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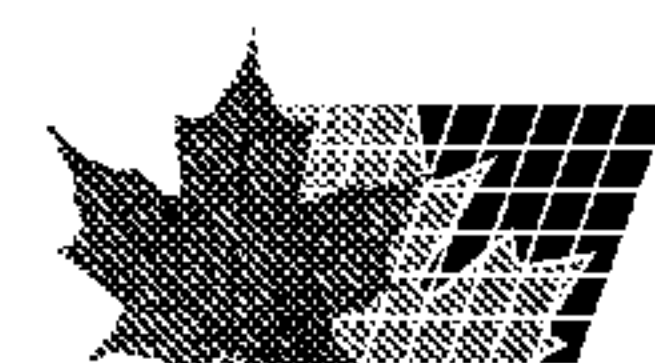
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(54) Titre : PROCEDE DE PRODUCTION DE SOLUTIONS DE HAUTE PURETE AU MOYEN D'ACIDE
FLUORHYDRIQUE GAZEUX

(54) Title: METHOD FOR PRODUCING HIGH-PURITY SOLUTIONS USING GASEOUS HYDROGEN FLUORIDE

(57) **Abrégé/Abstract:**

The invention relates to a method for producing a high-purity solution that contains hydrogen fluoride or a salt thereof or a mixture of two or more thereof. The inventive method comprises the following step (i): hydrogen fluoride is passed into at least one anhydrous solvent. The method is characterised in that hydrogen fluoride is passed into the at least one anhydrous solvent as a gas or liquid gas or as a mixture of gas and liquid gas.



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Abstract

Method for producing a highly pure solution, containing hydrogen fluoride or a salt thereof or a mixture of two or more thereof, comprising the following step (i):

5

(i) introducing hydrogen fluoride into at least one water-free solvent,

characterized in that hydrogen fluoride is introduced into the at least one water-free solvent in the form of gas or as liquified gas or as a mixture of gas and liqui-

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fied gas.

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TRANSLATION OF THE PCT-APPLICATION AS ORIGINALLY FILED

Method for producing highly pure solutions in using gaseous hydrogen fluoride

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The present invention relates to a method for producing a highly pure solution containing hydrogen fluoride or a salt thereof, or a mixture of two or more thereof, wherein hydrogen fluoride is introduced into a water-free solvent in a first step, wherein the used hydrogen fluoride is used as gas and/or as liquified gas.

10 The present invention also relates to the use of the highly pure solution produced in accordance with the invention as etchant.

A number of industrial fields of use, among which e.g. electronics and semiconductor industry are to be mentioned, have the requirement to use highly pure solutions. Among these solutions, e.g., those are to be mentioned which are produced from hydrogen fluoride, possibly among other educts.

One problem of the present invention is therefore to provide a method allowing to produce such highly pure solutions in a simple way using hydrogen fluoride for
20 their production.

Therefore, the present invention relates to a method for producing a highly pure solution containing hydrogen fluoride or a salt thereof or a mixture of two or more thereof, comprising the following step (i):

25

(i) passing hydrogen fluoride into at least one water-free solvent,

characterized in that hydrogen fluoride is introduced as a gas and/or liquified gas into the at least one water-free solvent.

Passing into of the hydrogen fluoride as gas and/or liquified gas can therein be performed in accordance with all appropriate methods as per the prior art.

5 In a preferred embodiment, the at least one water-free solvent is placed in an appropriate container. The container materials can be made of all materials appropriate for the method, guaranteeing high purity of the solution. Containers are preferred that have inner walls contacting the highly pure solution, which are made of metal-free polymers such as HDPE, PFA, polypropylene, PVDF, and
10 perfluorinated polyethylene propylene (FEP).

Unstabilized HD-polyethylenes such as e.g. HD-polyethylenes with a specific density of $0.940 - 0.970 \text{ g/cm}^3$, in particular $0.942 - 0.961 \text{ g/cm}^3$ are to be mentioned among them. In particular polyethylenes being distributed in commerce
15 under the trademark Lupolen are part of them. Lupolen® 6021D, Lupolen® 5021D, Lupolen® 4261AQ149, and Lupolen® 4261AQ135 are mentioned. The containers used in the method as per the invention can consist of one or more layers, wherein the one or more external layers can be made of all thinkable materials.

