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ON-SITE WASTE RECOVERY FOR SOLID STATE MANUFACTURING PROCESS

The present invention concerns generally reduction in waste for solid state manufacturing processes. More specifically, the present invention pertains to synthesis of useful chemicals using waste streams, for example, from a solid state (semiconductor) manufacturing process.

Solid state device manufacturing can be divided into four stages: material preparation, crystal growth and wafer preparation, wafer fabrication and packaging. During the first three stages, a plethora of chemicals are used for various steps involving growth, patterning, doping, deposition, etching, polishing and cleaning. For example, C_2F_6 , NF_3 , and ClF_3 gases are used during the etching process; BF_3 , AsH_3 , PH_3 , trimethylborane (TMB), trimethylphosphine (TMP) are used for doping; and aqueous solutions containing HCl , HF , NH_4F , H_2O_2 , or H_2SO_4 are used for wafer surface cleaning. The purity requirement for these chemicals are very high (the impurity level in these chemicals are typically below parts per million (ppm) level). The chemical utilization rate of these processes are very inefficient. The exhaust gases from these processes are usually treated before release to atmosphere to remove toxic or otherwise unfriendly gases.

Since the cost of treatment units are normally very high and with no added value to the manufacturers, some reclaiming processes are gaining attention in the industry. For example, several units of on-site recovery/purification of H_2SO_4 have been installed in semiconductor fabrication facilities.

In order to reduce the cost of transportation and storage of high purity aqueous solutions, several on-site generators of high purity aqueous solutions involving NH_4OH , HCl , HF and NH_4F have also been commercialized for the industry, for example the system known under the trade designation "Gas-to-Chemical Generation" or "GCG", marketed by Air Products and Chemicals, Inc.

Most specialty gases used in the solid state device manufacturing processes are either toxic (e.g. AsH_3 , HF), pyrophoric (e.g., SiH_4) or corrosive (e.g., HCl , HF) in nature. It is not uncommon, therefore, that these gases must pass through some abatement process before being released into the atmosphere. Normally, the material utilization rate of the gases in the processes is very low and some of the toxic gases are generated during the process. For example, in the epitaxial process, HCl is generated via the reaction of $SiCl_4$ with adsorbed H_2 on a wafer surface.

Thus, there is presently needed for the solid state device manufacturing industry, indeed in any industry which discards waste streams, for processes and systems which utilize a waste stream

as a feed to an on-site or off-site chemical generator which can generate chemicals needed either in the facility or process where the waste is produced, or elsewhere, thereby reducing the overall hazardous material emission, decreasing the abatement cost, and lowering the total amount of raw material input. In other words, there is presently needed processes and systems which not only serve the environment via reducing hazardous material generation, but also benefit the device manufacturer by reducing the total cost of handling these materials.

In accordance with the present invention, processes and systems are provided which combine waste recovery and chemical generation (or synthesis), preferably on-site chemical generation.

Thus one aspect of the present invention is a waste recovery process characterized by the steps of:

- a) providing a waste stream comprising halogenated gases;
- b) wet scrubbing the waste stream using a composition comprising an inorganic hydroxide (for example calcium hydroxide, sodium hydroxide, and the like) to generate a stream comprising an inorganic salt such as CaX_2 , wherein X is selected from the group consisting of Cl, F, and I; and
- c) passing the stream comprising the inorganic salt through a generator with sulfuric acid to produce a stream comprising HX gas. Preferred processes in accordance with this aspect are those wherein the waste stream is generated from a SACVD process, and those process wherein the halogenated gases are selected from the group consisting of COF_2 , HF, and the like. Particularly preferred are those processes wherein the stream comprising HX gases is routed to a wet chemical generator, wherein the HX gas is dissolved in ultra high purity water to form ultra high purity aqueous HX, preferably HF

Another process embodiment of the invention is a process for production of aqueous HNO_3 characterized by the steps of:

- a) providing a gas stream comprising at least one gas which, when combusted with oxygen, produces one or more oxides of nitrogen (NO_x);
- b) routing the gas stream to a combustion process with an oxidant gas comprising oxygen;
- c) combusting the at least one gas with the oxygen to form an NO_x -containing stream;

d) routing the NO_x containing stream to a separator and separating the NO_x from non- NO_x species; and

e) routing the NO_x to a chemical generator to generate aqueous HNO_3 .

