METHOD FOR RECYCLING SILANE (SiH4)

The invention relates to a method for recycling silane that comprises the following consecutive steps: a) injecting a mixture of pure silane/pure hydrogen (SiH4/H2) in a reaction chamber for making silicon-containing thin layers; b) extracting from the mixture the excess of silane not used during step a) by hydrogen (SiH4/H2) via a pump using a supply gas; c) discharging from said pump, at a pressure close to the atmospheric pressure, a mixture containing at least silane (SiH4), hydrogen (H2) and an amount different from zero of said supply gas; d) separating the silane (SiH4) from the hydrogen/supply gas mixture resulting from the mixture from step c), the silane thus obtained containing less than 100 ppm of supply gas, preferably less than 10 ppm of supply gas and more preferably less than 1 ppm of supply gas; characterised in that at least 50%, preferably 70%, and more preferably 80% of the silane (SiH4) from step b) is reused after step d) for a new step a).
METHOD FOR RECYCLING SILANE (SiH₄)

[0001] The present invention relates to a plant and a method for silane (SiH₄)/hydrogen (H₂) recycling. The first intended application is for the deposition of thin silicon films. However, this system can be used for other applications for which the specifications are similar.

[0002] The cost of solar energy can be reduced by reducing the fabrication cost of the photovoltaic cells. In what is called “thin film” technology, in particular for the application in which silicon is deposited as a thin film, and more particularly for the microcrystalline amorphous silicon solution, a reduction in the consumption of gases used for depositing the active films contributes to the overall reduction in fabrication cost.

[0003] The production of photovoltaic cells with thin microcrystalline and/or amorphous silicon films requires the use of gases such as H₂, SiH₄, dopant gases such as TMB (trimethylboron), PH₃ (phosphine), B₂H₆ (diborane), and also N₂, argon, etc. These solar cells will soon be produced in plants having production capacities partly exceeding several hundred megawatts each year.

[0004] The production of thin silicon films for solar cells requires the sequential deposition of p-doped silicon films, undoped silicon films and n-doped silicon films on a substrate. Each silicon deposition is carried out in a chamber in which a method chosen from CVD (including MOCVD, PECD, ALD, HWCVD, APCVD, VTD, etc.) or PVD (in particular evaporation and sputtering) is implemented.

[0005] For example, the substrate is placed in a first chamber in which a gas mixture containing silane, a dopant such as TMB and hydrogen as carrier gas is delivered so as to produce a p-type silicon layer on the substrate. The substrate is then moved into a second chamber in which a hydrogen/silane gas mixture is delivered for the formation of an undoped film. The substrate can then be moved into a third chamber in which a gas mixture comprising hydrogen as carrier gas, silane and a dopant, such as phosphine PH₃, is delivered for producing an n-doped film on the substrate. There is a trend in this type of process for fabricating such devices, namely the substrates on which these films are deposited are becoming larger and larger. Thus, the size of the deposition chambers and the volumes of gases introduced, particularly hydrogen as carrier gas, must also be increased. In current plants, the gases not used in the deposition chambers are extracted by a pump before being treated so as to destroy the dangerous effluents.

[0006] The amounts of gases needed to deposit the target active films are very large. Because of the size of projected plants and the intrinsic need for gases linked to the nature of the technology, the necessary flow rates will reach tens or even hundreds of m³ per hour in the case of hydrogen. Gas delivery therefore becomes problematic in the case of hydrogen, but also in the case of silane. The volumes required must be a brake on the development of these technologies.

[0007] One way of reducing the delivery/logistic handling cost of silane (SiH₄) and hydrogen (H₂) is to recycle these gases upon exiting the deposition reactors.

[0008] However, the gases reintroduced into the reactor must meet the specifications required for obtaining good-quality films.

[0009] The main specifications are the following: H₂O, O₂, and N₂ concentrations <1 ppm in SiH₄ and H₂ so as to prevent the formation of oxides and/or nitrides; concentrations of dopant gases, such as PH₃, B₂H₆, and TMB, that are controlled according to the type and level of doping required. In addition, powders may form in large amounts during the reaction; their concentration must therefore be reduced to an acceptable value, i.e. to a level low enough to be compatible with the mode of operation of the various components into which the gases containing these powders will flow and with the intended application (for example thin-film deposition for the production of solar cells). These components are for example compressors, adsorption units, etc. Furthermore, the SiH₄/H₂ ratio and the flow rate of these gases must be able to be controlled.

