# A chamber cleaning method using $F_2$ and a process for manufacture of $F_2$ for this method

The invention concerns a chamber cleaning method using $F_2$ with a specific content of HF and a process for manufacture of $F_2$ for this method.

$F_2$ (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 $F_2$ intended for etching or chamber cleaning. WO 2012/016997 for example provides a purification process for the manufacture of highly pure $F_2$, useful as etching agent and chamber cleaning agent, with a content of equal to or less than 10 ppm of HF.

$F_2$ 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 $KF \cdot (1.8 - 2.3)HF$ are electrolyzed. Often, production of $F_2$ 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 $F_2$ is used as chamber cleaning agent and a technically and economically advantageous process for providing $F_2$ 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.

One aspect of the invention relates to a method for the cleaning of chambers using $F_2$ which contains more than 0.01% by weight and less than 0.5% by weight HF.

It was observed that $F_2$ 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 $F_2$ 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 $F_2$ with a content of equal to or more

CLAIMS

1. A method for the cleaning of chambers using $F_2$ which contains more than 0.01 % by weight and less than 0.5~~10~~ % by weight of HF.

~~2. The method of claim 1 wherein the $F_2$ contains equal to or more than 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~~or claim 2 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.

4The method of any one 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

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

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 a t least one step of chamber cleaning.

5. The method of claim 4 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

B) a step of removing particles entrained in the raw $F_2$ obtained in step A)

C) A step of filtering any remaining particles out of the $F_2$ leaving step B)

and

D) a step of delivering $F_2$ to a buffer tank or a storage tank.

~~7~~6. 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~~.

~~9~~7. The method of ~~anyone of~~ claims ~~5~~5 ~~to 8~~ or 6 wherein the steps A) to D) are performed on the site of chamber cleaning.

~~8~~10.The method of claim ~~9~~7 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 $F_2$ 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 $F_2$ in each of the steps B) to D) and (II) is lower than the pressure of $F_2$ in the preceding step.~~

~~9~~12.The method of any one of claims ~~4~~5 to ~~11~~8 wherein the $F_2$ 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).

~~13~~10. The method of claims ~~11 or 12~~ 8 wherein the $F_2$ 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).

11~~4~~. A process for the manufacture of $F_2$ 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 :

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)

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.

~~15~~12. The process of claim 14~~1~~ for the manufacture of $F_2$ which contains 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 $F_2$ from HF in the presence of KF

B) a step of removing particles entrained in the raw $F_2$ obtained in step A)

C) A 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,

wherein the $F_2$ 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 $F_2$ 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 $F_2$ in each of the steps B) to D) is lower than the pressure of $F_2$ in the preceding step.

~~16. The method of claim 11 or the process of claim 15 wherein the $F_2$ is not subjected to a pressurizing treatment.~~

~~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.~~

~~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.~~