Preferred processes in accordance with this aspect of the invention are those wherein the gas stream is an effluent stream of a nitride process, the nitride process having a feed gas comprising one or more of SiH_4 , NF_3 , N_2 , N_2O and NH_3 , and those wherein the at least one gas is selected from the group consisting of NF_3 , N_2 , N_2O , and NH_3 .

A third process embodiment in accordance with the present invention is a process for the production of aqueous HCl and gaseous NH_3 , characterized by the steps of:

a) providing a gas composition comprising SiCl_4 , H_2 , N_2 and HCl ;

b) wet scrubbing the gas composition with water to produce a wet HCl gas stream and a stream rich in N_2 and H_2 ;

c) routing the wet HCl gas stream to a chemical generator wherein water is admixed with the wet HCl to produce aqueous HCl ; and

d) routing the stream rich in N_2 and H_2 to an ammonia NH_3 synthesizer.

Preferred are those processes of this aspect of the invention wherein the NH_3 is further routed to a nitride process, and those processes wherein the NH_3 is routed to an aqueous HNO_3 generator. The NH_3 may also be routed directed to an aqueous NH_4OH generator, wherein the NH_4OH is routed to an NH_4F generator or an NF_3 generator. The NF_3 may further be routed to a nitride process or a chamber cleaning process.

Systems for carrying out the processes of the present invention are also considered aspects of the invention.

One system embodiment is characterized by:

a) a source of a waste stream comprising halogenated gases;

b) a wet scrubber connected to the source by a conduit, the conduit adapted to carry the waste stream to the wet scrubber, the wet scrubber adapted to contact the waste stream with a composition comprising an inorganic hydroxide (such as calcium hydroxide, sodium hydroxide, and the like) to generate a stream comprising an inorganic salt such as CaX_2 ; and

c) a generator connected to the wet scrubber by a second conduit, the second conduit directing the stream comprising the inorganic salt to the generator, the generator adapted to contact the stream comprising the inorganic salt with sulfuric acid to produce a stream comprising HX gas. Preferred systems in accordance with this aspect are those wherein the

source of the waste stream is a SACVD tool, and those systems wherein the halogenated gases are selected from the group consisting COF_2 , HF , and the like. Particularly preferred are those systems wherein the stream comprising HX gases is routed to a wet chemical generator, as described previously in the corresponding process embodiment of the invention.

Another system embodiment of the invention is a system adapted to produce aqueous HNO_3 , the system characterized by:

- a) a source of a gas stream comprising at least one gas which, when combusted with oxygen, produces NO_x species and non- NO_x species;
- b) a combustion unit connected to the source via a conduit, the conduit adapted to route the gas stream to the combustion unit, the combustion unit adapted to combust the at least one gas to form the NO_x species with an oxidant gas comprising oxygen;
- c) a separator connected to the combustion unit by a second conduit, the second conduit adapted to route the NO_x containing stream to the separator, the separator adapted to separate the NO_x species from the non- NO_x species; and
- e) an HNO_3 generator connected to the separator by a third conduit, the third conduit adapted route the NO_x species to the HNO_3 generator, the HNO_3 generator adapted to generate aqueous HNO_3 from the HNO_3 and water. Preferred systems in accordance with this aspect of the invention are those wherein the source of the gas stream is a nitride process tool, although this is by no means required.

A third system embodiment in accordance with the present invention is a system adapted to produce aqueous HCl and gaseous NH_3 , characterized by:

- a) a source of a gas composition comprising SiCl_4 , H_2 , N_2 and HCl ;
- b) a wet scrubber connected to the source by a first conduit, the first conduit adapted to direct the gas composition to the wet scrubber in the presence of water to produce a wet HCl gas stream and a stream rich in N_2 and H_2 ;
- c) a chemical generator connected to the wet scrubber by a second conduit, the second conduit adapted to direct the wet HCl gas stream to the chemical generator wherein water is admixed with the wet HCl to produce aqueous HCl ; and
- d) an ammonia synthesizer connected to the wet scrubber by a third conduit, the third conduit routing the stream rich in N_2 and H_2 to the ammonia NH_3 synthesizer.