20

The feeders passing the hydrogen fluoride as gas and/or liquified gas into the container wherein the at least one water-free solvent is placed, can also consist of all materials appropriate for it. Hose couplings being made of highly pure PFA are preferably used in the method as per the invention.

25

Should the gaseous hydrogen fluoride be liquified within the framework of the present invention prior to the introduction of the at least one water-free solvent, this liquefaction can be performed in accordance with all thinkable methods according to prior art.

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If the introduction of the hydrogen fluoride into the at least one water-free solvent in gaseous form as well as in the form of liquified gas is provided within the framework of the present invention, it is possible to first introduce gaseous and the liquified hydrogen fluoride. It is also possible to first introduce liquified and
5 then gaseous hydrogen fluoride. It is further possible to simultaneously introduce gaseous and liquified hydrogen fluoride, wherein gaseous and liquified hydrogen fluoride can be combined prior to introduction.

Within the framework of the present invention, it is possible to bring the hydrogen
10 fluoride, introduced as gas and/or liquified gas into the at least one water-free solvent, to a certain desired temperature prior to passing into. It also is possible to bring the at least one water-free solvent to a desired temperature prior to introduction. It also can be provided for the solution being brought to a desired temperature and/or being held at a desired temperature during the introduction of the hydrogen fluoride into the at least one water-free solvent. All methods known to be
15 appropriate from the prior art can be used for this temperature adjustment.

During passing or after passing the hydrogen fluoride into the at least one water-free solvent, it is possible to homogenize the solution. This is possible in accordance with all thinkable methods. In a preferred embodiment of the present invention, the solution is herein recirculated via one or more pump-over lines after finishing the passing into of the hydrogen fluoride.
20

All water-free solvents in which hydrogen fluoride is soluble can be used as the at
25 least one water-free solvent. Generally, these are polar water-free solvents.

Thus, the present invention also relates to a method as described above, characterized in that the at least one water-free solvent is a polar solvent.

30 In a preferred embodiment of the method as per the invention, the at least one water-free solvent is chosen from the group consisting of polyols, carboxylic ac-

ids, derivatives of carboxylic acids, organic sulfur compounds, aliphatic or aromatic nitrogen compounds, and mixtures of two or more thereof.

Among others, ethylene glycol, propylene glycol, polymethylene glycol, polyethylene glycol, or glycerol are to be mentioned as examples for polyols, wherein in particular polyols with relatively low viscosity are to be mentioned. Further, polyalkylene glycols, in particular polyethylene glycols are to be mentioned as preferred, with an average number of molecular weight of 250 to 6,000, more preferably 250 to under 5,000 and in particular 250 to 1,000.

10

As carboxylic acids, aliphatic, cycloaliphatic and aromatic acids, being liquid at ambient conditions, are mentioned, which may respectively carry one or more acid groups. Among others, these are formic acid, acetic acid, or propionic acid. Acid derivatives of carboxylic acid such as their esters or their amides are appropriate solvents. It is further possible to substitute the acrylic residua of the carboxylic acids or the carboxylic-acid derivatives. Hydroxyl groups or halogenid residua are to be mentioned as possible substituents. Amino carboxylic acids are also mentioned as possible solvent.

20 Water-free organic sulfur compounds, such as sulfates, sulfonates, sulfoxides, sulfones, or sulfites are appropriate solvents. Mentioned besides DMSO are dimethyl sulfite, diethyl sulfite, glycol sulfite, dimethyl sulfone, diethyl sulfone, dipropyl sulfone, dibutyl sulfone, tetramethylene sulfone, methyl sulfolane, diethyl sulfoxide, dipropyl sulfoxide, dibutyl sulfoxide, tetramethylene sulfoxide, ethyl methane sulfonate, 1,4-butane diolbis(methane sulfonate), diethyl sulfate, 25 dipropyl sulfate, dibutyl sulfate, dihexyl sulfate, dioctyl sulfate.

Furthermore, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate are 30 appropriate water-free solvents in the method as per the invention.

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Water-free aliphatic compounds, substituted such that hydrogen fluoride is soluble therein, can also be used as solvents. Halogen substituents are mentioned as possible substituents, among others.

5 Another group of possible solvents are aliphatic or aromatic amines, substituted, if need be. E.g. amino alcohols such as ethanolamine fall under this group.

Of course it is possible in the method as per the invention to first pass the hydrogen fluoride into a part of the at least one solvent and to add further solvent after
10 introduction.