[0010] Because of the current technology, the problems mentioned above are new. However, the literature reveals a few characteristics.

[0011] A waste gas recycling method is for example described in document JP 58225612A “Apparatus for forming amorphous silicon, film”. The patent application, published in 1983, provides a solution for improving the level of use of silane when depositing an amorphous silicon film by PECD (plasma-enhanced chemical vapour deposition): this involves separating the hydrogen from the gases recovered at the outlet of the deposition reactor and then recycling the silane into the inlet of this same reactor. The above document presents a solution in which the separation and the recycling require in particular the use of a cold trap using liquid nitrogen. However, it does not tackle the problem of recycling the hydrogen. Moreover, the process is a vacuum process, thereby representing a hazard difficult to completely control when handling silane, which is a very violent reducing agent, and therefore with a high affinity for an oxidizing agent, such as the oxygen contained in the air that could for example get back into the process.

[0012] In the photovoltaic field, the solution detailed in patent application JP 58225612A commented upon above has not hitherto been implemented for separating and then recycling the gases used as thin-film deposition precursors. Moreover, no solution is currently used on an industrial scale to recover the silane and/or hydrogen gases and to reuse them in the silicon film deposition process. The gases discharged are simply treated and removed.

[0013] Moreover, the patent U.S. Pat. No. 5,785,741 “Process and system for separation and recovery of perfluorocompounds gases” presents a solution for separating PFC gases for the purpose of recycling them. This solution may be employed in the microelectronics industry. Scrubbers, filters, membranes, cold traps and PSA (pressure swing adsorbers) are required for recycling these PFC gases. The above solution is useful, but an improved and simplified form of this method is essential in order to employ other gases (for example silane and hydrogen) and in another field (for example in the case of the photovoltaic industry).

[0014] To separate the silane from the hydrogen, solutions have been described in document EP 0 644 153 “Procédé de séparation du silane à l’aide d’une membrane” [method of separating silane using a membrane] and “Separation of hydrogen from silane via membranes: a step in the production of ultra-high purity silicon” dealing with the use of a membrane to separate the silane from the hydrogen used in the fabrication of high-purity silicon. This element can be employed for the solution developed for recycling silane and hydrogen for the application relating to the thin-film deposition of amorphous silicon. Nevertheless, this is one building block in the technological solution devised for carrying out this recycling. Moreover, membrane separation cannot
deliver high-purity gases, something which is however essential in the intended applications mentioned above.

[0015] To finish, patent EP 0645 345 discloses a membrane separation process for separating a gaseous hydride or a mixture of gaseous hydrides (such as PH₃, AsH₃, SiH₄) from a gas mixture containing at least argon, helium and/or hydrogen. The proposed solution therefore makes it possible to concentrate, on one side, the gaseous hydrides (in this case the gases used for doping in the case of an application in the photovoltaic industry) and let through the membrane, on the other side, also called the permeate side, only the mixture of argon, helium and/or hydrogen. Such a separation is carried out using a polymer membrane of the polyimide or polyamide type.

[0016] Consequently, no satisfactory solution has been implemented hitherto for efficiently and integrally carrying out the various steps required to recycle the gases used in the fabrication of structures formed in particular by depositing thin films of silicon, whether or not these are doped.

[0017] In summary, to reduce the consumption of hydrogen and/or silane for the fabrication of systems made up of thin silicon films deposited for example by CVD or PVD, such as especially photovoltaic cells made from thin silicon films, the benefits that the solution must provide are for example:

[0018] the separation of powders from a gaseous effluent (the effluent recovered at the outlet of a reactor for depositing thin amorphous silicon films);

[0019] the concentration of the silane in a silane/hydrogen mixture;

[0020] the separation of the gases to be recycled from the nitrogen used in the pumping unit, either as ballast or diluted downstream of the chamber(s);

[0021] the separation of the dopant gases from the silane or from the hydrogen; and

[0022] the collection of the silane and hydrogen gases for the purpose of reintroducing them into the deposition reactor and reusing them for said deposition processes.