Preferred are those systems of this aspect of the invention further including an aqueous NH_4OH generator to which the NH_3 is directed, and further including a NH_4F generator where the NH_4OH is directed, as previously mentioned.

FIG. 1 is a schematic diagram of one embodiment of the invention wherein aqueous HF is generated from the effluent of an SACVD chamber;

FIG. 2 is a schematic diagram of a second embodiment of the present invention where aqueous HNO_3 is generated on-site using a waste stream from a PE nitride chamber; and

FIG. 3 is a third embodiment of the present invention wherein a variety of useful chemicals are generated using a waste stream from a silicon epitaxial chamber.

The essential concept of the present invention is the incorporation of waste recovery with chemical generation in any one of a variety of industrial processes. For example, Table 1 lists some of the gases used in the solid state device manufacturing processes.

Table 1: Commonly Used Chemicals In the Solid State Fabrication Process	
Gases	Aqueous Inorganic Chemicals
SiCl_4	HF
SiHCl_3	HNO_3
SiH_2Cl_2	HCl
SiH_3Cl	NH_4OH
SiH_4	H_2SO_4
Si_2H_6	NH_4F
WF_6	H_3PO_4
BF_3	H_2O_2
BCl_3	
B_2H_6	
PH_3	
AsH_3	Organic Chemicals
	TEOS
HCl	TMP
HBr	TMB
HF	IPA
Cl_2	CH_3OH
Br_2	Acetone
BrCl	Toluene
ClF_3	Methylene chloride
NH_3	
N_2O	

CF ₄	
C ₂ F ₆	
CHF ₃	
CH ₃ F	
NF ₃	
C ₃ F ₈	
Ar	
N ₂	
O ₂	
H ₂	
He	
O ₃	

In accordance with the present invention, processes and systems are provided which combine waste recovery and chemical generation (or synthesis), preferably on-site chemical generation.

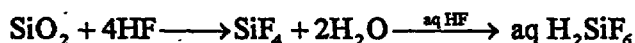
Thus one aspect of the present invention is a waste recovery process characterized by the steps of:

- a) providing a waste stream comprising halogenated gases;
- b) wet scrubbing the waste stream using a composition comprising calcium hydroxide to generate a stream comprising CaX₂; and
- c) passing the stream comprising CaX₂ through a generator with sulfuric acid to produce a stream comprising HX gas. Preferred processes in accordance with this aspect are those wherein the waste stream is generated from a SACVD process, and those process wherein the halogenated gases are selected from the group consisting COF₂, HF, and the like. Particularly preferred are those processes wherein the stream comprising HX gases is routed to a wet chemical generator, wherein the HX gas is dissolved in ultra high purity water to form ultra high purity aqueous HX, wherein X is selected from the group consisting of Cl, F, I, and the like.

Particularly preferred for the solid state device manufacturing industry is where HX = HF. Anhydrous HF is almost invariably made by the action of concentrated H₂SO₄ (≥ 95%) on "acid grade" fluorspar (≥98% CaF₂):



As the reaction is endothermic heat is preferably supplied to obtain good yields in reasonable time (e.g. 30-60 min at 200-250°C). Silica is a particularly undesirable impurity in the fluorspar since it consumes up to 6 moles of HF per mole of SiO_2 by reacting to form SiF_4 and then H_2SiF_6 . A typical unit, producing up to 20,000 metric tons of HF, consists of an externally heated, horizontal steel kiln about 30 meters long rotating at 1 revolution per minute. The product gas emerges at 100-150°C and, after appropriate treatment to remove solid, liquid, and gaseous impurities, is condensed to give a 99% pure product which is then redistilled to give a final product of 99.9% purity. The technical requirements to enable the safe manufacture and handling of so corrosive a product are considerable. In principle, HF could also be obtained from the wet-processing of fluorapatite to give phosphoric acid but the presence of SiO_2 preferentially yields SiF_4 and H_2SiF_6 from which HF can only be recovered uneconomically.



