 % by weight of HF, comprising step (I) comprising the following steps :

- A) at least one step of electrolytically producing raw F₂ from HF in the presence of KF
35 B) at least one step of removing particles entrained in the raw F₂ obtained in step A)

C) at least one step of filtering any remaining particles out of the F₂ leaving step B)

and

5 D) a step of delivering the F₂ to a buffer tank or a storage tank, wherein the F₂ pressure in step A) is equal to or lower than 1.1 bar (abs), preferably equal to or lower than 1.05 ± 0.02 bar (abs), the pressure of the F₂ provided to the chamber to be cleaned is from equal to or greater than 0.2 bar (abs) to equal to or lower than 0.55 bar (abs), and wherein the pressure of the F₂ in each of the steps B) to D) is lower than the pressure of F₂ in the preceding step.

10 Preferably, the F₂ is not subjected to a pressurizing treatment throughout the process and method.

The F₂ provided by the invention, containing HF from 0.1 to 2.5 % by weight is very well suited as chamber cleaning agent. An F₂ containing 1 to 2 % by weight of HF can be manufactured technically easy (only a short contact time
15 in the static scrubber is necessary, for example), and nevertheless very suitable as chamber cleaning agent. If it is desired to provide F₂ with a very low content of HF, e.g. with an HF content from equal to or greater than 0.1 % by weight to equal to or lower than 0.5 % by weight, it is an option to contact the F₂ for further HF removal between step B) and step C), especially with an adsorbent,
20 e.g. with NaF. This complicates the process, though, without improving the suitability of the treated F₂ as chamber cleaning agent.

The F₂ which is provided according to the invention is used as chamber cleaning gas for chambers used in the manufacture of the a semiconductor, a TFT or a solar panel.

25 In a preferred embodiment, step (I), i.e., the electrolytic manufacture of F₂, purification and delivery, optionally including storage, as described above are performed on site in combination with step (II). The electrolyzer apparatus, scrubber, filter or filters and storage tank are connected through lines in this embodiment.

30 The method of chamber cleaning and the process of providing F₂ according to the invention have many advantages over the prior art. Contrary to the common belief that highly pure F₂, notably F₂ essentially free of HF, is needed for chamber cleaning, it was found that F₂ containing HF with a content of up to 2.5 % by weight of HF is very suitable. Consequently, it is not necessary to
35 subject F₂ to thorough and careful purifying operations to remove even minute amounts of HF. An added advantage is the finding that the purifying steps

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according to the process of the invention can be performed such that no pump or compressor is needed to subject purified F_2 to pressurization. The combination of both observations – simple purification with low pressure drop, and consequently, no need for pressurization – provides an economic advantage because of less energy consumption and less equipment ; the latter also has technical advantages because less equipment and less treatment steps mean less incidents due to failure of apparatus, less maintenance costs and less downtime. Less apparatus, less treatment steps and a lower F_2 pressure also provide a higher degree of safety.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

The following example is intended to explain the invention further without limiting it. It is performed according to the embodiment wherein the pressure in the electrolytic cell is 1.05 bar (abs).

EXAMPLE 1 : MANUFACTURE OF F_2 , ITS PURIFICATION AND ITS DELIVERY FOR CHAMBER CLEANING

Step A). Manufacture of F_2

An electrolyte salt with a composition of about $KF \cdot 2HF$ is filled into an electrolysis cell, heated to about 80 - 120°C and molten therein. A voltage between 8 to 10 V is applied, and current is passed through the composition of electrolyte salt dissolved in the hydrogen fluoride. HF is introduced into the electrolytic cell in an amount corresponding to consumed HF. Raw F_2 under a pressure of about 1.05 bar (abs) and H_2 form in the respective electrode compartments. H_2 is passed through a water scrubber to removed entrained HF and is then released to the atmosphere.

Step B). Removal of HF and solids

The raw F_2 in the anode compartment of the electrolytic cells contains HF and entrained solids (mainly electrolyte salt). The raw F_2 is withdrawn from the electrolytic cells at a pressure of about 1.05 bar (abs) and contacted in a static scrubber with liquid HF which has a temperature of about -80°C. Most of the solids and the major part of HF entrained in the F_2 are removed in the static scrubber. The F_2 leaving the static scrubber has an HF content of about 1 % by weight, and its pressure is about 0.95 bar (abs.).

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Step C) : Additional solids removal in a filter

The F₂ leaving step B) is passed through a Monel metal frit with pores having a diameter of approximately 1 µm to further reduce the solids content. The F₂ leaving the metal frit has a pressure of approximately 0.8 bar (abs.) and a very low content of entrained solids. The frits are plugged from time to time by filtered solids. They can be cleaned by a treatment with liquids to dissolve the solids.