[0023] The aim of the present invention is to alleviate all or some of the abovementioned drawbacks of the prior art.

[0024] For this purpose, one subject of the invention is a silane recycling method comprising the following successive steps:

[0025] a) injection of a pure silane/pure hydrogen (SiH₄/H₂) mixture into a reaction chamber in order to fabricate thin films containing silicon;

[0026] b) extraction of the mixture comprising the excess silane unused in step a) and hydrogen (SiH₄/H₂) by means of a pump employing a feed gas;

[0027] c) delivery by said pump at a pressure close to atmospheric pressure of a mixture comprising at least silane (SiH₄), hydrogen (H₂) and a non-zero amount of said feed gas; and

[0028] d) separation of the silane (SiH₄) from the hydrogen/ feed gas mixture resulting from the mixture resulting from step c), said silane obtained comprising less than 100 ppm of feed gas, preferably less than 10 ppm of feed gas and preferably less than 1 ppm of feed gas, characterized in that at least 50%, preferably 70% and more preferably 80% of the silane (SiH₄) resulting from step b) is reused after step d) for a new step a).

[0029] Said feed gas is a heavy gas enabling the hydrogen to be entrained out of said reaction chamber and providing the pump with satisfactory lubrication. For example, the feed gas is nitrogen or argon. Preferably, the feed gas is nitrogen.

[0030] The term “pure gas” is understood to mean a gas comprising less than 1 ppm of impurities, for example less than 1 ppm of nitrogen. The dopants, such as those mentioned above, are not considered as impurities.

[0031] Another subject of the invention is a silane/hydrogen recycling method employing the method as defined above, which further includes a step of:

[0032] e) purification of the hydrogen (H₂) resulting from step d) in such a way that the feed gas content in the hydrogen is not greater than 100 ppm, preferably not greater than 10 ppm and preferably not greater than 1 ppm, characterized in that at least 50%, preferably 70% and more preferably 85% of the hydrogen (H₂) resulting from step b) is reused after step e) for a new step a).

[0033] The technique of thin-film fabrication by deposition of metal in a vacuum is widely practiced. At very low pressure (of the order of 100th of a Pascal) the molecules of a metal vapour travel with a very low risk of colliding with other molecules. The metal vapour molecules are sputtered onto a substrate without being impeded by diffusion phenomena and without the risk of being oxidized. The film obtained is thus very pure and very regular.

[0034] Moreover, ways of implementing the method of the invention may include one or more of the following features:

[0035] method as defined above, characterized in that said feed gas employed by the pump is nitrogen (N₂);

[0036] method as defined above, characterized in that the mixture resulting from step c) comprises 30% to 90% nitrogen (N₂), preferably 60% to 80% nitrogen (N₂);

[0037] method as defined above, which further includes a compression step between steps c) and d), during which step the delivery pressure of the pump, which is close to atmospheric pressure, is increased to a pressure of between 2 bars and 35 bars, preferably between 5 bars and 15 bars and more preferably between 8 bars and 10 bars;

[0038] method as defined above, which further includes, before step d), a filtration step for filtering the impurities contained in the mixture resulting from step c);

[0039] method as defined above, which further includes, after compression and before step d), a water adsorption step. This is because among the impurities present in the mixture resulting from step c) there may be water. The adsorption means is for example a PSA unit or a TSA unit, said adsorption means then being present in the plant (defined below) employing the method according to the invention;

[0040] method as defined above, characterized in that step d) is carried out by cryogenic distillation and/or separation;

[0041] method as defined above, characterized in that the mixture injected at step a) comprises less than 50%, and preferably less than 25%, silane (SiH₄) in hydrogen (H₂). The method according to the invention may also be employed for a mixture injected at step a) that contains more than 50% silane;

[0042] method as defined above, characterized in that the ratio of the concentration of silane (SiH₄) to the concentration of hydrogen (H₂) is controlled and adjusted, if necessary, before re-injection, for a new step a), of the silane/hydrogen (SiH₄/H₂) mixture comprising at least silane (SiH₄) recycled according to said method; and
method as defined above, characterized in that the thin-film fabrication in the reaction chamber is carried out in a vacuum.