In the case that two or more different water-free solvents are used in the method as per the invention, it is possible to pass the hydrogen fluoride into first one or more of these solvents, and then to add one or more of the other solvents. It is also
15 possible to produced two or more solutions of hydrogen fluoride as per the above described method and to combine these two or more solutions subsequently.

In another preferred embodiment of the method as per the present invention, a highly pure solution is produced, wherein at least one other educt is used besides
20 hydrogen fluoride and the at least one water free solvent.

Accordingly, the present invention relates to a method as described above, characterized in that at least one other gas or at least one other liquid or at least one solid or a mixture of two or more thereof besides hydrogen fluoride is introduced
25 into the at least one water-free solvent.

In the case that the further educt does not react with hydrogen fluoride, the order of the introduction of the educts is not critical. It is possible that the at least one further educt is introduced into the solution of hydrogen fluoride in the at least
30 one water-free solvent. It is also possible to first combine the at least one water-free solvent with the at least one further educt and than to introduce hydrogen

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fluoride. Furthermore, it is possible to introduce the at least one further educt together with the hydrogen fluoride into the at least one water-free solvent. If need be, the hydrogen fluoride can be mixed with the at least one further educt prior to introducing into the at least one water-free solvent, and the resulting mixture can
5 be added to the at least one water-free solvent.

In another preferred embodiment of the method as per the invention, ammonia is used as further educt besides hydrogen fluoride, whereby an ammonium fluoride solution is produced. Therein, it is possible in principle to use ammonia as liquid.
10 Preferably, however, gaseous ammonia is used.

Thus, the present invention also relates to a method for procuring a highly pure solution, as described above, characterized in that ammonia is used as the at least one further educt.

15 Ammonium fluoride solutions, to which higher requirements regarding degree of purity are posed, are generally produced by solving crystalline ammonium fluoride in the corresponding solvent, as is e.g. described in US-A-5,320,709.

20 One disadvantage of this method is that the metallic impurities of the thus produced solutions are generally within the ppm range, and that the solutions are therefore inappropriate for some fields of use, having much higher requirements on purity regarding the metal content. The purification of the crystalline ammonium fluorides which would be necessary for producing highly pure solutions
25 with a substantially lower content of metal is, however, experimentally difficult.

In a preferred embodiment of the present invention therefore a highly pure ammonium fluoride solution is produced in accordance with the above described method.

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Herein, it is possible to treat the at least one water-free solvent with the desired amount of gaseous hydrogen fluoride and to then introduce the corresponding amount of gaseous ammonia into it. It is also possible to first treat the at least one solvent with the desired amount of gaseous ammonia and then to introduce the
5 corresponding amount of gaseous hydrogen fluoride into it. The two gaseous components can also be introduced into the at least one solvent simultaneously and spatially separated. It is also possible to introduce one of the two gaseous components and then to start the introduction of the other gaseous component after a certain time.

10

In a particularly preferred embodiment of the present method, the at least one water-free solvent is first treated with the desired amount of gaseous hydrogen fluoride and this solvent is recirculated, as described above. Then, gaseous ammonia is introduced into this homogenized solution and the resulting solution is in
15 turn recirculated by pumping over and thus homogenized.

The temperature in the reaction container is controlled in that during introduction of the gaseous ammonia that it amounts to a maximum of 35°C, preferably a maximum of 30°C, and particularly preferably to less than 30°C.

20

The concentrations of the highly pure solutions of ammonium fluoride which are produced within the framework of the method as per the invention are essentially only dependent on the solubility of ammonium fluoride in the at least one solvent and can deliberately be chosen within this framework. Of course, it is also possible to produce saturated solutions of ammonium fluoride in the at least one solvent, wherein it is herein also generally possible that such an amount of ammonia and hydrogen fluoride are introduced into the at least one solvent that ammonium fluoride precipitates as solid.

25

30 In a preferred embodiment of the present invention, highly pure solutions of ammonium fluoride are produced in the at least one solvent within the framework of

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the method as per the invention, the concentration of which solutions generally ranges from 0.1 to 50 weight percent, preferably from 1 to 30 weight percent, and particularly preferably from 2.5 to 10 weight percent.