Step D) : Delivery to the buffer tank

The F₂ leaving the Monel filter frit in step C) still has a content of about 1 % by weight of HF, but a very low solids content. It is passed into a buffer tank having an internal volume of 25 m³; four such buffer tanks are assembled. In the buffer tank, the F₂ is stored under a pressure of approximately 0.8 bar (abs.). If desired, a control valve can be foreseen between the Monel filter of step C) and the buffer tank ; by means of the control valve, the pressure of the F₂ in the buffer tank can be reduced to a still lower level (e.g., it can be stored at a pressure ranging from 0.2 to 0.55 bar).

Step (II) : As soon as F₂ is needed as chamber cleaning agent, it is provided from the buffer tank through a delivery line. It is passed through a control valve which further reduces the pressure, e.g. to 0.5 bar (abs) if the F₂ pressure in the buffer tank is greater than 0.5 bar (abs). The F₂ which finally is delivered to a chamber (used for the manufacture of photovoltaic cells) as cleaning agent has an HF content of 1 % by weight and a pressure of approximately 0.5 bar (abs).

In the chamber, F₂ containing HF is introduced as the cleaning agent, an in-situ plasma is ignited and the cleaning agent, having a pressure of about 0.5 bar (abs), removes deposits, e.g. deposits of Si and SiO₂, from the walls and parts inside the chamber.

EXAMPLE 2 : MANUFACTURE OF F₂, ITS PURIFICATION AND ITS DELIVERY FOR CHAMBER CLEANING

Step A). Manufacture of F₂

An electrolyte salt with a composition of about KF·2HF is filled into an electrolysis cell, heated to about 80 - 120°C and molten therein. A voltage between 8 to 10 V is applied, and current is passed through the composition of electrolyte salt dissolved in the hydrogen fluoride. HF is introduced into the electrolytic cell in an amount corresponding to consumed HF. Raw F₂ under a pressure of about 1.05 bar (abs) and H₂ form in the respective electrode

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compartments. H_2 is passed through a water scrubber to removed entrained HF and is then released to the atmosphere.

Step B). Removal of solids

5 The raw F_2 in the anode compartment of the electrolytic cells contains HF and entrained solids (mainly electrolyte salt). The raw F_2 is withdrawn from the electrolytic cells at a pressure of about 1.05 bar (abs) and introduced into a settling box where most of the solids entrained in the F_2 are removed by gravity. The F_2 leaving the settling box has an HF content of about 5% by weight, and its pressure is about 0.95 bar (abs.).

10 *Step C). Final solids removal in a filter*

The F_2 leaving step B) is passed through a into a filtering device composed of a first Monel metal frit with pores having a diameter of approximately 30 μm and a second Monel metal frit with pores having a diameter of approximately 0.003 μm . The F_2 leaving the metal frit has a pressure of approximately 15 0.8 bar (abs.) and a very low content of entrained solids. The frits are plugged from time to time by filtered solids. They are cleaned by a treatment with liquid HF to dissolve the solids. The HF recovered from the washing of the frits is recovered and fed in the liquid phase to step A).

Step D) : Delivery to the buffer tank

20 The F_2 leaving the Monel filter frit in step C) still has a content of about 5 % by weight of HF, but a very low solids content. It is passed into a buffer tank having an internal volume of 25 m^3 ; four such buffer tanks are assembled. In the buffer tank, the F_2 is stored under a pressure of approximately 0.8 bar (abs.). If desired, a control valve can be foreseen between the Monel 25 filter of step C) and the buffer tank ; by means of the control valve, the pressure of the F_2 in the buffer tank can be reduced to a still lower level (e.g., it can be stored at a pressure ranging from 0.2 to 0.55 bar).

Step (II) : As soon as F_2 is needed as chamber cleaning agent, it is provided from the buffer tank through a delivery line. It is passed through a control valve 30 which further reduces the pressure, e.g. to 0.5 bar (abs) if the F_2 pressure in the buffer tank is greater than 0.5 bar (abs). The F_2 which finally is delivered to a chamber (used for the manufacture of photovoltaic cells) as cleaning agent has an HF content of 5 % by weight and a pressure of approximately 0.5 bar (abs).

35 In the chamber, F_2 containing HF is introduced as the cleaning agent, an in-situ plasma is ignited and the cleaning agent, having a pressure of about

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0.5 bar (abs), removes deposits, e.g. deposits of Si and SiO₂, from the walls and parts inside the chamber.

C L A I M S

1. A method for the cleaning of chambers using F_2 which contains more than 0.01 % by weight and less than 10 % by weight of HF.

2. The method of claim 1 wherein the F_2 contains equal to or more than
5 1 % by weight of HF, and a content of equal to or less than 2 % by weight of HF.