One essential feature of the method according to the invention is the silane recycling, and if necessary the hydrogen recycling, carried out other than in a vacuum. This is because silane is a gas that reacts very strongly with the air, and therefore is very difficult to handle other than by using membranes or else by absorption, but these techniques are not satisfactory when there is a purity requirement on a gas to be recycled. In addition, handling silane under vacuum presents a great hazard in terms of safety due to the risk of air, oxygen or moisture ingress.

Moreover, the fact that a method is employed at a relatively high pressure (at atmospheric pressure or higher) means that the elements of the plant for carrying out the method according to the invention can be optimized.

Another subject of the invention is a plant operating at a pressure at least equal to atmospheric pressure, for recycling at least one gas employed in a vacuum reaction chamber during a thin-film deposition process, which comprises:

- a vacuum pump fed with feed gas;
- at least one purification means, for purifying the gas mixture extracted by said pump;
- at least one separation means, for separating the gases resulting from the purified mixture; and
- at least one recycling means, for recycling the separated gases into said reaction chamber.

Moreover, embodiments of the plant according to the invention may comprise one or more of the following features:

- a plant as defined above, which further includes a compression means located downstream of the purification means and upstream of the separation means;
- a plant as defined above, characterized in that the separation means consists of a cryogenic phase separation and/or cryogenic distillation unit; and
- a plant as defined above, characterized in that said feed gas is nitrogen (N₂).

Another subject of the invention is the use of the plant defined above for implementing a method defined according to the invention.

Yet another subject of the invention is a process for depositing a silicon-containing film employing at least one gas recycled according to the method defined above. Preferably, this deposition process is carried out using an SiH₄ (precursor)/H₂ mixture comprising less than 50%, preferably less than 25%, silane. The recycled gas described in the above method employed in the deposition process according to the invention is either the precursor silane or the precursor silane and hydrogen.

Other features and advantages will become apparent on reading the following description given with reference to FIG. 1:

FIG. 1 shows a diagram of an exemplary recycling circuit according to the invention and suitable for implementing the method that is the subject of the present invention.

FIG. 1 shows a recycling circuit (C) comprising a source 1 of silicon precursor, in particular the gas silane (SiH₄), and a hydrogen source 2. The hydrogen may be employed as carrier gas. The plant also includes a source 3 of dopant gases, such as TMB (trimethyl boron), PH₃ (phosphine) or B₂H₆ (diborane), intended for thin-film fabrication for the abovementioned applications. Other gases may be used, depending on the intended application. The gases output by these sources are then injected via the gas lines 4, 5, 6 into the reaction chamber 7, where the thin-film deposition takes place.

For example, said mixture comprises at most 50% silane, preferably less than 25% silane, in hydrogen. The concentration of dopant elements is generally less than 5% and depends on the desired level of doping and on the doping efficiency of the precursor used. Thus, the ratio of H₂ concentration to SiH₄ concentration is chosen precisely and must be controlled before the mixture is introduced into the reaction chamber 7.

Once said mixture has been injected into the reaction chamber 7, the deposition takes place. During the deposition, a quantity of the silicon precursor, particularly silane, introduced beforehand, which may amount up to 85%, is not used during the reaction inside the chamber. Since one objective of the present invention is to recycle all or practically all this unused quantity, the other components of the plant are used to recycle this silane. According to a variant of the method according to the invention, in addition to the silane, the hydrogens is also recycled. A pump 8 is placed downstream of the reaction chamber 7. This pump 8 takes in a mixture comprising the excess silane not used in the chamber 7 hydrogen (SiH₄/H₂) through a line 9 in which the pressure is a few millibars. Said mixture may further include impurities such as, for example, H₂O, O₂, traces of dopants, such as PH₃, B₂H₆, TMB, and particles formed in the reactor that result from the decomposition of the injected plasma. The pump 8 is for example supplied with nitrogen (N₂) (used here as “feed gas” as defined above) in particular for its inerting, lubricating and light-gas entraining properties. This results at the outlet of the pump 8 in a mixture comprising inter alia nitrogen, silane (in general 10.01% to 15%) and hydrogen (10% to 80%), which mixture flows at a pressure close to atmospheric pressure in a line 10.