Some of the H_2SiF_6 so produced finds commercial outlets, but it has been estimated that ~50,000 metric tons of H_2SiF_6 is discarded annually by the US phosphoric acid industry, equivalent to ~1 million tonnes of fluorspar-enough to supply that nation's entire requirements for HF.

Processes in accordance with this aspect of the invention typically also produce a gas stream comprising gases which are insoluble in water. These insoluble gases are preferably routed to a recovery unit to separate useful gases from carrier gases. For example, if the insoluble gases comprise C_2F_6 and CF_4 in a carrier gas of nitrogen (see for example FIG. 1, discussed herein below), the recovery unit is preferably a membrane separator which separates substantially all of said C_2F_6 and CF_4 from the nitrogen.

Membranes useful in the invention are preferably glassy membranes, such as polymer membranes made preferably from polyimides, polyamides, polyamide-imides, polyesters, polycarbonates, polysulfones, polyethersulfone, polyetherketone, alkyl substituted aromatic polyesters, blends of polyethersulfone, aromatic polyimides, aromatic polyamides, polyamides-imides, fluorinated aromatic polyimide, polyamide and polyamide-imides, glassy polymeric membranes, cellulose acetates, and blends thereof, copolymers thereof, substituted polymers (e.g. alkyl, aryl) thereof and the like.

Asymmetric membranes are prepared by the precipitation of polymer solutions in solvent-miscible nonsolvents. Such membranes are typified by a dense separating layer supported on an anisotropic substrate of a graded porosity and are generally prepared in one step. Examples of such membranes and their methods of manufacture are disclosed in U.S. Patents 4,113,628; 4,378,324; 4,460,526; 4,474,662; 4,485,056; 4,512,893, 5,085,676, and 4,717,394. The '394 and '676 patents disclose preparation of asymmetric separation membranes from selected polyimides. Particularly preferred membranes are polyimide asymmetric gas separation membranes as disclosed in the '676 patent.

In a pressure driven gas membrane separation process, one side of the gas separation membrane is contacted with a complex multicomponent gas mixture and certain of the gases of the mixture permeate through the membrane faster than the other gases. Gas separation membranes thereby allow some gases to permeate through them while serving as a barrier to other gases in a relative sense. The relative gas permeation rate through the membrane is a property of the membrane material composition and its morphology. It has been suggested in the prior art that the intrinsic permeability of a polymer membrane is a combination of gas diffusion through the membrane, controlled in part by the packing and molecular free volume of the material, and gas solubility within the material. Selectivity is the ratio of the permeability's of two gases being separated by a material. It is also highly desirable to form defect-free dense separating layers in order to retain high gas selectivity.

Composite gas separation membranes typically have a dense separating layer on a preformed microporous substrate. The separating layer and the substrate are usually different in composition. Composite gas separation membranes have evolved to a structure of an ultrathin, dense separating layer supported on an anisotropic, microporous substrate. These composite membrane structures can be prepared by laminating a preformed ultrathin dense separating layer on top of a preformed anisotropic support membrane. Examples of such membranes and their methods of manufacture are disclosed in U.S. Patents 4,664,669; 4,689,267; 4,741,829; 2,947,687; 2,953,502; 3,616,607; 4,714,481; 4,602,922; 2,970,106; 2,960,462; 4,713,292, 4,086,310; 4,132,824; 4,192,824; 4,155,793; and 4,156,597.

Alternatively, composite gas separation membranes may be prepared by multistep fabrication processes, wherein first an anisotropic, porous substrate is formed, followed by contacting the substrate with a membrane-forming solution. Examples of such methods are described in U.S. Patents 4,826,599; 3,648,845; and 3,508,994.

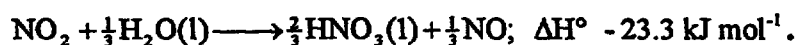
U.S. 4,756,932 describes how composite hollow-fiber membranes may also be prepared by co-extrusion of multiple polymer solution layers, followed by precipitation in a solvent-miscible nonsolvent.

The membrane can be post-treated with, or coated by, or coextruded with, a fluorinated or perfluorinated polymer layer in order to increase its ability to withstand harmful constituents in the gas mixture from which PFCs are to be separate, at low levels or temporary contact with such components.