3. The method of claim 1 or 2 wherein the chamber is a CVD chamber.

4. The method of anyone of claims 1 to 3 wherein the chamber is used during the manufacture of a semiconductor, a micro-electromechanical system, TFT (flat panel display) or a solar cell for depositing at least one layer.

10 5. The method of anyone of claims 1 to 4 wherein an F_2 is applied which was obtained in a process comprising the following steps (I) and (II) :

A step (I) comprising

A) at least one step of electrolytically producing raw F_2 from HF in the presence of KF

15 B) at least one step of removing particles entrained in the raw F_2 obtained in step A)

C) At least one step of filtering any remaining particles out of the F_2 leaving step B)

and

20 D) a step of providing F_2 to a buffer tank or a storage tank ;

and

A step (II) wherein F_2 is withdrawn from the buffer tank or storage tank and delivered to a chamber to perform at least one step of chamber cleaning.

25 6. The method of claim 5 wherein the F_2 was obtained in step (I) in a process comprising the following steps :

A) a step of electrolytically producing raw F_2 from HF in the presence of KF

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- B) a step of removing particles entrained in the raw F₂ obtained in step A)
- C) A step of filtering any remaining particles out of the F₂ leaving step B)
- and
- D) a step of delivering F₂ to a buffer tank or a storage tank.

5 7. The method of claims 5 or 6 wherein the particle filter of step C) comprises pores having a diameter between 0.01 and 20 µm.

8. The method of anyone of claims 5 to 7 wherein the particle filter in step C) comprises pores having a diameter less than 10 nm.

10 9. The method of anyone of claims 5 to 8 wherein the steps A) to D) are performed on the site of chamber cleaning.

15 10. The method of claim 9 wherein step A) is performed in an electrolyzer, step B) is performed in a static scrubber, step C) is performed using a metallic filter, step D) is performed in a buffer tank or storage tank, and the F₂ leaving step D) is delivered to at least one chamber and used in the chamber in a chamber cleaning step (II), wherein the electrolyzer, the static scrubber, the metallic filter, the buffer tank or storage tank, the buffer tank or storage tank, and the at least one chamber are operably connected.

11. The method of claim 11 wherein the pressure of the F₂ in each of the steps B) to D) and (II) is lower than the pressure of F₂ in the preceding step.

20 12. The method of anyone of claims 5 to 11 wherein the F₂ pressure in step A) is equal to or lower than 1.1 bar (abs), preferably equal to or lower than 1.05 ± 0.02 bar (abs).

25 13. The method of claims 11 or 12 wherein the F₂ is delivered to the chamber in step (II) at a pressure from equal to or greater than 0.2 bar (abs) to equal to or lower than 0.55 bar (abs).

14. A process for the manufacture of F₂ which contains more than 0.1 % by weight and equal to or less than 10 % by weight, preferably equal to or less than 5 % by weight, and especially preferably, equal to or less than 2.5 % by weight of HF, comprising the following steps :

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- A) at least one step of electrolytically producing raw F₂ from HF in the presence of KF
 - B) at least one step of removing particles entrained in the raw F₂ obtained in step A)
 - 5 C) at least one step of filtering any remaining particles out of the F₂ leaving step B)
- and
- D) a step of delivering the F₂ to a buffer tank or a storage tank.

15. The process of claim 14 for the manufacture of F₂ which contains
10 more than 0.1 % by weight and equal to or less than 2.5 % by weight of HF, comprising the following steps :

- A) a step of electrolytically producing raw F₂ from HF in the presence of KF
- B) a step of removing particles entrained in the raw F₂ obtained in step A)
- C) A step of filtering any remaining particles out of the F₂ leaving step B)
- 15 and
- D) a step of delivering the F₂ to a buffer tank or a storage tank,

wherein the F₂ pressure in step A) is equal to or lower than 1.1 bar (abs), preferably equal to or lower than 1.05 ± 0.02 bar (abs), the pressure of the F₂ provided to the chamber to be cleaned is from equal to or greater than
20 0.2 bar (abs) to equal to or lower than 0.55 bar (abs), and wherein the pressure of the F₂ in each of the steps B) to D) is lower than the pressure of F₂ in the preceding step.