A three-way valve 11 may be installed so as to direct the mixture either into the line 12, so as to recycle it, or into the line 13 and the reprocessing and venting equipment. This makes it possible, for example, to select the mixtures, exiting the reaction chamber 7, to be recycled according to the mixtures injected into the same reaction chamber 7. The valve 11 is also used to discharge the mixture coming from the line 10 into the line 13 in the event of the recycling circuit failing, so that if the recycling method according to the invention cannot operate, the gases output from the reaction chamber 7 are removed as in the standard systems of the prior art.

The mixture flowing in the line 12 may also include impurities, such as those described above. The purity requirements in the applications intended by the present invention therefore necessitate maximum removal of these impurities, which is why a filter 14 may be placed at the end of the line 12. Said filter 14 is for example of the centrifugal separator, inertial/sedimentation separator, electrical separator, electrofilter, bag filter, wet separator or scrubber type. The position of the filter may be downstream or upstream of a compression means 16 (for example a compressor), depending on the characteristics of said compression means 16. Specifically, if the suction force of the compressor is sufficient, the filter can be placed upstream with, however, a risk of partial vacuum downstream of the filters. If the suction force of the compressor is insufficient, the filters must be placed downstream of the compressor.
The mixture thus filtered flows in a line 15 to a compression means 16. The pressure of the mixture, comprising at least silane, hydrogen and nitrogen, leaving this compression means 16 is between 2 bars and 35 bars, preferably between 8 bars and 10 bars. The preferred pressure is that which achieves the best compromise between the size of the equipment of the plant (C) according to the invention and the cost of the energy for raising the working pressure. The size of said equipment is reduced when the pressure is raised, but the cost of the energy to be expended in order to achieve a high pressure is to be taken into consideration. Note, 1 bar = 10^5 Pa.

According to a variant of the invention, a buffer tank 18 may be installed so as to smooth out the variations in the flow rate of the mixture flowing in the line 17 downstream of said compression means 16. The size of this tank 16 and the way in which it is connected to the line 17 depend on the flow rates used and on the desired mode of operation.

According to a variant of the invention, one or more impurity removal systems may be placed around the compression module. This is because the precise location will enable most of one or more impurities prejudicial to the rest of the process to be removed.

The presence of fluorinated compounds may cause problems, for example corrosion problems or mechanical strength problems of the materials present in the plant according to the invention. The cost may also be high if the presence of fluorinated compounds requires the use of particularly suitable, and therefore expensive, materials. The compressor 16 is particularly prone to these possible problems. Therefore, a removal system 19 will be preferably placed upstream of the compression system 16.

Of course, in the absence of prejudicial impurities, no removal system need be added.

According to a variant of the invention, a separation means 19 operating for example on the adsorption principle (for example PSA (pressure swing adsorption) or TSA (temperature swing adsorption)) is located downstream of the compression means 16 for the purpose of adsorbing the impurities, such as for example H_2O, O_2 or fluorinated or even chlorinated compounds. Flowing in the line 20 downstream of the separation means 19 is a nitrogen/silane/hydrogen mixture, the pressure being a few bar. One of the objectives of the present invention is to recycle gases such as pure silane and pure hydrogen. The term “pure gas” is understood to mean a gas containing less than 100 ppm of impurities, for example less than 100 ppm of nitrogen, or even less than 1 ppm of impurities, for example less than 1 ppm of nitrogen. These specifications depend on the intended application. Now, the recycling at a pressure of a few bar of a gas (silane/hydrogen) mixture containing less than 100 ppm of nitrogen, preferably less than 1 ppm of nitrogen, resulting from an initial (silane/hydrogen) mixture, which may contain up to 90% nitrogen, is a technical problem to be solved by the present invention. This is why a cryogenic separation device 21 is placed downstream of said line 20. A cryogenic system 21 is used to condense, or even solidify, the silane (SiH₄) and therefore ensure SiH₄ separation. Depending on the separation conditions (pressure and temperature), the condensed silane phase may contain a greater or lesser amount of nitrogen and other heavy products. An additional silane purification step (using for example a distillation column or TSA) may be envisaged, depending on the required specifications. In particular, a nitrogen content of less than 1 ppm may be effectively achieved using a distillation column 23 which is fed with the mixture that has condensed in the separator 21 and is flowing in the line 22. For example, the distillation column 23 may be configured so as to remove what are called the light impurities via the line 25 and what are called the heavy impurities via the line 26. The silane having the desired purity is then recovered in the line 24.