5 In order to avoid creation of explosive ammonia-air mixtures, it is possible within the framework of the present method to inertize the container, wherein the gaseous ammonia is introduced into the at least one water-free solution, and wherein hydrogen fluoride may already have been dissolved. In principle, any inert gas such as, among others, nitrogen and argon is appropriate. Preferably, the container
10 is inertized prior to filling with solvents and, if need be, hydrogen fluoride.

In principle, all above described solvents can be used as solvents in which the ammonium fluoride is produced. In a preferred embodiment, water-free polyols are used, in a particularly preferred embodiment water-free ethylene glycol is
15 used.

A further disadvantage of the method according to the prior art, already described above, wherein crystalline ammonium fluoride is dissolved in a corresponding solvent, is the fact that it is very difficult in manufacturing to set the amount of
20 the free hydrogen fluoride contained in the ammonium fluoride solution to be produced in such a reproducible way that two or more ammonium fluoride solutions have a constant value of content of free hydrogen fluoride. For some industrial applications, however, a constant content of free hydrogen fluoride is decisive.

25 Another problem of the present invention therefore was providing a method allowing for production of highly pure ammonium fluoride solutions, having a constant content of free hydrogen fluoride which can reproducibly be set.

30 The content of free hydrogen fluoride contained in the highly pure ammonium fluoride solutions produced as per the present invention can be set in a simple way

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by means of the stoichiometric method wherein the gaseous hydrogen fluoride and the gaseous ammonia are introduced into the at least one solvent. By the possibility of exact dosage which is provided for by the use of the gaseous educts, it is in particular possible to produce highly pure solutions which have an exactly defined content of free hydrogen fluoride which is therein reproducibly settable. In particular, highly pure solutions of ammonium fluoride can be produced, having free hydrogen fluoride in a range of less than 0.01 weight percent.

A technical application of the solutions made in accordance with the present invention and in using gaseous hydrogen fluoride is etching. Therefore, another problem of the present invention was providing a method wherein the highly pure solutions can be adapted to the desired requirements of the respective etching process.

In another embodiment of the method in accordance with the invention, the at least one other educt used besides hydrogen fluoride is another gas acting as reactive gas in etching. Examples are, among others, hydrogen chloride and hydrogen bromide.

Accordingly, the present invention also relates to a method, as described above, which is characterized by the use of gaseous hydrogen chloride or gaseous hydrogen bromide or a mixture thereof as the at least one other educt.

Referring to the production of these solutions, the order of adding the gases to the at least one water-free solvent is not critical. It is possible to pass the gases into the at least one water-free solvent in sequence or simultaneously, if need be spatially separated or together in one feeder. It is further possible to liquify the at least one other gaseous educt prior to introducing it into the at least one water-free solvent in accordance with the common methods as per the prior art, as described above for the introduction of hydrogen fluoride, and to introduce the at least one liquified gas into the at least one water-free solvent.

- 10 -

In principle, all above-mentioned, water-free solvents can be used for this preferred embodiment of the method in accordance with the present invention, provided that the at least one additional gaseous educt is soluble in the solvents. In preferred embodiments, acetic acid or a mixture of acetic acid and acetic ester, respectively, or a mixture of DMSO and DMA are used as the water-free solvents, respectively. If a mixture of DMSO and DMA is used, the mixing ratio of the two components can in general be deliberately chosen. Preferably, the stoichiometric mixing ratio of DMSO and DMA is in the range from 30 : 70 to 70 : 30. In a particularly preferred embodiment of the present invention, highly pure solutions of hydrogen fluoride are produced in a DMSO / DMA mixture, wherein hydrogen fluoride, DMSO, and DMA have the same weight portions.

In highly pure solutions made in accordance with the present invention, containing hydrogen bromide and/or hydrogen chloride besides hydrogen fluoride, the stoichiometric ratio of hydrogen fluoride to hydrogen chloride and/or hydrogen bromide is preferably in the range of less than or equal to 1, preferably in the range of less than 1.

It is further possible within the framework of the method in accordance with the present invention to also introduce gaseous hydrogen chloride and/or gaseous hydrogen bromide besides hydrogen fluoride and gaseous ammonia into the at least one water-free solvent. Herein, the order of introducing the individual components is in principle not limited.

25

Of course, the field of use of the highly pure solutions, wherein at least one further reactive gas is also used as educt besides gaseous hydrogen fluoride, is not limited to the above-mentioned etching.

In principle, the term "purity" as used herein relates to all imaginable impurities which a solution, made in accordance with the present invention, can show.