The hollow-fiber spinning process depends on many variables which may affect the morphology and properties of the hollow-fiber membrane. These variables include the composition of the polymer solution employed to form the fiber, the composition of fluid injected into the bore of the hollow-fiber extrudate during spinning, the temperature of the spinneret, the coagulation medium employed to treat the hollow-fiber extrudate, the temperature of the coagulation medium, the rapidity of coagulation of the polymer, the rate of extrusion of the fiber, takeup speed of the fiber onto the takeup roll, and the like. The nitrogen stream may also be used in a variety of processes, such as inerting a circuit board wave soldering machine atmosphere, as described in U.S. Pat. No. 5,411,200.

Preferred processes in accordance with the HNO_3 production process of the invention are those wherein the gas stream is an effluent stream of a nitride process, the nitride process having a feed gas comprising one or more of SiH_4 , NF_3 , N_2 , N_2O and NH_3 , and those wherein the at least one gas is selected from the group consisting of NF_3 , N_2 , N_2O , and NH_3 .

Nitric acid may be generated in known fashion by passing a gaseous stream of NO_2 and NO through an absorber column wherein water flows countercurrently to the flow of the feed gas. For example, the following reaction takes place, wherein the absorption column typically yields 60% aqueous nitric acid at about $40^\circ\text{C}.$:

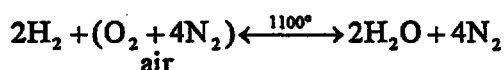


Processes in accordance with this aspect of the invention may have as the oxidant gas an oxygen-rich stream emanating from a separation process selected from the group consisting of cryogenic air separation, vacuum swing or pressure swing adsorption separation units, and membrane separation units as are known in the air separation art.

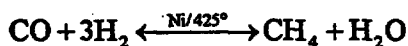
As stated previously, particularly preferred processes in accordance with this aspect invention are those wherein the chemical generator is on-site of a semiconductor fabrication facility.

Another process embodiment in accordance with the present invention is a process for the production of aqueous HCl and gaseous NH₃, as discussed above. Preferred are those processes of this aspect of the invention wherein the NH₃ is further routed to a nitride process, and those processes wherein the NH₃ is routed to an aqueous HNO₃ generator. The NH₃ may also be routed directed to an aqueous NH₄OH generator, wherein the NH₄OH is routed to an NH₄F generator or an NF₃ generator. The NF₃ may further be routed to a nitride process.

The production of NH₃ from H₂ and N₂ may proceed as follows. Sufficient air is injected via a compressor to give a final composition of about 1:3 N₂:H₂ and the air burns in the hydrogen thereby heating the gas to ~1100°C in a reforming reaction:



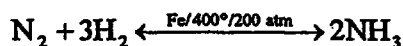
Any remaining trace quantities of CO (which would poison the iron catalyst during ammonia synthesis) are preferably converted to CH₄ by passing the damp gas over a Ni methanation catalyst at about 325°C.



The synthesis gas now emerging has the approximate composition:

H₂ 74.3%, N₂ 24.7%, CH₄ 0.8%, Ar 0.3%, CO 1-2 ppm;

This gas is compressed in typically multiple (usually) three stages from 25 atm to 1200 atm and then passed over a promoted iron catalyst at about 380-450°C:



The gas leaving the catalyst beds contains about 15% NH_3 ; this is condensed by refrigeration and the remaining gas mixed with more incoming synthesis gas and recycled. Variables in the final reaction are the synthesis pressure, synthesis temperature, gas composition, gas flow rate and catalyst composition and particle size. Since the earliest days the "promoted" Fe catalysts have been prepared by fusing magnetite (Fe_3O_4) on a table with KOH in the presence of a small amount of mixed refractory oxides such as MgO , Al_2O_3 and SiO_2 ; the solidified sheet is broken up into chunks 5-10 mm in size. These chunks are then reduced inside the ammonia synthesis converter to give the active catalyst which consists of Fe crystallites separated by the amorphous refractory oxides and partly covered by the alkali promoter which increases the activity by at least an order of magnitude.

Several examples are given to illustrate the conceptual processes and systems incorporating waste recovery for chemical generation.