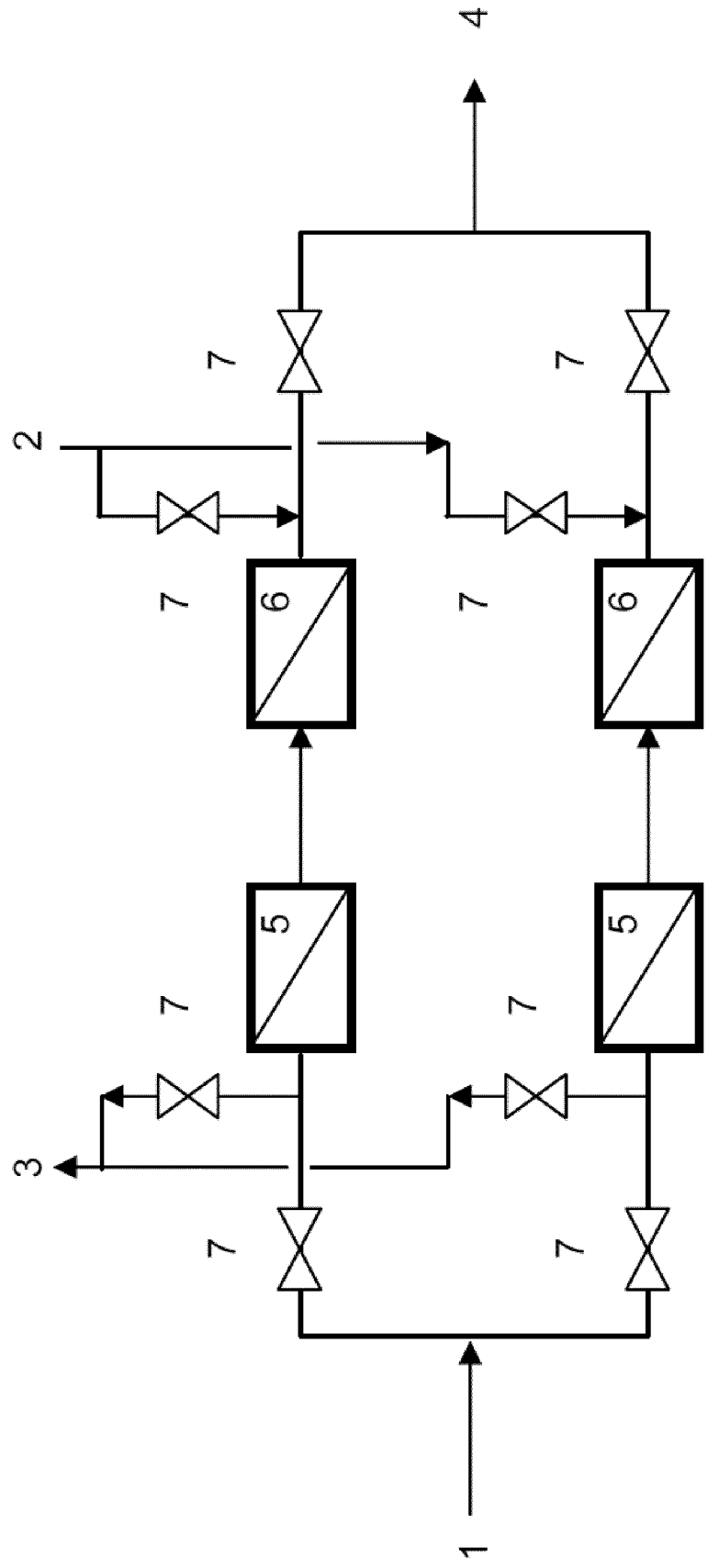
16. The method of claim 11 or the process of claim 15 wherein the F₂ is not subjected to a pressurizing treatment.

25 17. The process or method according to anyone of claims 5 to 16 wherein the filter used in step C) is cleaned with liquid HF.

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18. The process or method according to claim 17 wherein the cleaning HF is recovered and fed to a step of electrolytically producing F_2 preferably in liquid form.

FIGURE 1



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/068437

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C23C16/44 C25B1/24
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C23C C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 3 293726 A (CENTRAL GLASS CO LTD) 25 December 1991 (1991-12-25)	1-4
Y	the whole document	5-13, 17, 18
Y	----- WO 2011/117234 A2 (SOLVAY [BE]; PAGANIN MAURIZIO [BE]) 29 September 2011 (2011-09-29) the whole document	5-13, 17, 18
A	----- US 6 602 433 B1 (BHARDWAJ JYOTI KIRON [GB] ET AL) 5 August 2003 (2003-08-05) the whole document	1-13
Y	----- WO 2012/016997 A1 (SOLVAY [BE]; DIANA OLIVIERO [BE]; PREDIKANT PETER M [DE]; MORELLE PHIL) 9 February 2012 (2012-02-09) the whole document	17, 18
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 October 2013

Date of mailing of the international search report

14/02/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Ekhult, Hans

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/068437

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/034978 A1 (SOLVAY [BE]; MORELLE PHILIPPE [BE]; DIANA OLIVIERO [BE]; PREDIKANT PET) 22 March 2012 (2012-03-22) the whole document -----	1-13, 17, 18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/068437

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-13(completely); 17, 18(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13(completely); 17, 18(partially)

Chamber cleaning method using specified gas composition.

2. claims: 14-16(completely); 17, 18(partially)

Method for obtaining fluorine.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/068437

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			WO 2012034978 A1	22-03-2012