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Among others, metal ions, halogenides such as chloride or bromide, further anions such as nitrate, phosphate or sulfate, organic compounds, generally particular impurities, virus, bacteria, and their by-products, such as endotoxines or mycotoxines, are mentioned as impurities.

5

The term "highly pure" as used herein denotes degrees of purity regarding a certain impurity, being in a range of less than 1 ppb.

10 In principle, highly pure solutions can be made in accordance with the method as per the present invention which are highly pure with regard to all imaginable impurities. In a preferred embodiment of the method as per the present invention, highly pure solutions are made which have a very low content of metal ions.

15 Within the framework of the method as per the present invention, educts are used which have a degree of impurity regarding all imaginable impurities which is so low that the highly pure solutions can be produced from educts without a further purifying step and with the purity required by the user.

20 According to the degree of purity required for the highly pure solution to be produced, it is possible within the framework of the present invention to use highly pure hydrogen fluoride gas and/or one or more highly pure solvents. In the case that at least one further educt as described above is used, this educt can also be highly pure.

25 With regard to producing the highly pure solutions which, as describe above, have very low contents of metal ions, gaseous hydrogen fluoride is used, the metal-ion content of which is lower than 1 ppb, preferably lower than 100 ppt.

30 Accordingly, the present invention also relates to a method, as described above, which is characterized by the used hydrogen fluoride having a metal-ion content of less than 1 ppb per metal.

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Examples for metals, referring to which the solutions made in accordance with the present invention is highly pure, are, among others, aluminum, antimony, arsenic, barium, beryllium, lead, cadmium, calcium, chromium, iron, gallium, germanium, gold, indium, potassium, cobalt, copper, lithium, magnesium, manganese, molybdenum, sodium, nickel, platinum, silver, silicon, strontium, thallium, titan, vanadium, bismuth, zinc, tin, or zirconium.

According to required purity of the solution to be made, it is possible, if required, to lower the content of the at least one water-free solvent in accordance with the common methods as per prior art so far that it ranges within the framework of lower than 1 ppb, preferably lower than 100 ppt. In particular, distillative purifying is to be mentioned for the at least one water-free solvent, wherein, among others, purification by means of common distillation or distillation in using microwave radiation is mentioned.

In another preferred embodiment of the method as per the present invention, highly pure solutions can be made, having an extremely low content of metal ions, ranging in general below 1 ppb per metal, preferably less than 100 ppt per metal.

Accordingly, the present invention also relates to a method as described above, characterized by the highly pure solutions having a metal-ion content of less than 100 ppt per metal.

The highly pure solutions made in accordance with the present invention can be used in all imaginable technical applications. In particular, applications in the field of semiconductor and electronics industry, analytics as well as (bio)pharmaceutics are to be mentioned.

Accordingly, the present invention also relates to the use of a highly pure solution, producible in accordance with one of the claims 1 to 8, in the field of semicon-

ductor and electronics industry, analytics, or pharmaceutical or biopharmaceutical applications.

Preferably, the highly pure applications made in accordance with the method as
5 per the present invention are used as etching agents. Herein the advantages are particularly applied which result from the fact that e.g. the content of free hydrogen fluoride in the solutions can be reproducibly set to a constant value in the production as per the invention of the highly pure ammonium fluoride solutions. Thus, it is possible to provide an extremely narrow process window for the etch-
10 ing rate of the solution.

Accordingly, the present invention also relates to the use, as described above, which is characterized by the highly pure solution being used as etching agent in the semiconductor and electronics industry.

15

In particular, the highly pure solutions made in accordance with the method as per the present invention are used as etching agents for selectively removing organo-metallic residues or organic silicone residues in plasma etching within the framework of producing wafers. With regard to this selectivity, the method as per the
20 present invention can be particularly advantageously used since the selectivity can be controlled, among others, by the intentional addition of further reactive gases such as hydrogen chloride or hydrogen bromide; their use has already been described above.

25 In another embodiment of the method as per the present invention, water can be mixed into the highly pure solution for affecting the etching selectivity. A considerable advantage of the method as per the invention is that the highly-pure solution is water-free, e.g. in producing a highly pure ammonium fluoride solution in using gaseous hydrogen fluoride, gaseous ammonia, and water-free solvent, and
30 that an extraordinarily precise and reproducible water content can be set by intentional addition of water after the production of the highly pure solution.