There are various methods for reintegrating the purified SiH₄ into the reactor: either directly, by sending the stream directly into the SiH₄ delivery system, or indirectly, by passing via buffer tanks or even by filling bottles. Preferably, the solution according to the invention employs buffer tanks (27) which enable the output streams from the column to be matched to the gas demand of the delivery system. In particular, a system employing two buffer tanks in parallel enables one tank to be filled while the other one is being emptied and therefore makes it possible to provide complete decoupling between the output stream from the column and the stream demanded by the delivery system. These tanks may for example be filled by cryogenic filling, a well-known method in the field of gases produced by cryogenic means.

According to a variant of the invention, the silane thus recycled and purified is reintegrated into the line 4 via the line 28.

The N₂/H₂ mixture emerging, at a few bar, from the separation step carried out by the system 21, via a line 29, can then be separated using a membrane 30, so as if necessary to allow the hydrogen H₂ to be recycled, since the distillation of the hydrogen/nitrogen mixture is not very easy owing to the very low temperatures needed. Pure hydrogen containing less than 100 ppm of nitrogen, or even less than 1 ppm of nitrogen, is conventionally obtained using adsorption (PSA, cryogenic adsorption, etc.)-based systems. However, to be fully operational, these types of equipment require an incoming stream having a limited nitrogen content (less than about 20% in the case of a PSA unit or less than 5000 ppm in the case of a cryogenic adsorption system). By using a membrane it is possible, for a lower cost, to deplete the mixture of nitrogen so as to make it correspond to the specifications of a possible purification system sited downstream. The nitrogen resulting from the separation with the pure hydrogen is preferably removed from the system (C), for example by means of a vent 31. Some of the nitrogen resulting from this separation may also be employed by recycling it in order to feed the pump 8, by means of a recycling line 32. Reactivation of the nitrogen is probably not financially worthwhile owing to the low cost of nitrogen. It is therefore preferable to take the nitrogen to the vent 31 rather than recycling it into the vacuum pump 8 of the reaction chamber 7.

At the outlet of the membrane 30 through which the purified hydrogen flows, the hydrogen leaving the membrane may be used to regenerate the separation system 19 via a line (not shown in FIG. 1) or else may be also reintegrated (recycled) into the reaction chamber 7 via a line 33 if necessary after having undergone an additional purification. This additional purification may for example take place by PSA or by cryogenic adsorption depending on the required purity specifications. According to a variant of the invention, the hydrogen flowing in the line 33 is compressed by a compression means 34 and then conveyed into the purification system 36 via the line 35. The fact that the gas is compressed enables the purification to be optimized. For example, using a PSA unit, the operating pressure is around 25 bar. The hydrogen thus recycled and purified may, for example, be reintegrated into the line 5 via the line 37.
one or more tanks 38 may be used to store the hydrogen and thus decouple the recycled hydrogen stream from the stream demanded by the application. According to another variant of the invention, the recycled hydrogen may be reinjected into the tank serving as hydrogen source 2.

According to a variant of the invention, the composition of the recycled gas streams may be controlled by a suitable system (FTIR, calorimeter, etc.) connected either to the lines 28 and/or 37 or to the tanks 27 and/or 38. The various quantities measured may thus be sent back to a supervision system, which can act on the flow rates of the fresh gases injected so as to control the process. Another method of controlling the quality of the recycled gases consists in taking samples of said gases from the lines 28 and/or 37 or from the tanks 27 and/or 38 and then carrying out ex situ analysis on these samples.