Of course, it is also possible to add general aqueous systems to the solution after producing the water-free, highly pure solution as per the invention. Herein, the advantage is, among others, that the water content of the solution to be produced
5 can be set precisely and based on the water-free solution. Examples are, among others acids such as e.g. phosphoric acid, aqueous hydrochloric acid, or aqueous acetic acid.

In a particularly preferred embodiment of the present invention, at least one sub-
10 stance is added to the water-free solvent as an additional educt to hydrogen fluoride, affecting the surface-active properties of the highly pure solution, among others in use as etching agent. Therein, appropriate polar as well as unpolar substances can be used in principle. Examples are, among others, aliphatic or aromatic amines. Aliphatic amines with a chain length of 5 to 12 C-atoms are preferably
15 used. The mentioned amines may be substituted, if need be, wherein OH groups or halogenide residues are possible substituents.

In order to guarantee the required degree of purity of the highly pure solution, it may be necessary to purify the at least one substance, affecting surface activity,
20 prior to use. Herein, all appropriate methods as per prior art may be used.

The following examples are to explain the method in accordance with the invention in more detail.

25 **Examples:**

Example 1: Production of a solution of hydrogen fluoride in ethylene glycol

800 g ethylene glycol were placed in a 1,000 ml batching container. By means of
30 an injector, approx. 80 g water-free, hydrogen fluoride was condensed and dissolved in the ethylene glycol. Therein, the increase of content of hydrogen fluo-

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ride was analytically monitored. Passing into of the liquid acid was terminated at a content of 10 weight percent.

After terminated dosage, the solution was recirculated and homogenized for 1
5 hour by means of a pump-over line. The contained solution had a metal-ion content of less than 100 ppt per metal.

Example 2: Production of a solution of ammonium fluoride in ethylene glycol

10 A 1,000 ml batching container was inertized by rinsing with nitrogen for 1 hour. Subsequently, the process as of example 1 was applied.

Gaseous ammonia was introduced into this solution of HF in ethylene glycol, wherein the molar ration of ammonia and hydrogen fluoride already introduced
15 amounted to 1 : 1. Therein, the temperature was controlled in such a way by external cooling and dosage speed of the ammonia passing-into that it did not exceed a value of 30°C.

After introducing the entire amount of ammonia, the solution was recirculated for
20 30 min while cooling was switched on. The achieved solution had a metal-ion content of less than 100 ppt per metal.

Claims 1 to 8 as enclosed to IPER (for further prosecution)

1. Method for producing a highly pure solution containing hydrogen fluoride
5 or a salt thereof or a mixture of two or more thereof, wherein the hydrogen fluoride is introduced into at least one water-free solvent, wherein hydrogen fluoride is introduced into the at least one water-free solvent in the form of gas or as liquified gas or as a mixture of gas and liquified gas, characterized in that at least gaseous ammonia is used besides hydrogen
10 fluoride.
2. Method for producing a highly pure solution containing hydrogen fluoride or a salt thereof or a mixture of two or more thereof, wherein the hydrogen fluoride is introduced into at least one water-free solvent, wherein hydrogen
15 fluoride is introduced into the at least one water-free solvent in the form of gas or as liquified gas or as a mixture of gas and liquified gas, characterized in that at least gaseous hydrogen chloride or hydrogen bromide or a mixture thereof is used besides hydrogen fluoride.
- 20 3. Method in accordance with claim 1 or 2, characterized in that the at least one water-free solvent is a polar solvent.
4. Method in accordance with any of claims 1 to 3, characterized in that the
25 at least one water-free solvent is chosen from the group consisting of polyols, carboxylic acids, derivatives of carboxylic acids, organic sulfur compounds, aliphatic or aromatic nitrogen compounds, and mixtures of two or more thereof.

5. Method in accordance with one of the claims 1 to 4, characterized in that the used hydrogen fluoride has a metal-ion content of less than 1 ppb per metal.
- 5 6. Method in accordance with any one of the claims 1 to 5, characterized in that the highly pure solution has a metal-ion content of less than 100 ppt per metal.
7. Use of a highly pure solution, produced in accordance with any one of the
10 claims 1 to 6, in the field of semiconductor or electronics industry, analytic chemistry, or pharmaceutical or biopharmaceutical applications.
8. Use of the solution in accordance with claim 7 as an etching agent in the semiconductor and electronics industry.