According to one embodiment of the invention, the plant includes mixing tanks or chambers (not shown in FIG. 1). These chambers are intended for mixing the recycled gases with pure gases coming for example from the sources 1 and 2. These types of mixtures make it possible for example to damp out the fluctuations in quality of the composition of the recycled gases to be mixed before being reinjected into the reaction chamber 7.

In order for the silane/hydrogen mixture to be injected into the reaction chamber 7 in the same proportions as the silane/hydrogen mixture flowing in the lines 4 and 5 containing the gases output from the sources 1 and 2, the silane/hydrogen concentration ratio is controlled before the mixture is injected into the reaction chamber 7.

According to a variant, the cryogenic separation system 21 includes exchangers for reducing the temperature of the mixture. These exchangers are designed and sized so as to optimize the energy balance. The principle is based on the liquefaction of silane. To do this, the temperature of the gas containing the silane to be liquefied is brought to a temperature below the silane liquefaction temperature (bubble temperature) using exchangers cooled by employing nitrogen for example, thereby enabling this temperature to be easily modulated. Other cold sources can be used. When the silane is predominantly in liquid form, it is then necessary to separate the droplets from the waste gas. A separation pot is then used which optionally is provided with one or more droplet recovery systems so as to recover most of the droplets. Some of the nitrogen contained in the gas liquefies and/or dissolves in the liquid silane. However, it is necessary to recycle a high-purity silane product, and it is therefore preferable to purify this (mainly) nitrogen/silane mixture. Preferably, a distillation column in which one of the outlets contains high-purity silane will be used.

Such cryogenic separation systems allow the method according to the invention to be carried out continuously.

10. A silane recycling method comprising the following successive steps:

a) injection of a pure silane/pure hydrogen (SiH₄/H₂) mixture into a reaction chamber in order to fabricate thin films containing silicon;

b) extraction of the pure silane/pure hydrogen mixture unused in step a) by means of a pump employing a feed gas;

c) delivery by said pump at a pressure close to atmospheric pressure of a mixture comprising at least silane (SiH₄), hydrogen (H₂) and a non-zero amount of said feed gas; and

d) separation of silane (SiH₄) from the mixture of step c), said silane obtained comprising less than 100 ppm of the feed gas,

wherein at least 50% of silane (SiH₄) in the pure silane/pure hydrogen mixture of step b) is reused after step d) for a new step a).

11. The method of claim 10, further comprising a step of:

e) separation of hydrogen (H₂) from a mixture resulting from step d), said hydrogen obtained comprising less than 100 ppm of the feed gas,

wherein at least 50% of the hydrogen (H₂) in the pure silane/pure hydrogen mixture of step b) is reused after step e) for a new step a).

12. The method of claim 10, wherein said feed gas is nitrogen (N₂).

13. The method of claim 12, wherein the mixture of step c) comprises 30% to 90% nitrogen (N₂).

14. The method of claim 10, further comprising a compression step between steps c) and d), during which step the pressure of the mixture is increased to between 2 bars and 35 bars.

15. The method of claim 10, wherein step d) is carried out by cryogenic distillation and/or separation.

16. The method of claim 10, wherein the silicon thin-film fabrication in the reaction chamber is carried out in a vacuum.

17. The method of claim 10, further comprising, before injection step a), controlling and adjusting a ratio of a concentration of hydrogen (H₂) to a concentration of silane (SiH₄) containing the silane obtained in step d).

18. The method of claim 10, further comprising depositing a silicon-containing film employing the silane obtained in step d).

19. A silane recycling method comprising the following successive steps:

a) injection of a pure silane/pure hydrogen (SiH₄/H₂) mixture into a reaction chamber in order to fabricate thin films containing silicon;

b) extraction of the pure silane/pure hydrogen mixture unused in step a) by means of a pump employing N₂;

c) delivery by said pump at a pressure close to atmospheric pressure of a mixture comprising at least silane (SiH₄), hydrogen (H₂) and between 50% and 90% N₂; and

d) cryogenic separation of silane (SiH₄) from the mixture of step c), said silane obtained comprising less than 10 ppm of N₂,

wherein at least 50% of silane (SiH₄) in the pure silane/pure hydrogen mixture of step b) is reused after step d) for a new step a).

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