Example 1

FIG. 1 illustrates conceptual and in schematic diagram fashion a process of generating aqueous hydrogen fluoride (HF) using a waste stream from an SACVD chamber. During SACVD, typically TEOS, ozone, C_2F_6 , CF_4 , argon, nitrogen and helium are used as illustrated in FIG 1. SACVD is primarily used during the deposition of inter-metal dielectric gas-fill. The SACVD process can be divided into three essential steps: precleaning of the wafer, deposition, and post-cleaning. During the cleaning step, C_2F_6 , NF_3 , or CF_4 together with O_2 are normally used under plasma condition. A combination of TEOS with O_3 is typically used for the deposition step. Physically, these gases flow sequentially into the chamber. Stream 2 containing the above-mentioned gases is fed to an SACVD chamber 4 creating an affluent stream 6 which comprises, in addition to the feed gases HF, COF_2 , O_2 and some trace amounts of halogenated gases. The affluent stream 6 is fed to a wet scrubber 8 wherein calcium hydroxide is fed through conduit 10. In wet scrubber 8, fluorinated gases (HF, COF_2 and like) react with the calcium hydroxide to form a stream 12 containing calcium fluoride (CaF_2). Stream 12 containing calcium fluoride then enters a hydrogen fluoride generator 14, in which the calcium fluoride in stream 12 reacts with sulfuric acid in stream 16 to generate gaseous hydrogen fluoride in stream 18. The gaseous HF is then feed into an on-site (could be off-site also) liquid chemical generator 20, wherein the gaseous HF combines with ultra pure water from stream 22 to form ultra high purity aqueous HF in stream 24. The ultra high purity aqueous HF may then be used in the wet bench for a wafer cleaning process.

Alternatively, the gaseous HF in stream 18 may be fed to a NH_4F generator (with aqueous NH_4OH , as further described in Example 3).

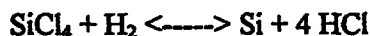
Exiting from wet scrubber 8 is a gas stream 26 typically comprising C_2F_6 , CF_4 , N_2 , He, and O_2 . This stream is preferably routed to a PFC recovery unit 28, preferably a membrane separator, as described herein, to produce a non-permeate, PFC-rich stream 32, and a permeate stream 30 rich in N_2 , O_2 , and He.

Example 2

FIG. 2 illustrates schematically a process of the invention to generate aqueous HNO_3 from a chamber upon stream from a plasma enhanced (PE) nitride chamber. In the PE nitride process, SiH_4 , NF_3 , N_2 , N_2O and NH_3 enter in stream 50 into a PE nitride chamber 52, forming an exhaust stream 54. In this example, a combustion detox unit 56 is chosen to treat exhaust line 54 using oxygen 58. In this particular process oxides of silicon and nitrogen will form as indicated at line 60 for the combustion detox unit 56 effluent. Effluent stream 60 comprising SiO_2 , NO, NO_2 , N_2 , and O_2 is sent to a separator unit 62, for example a membrane separation unit or a cryogenic separation unit, in which the NO_x are separated from the SiO_2 , oxygen and nitrogen. The separated NO_x may then be fed via conduit 64 to an on-site HNO_3 generator 68 in which the NO_x react with hydrogen peroxide or a combination of ozone and water to create an aqueous HNO_3 stream 72. Aqueous HNO_3 is one of the highly preferred liquid chemicals for wafer surface cleaning.

Example 3

FIG. 3 illustrates schematically a process to generate various chemicals from an effluent stream from a silicon epitaxial chamber. In the silicon epitaxial process, SiCl_4 , H_2 and N_2 are typically involved and enter the chamber in stream 80. In silicon epitaxial chamber 82, a large amount of HCl is generated via the following reaction:



The gases in exhaust line 84 typically comprise SiCl_4 , H_2 , N_2 , and HCl, and is fed to a wet scrubber 86 wherein water enters wet scrubber 86 through line 88 wherein the HCl is absorbed in a preferably countercurrent water stream to produce a wet HCl gas 90 which is then fed to an on-site or off-site HCl generator 92, wherein the wet HCl in stream 90 is mixed with ultra high purity water and stream 94 to produce ultra high purity aqueous HCl stream 96. Another effluent

stream from the wet scrubber 98, comprising hydrogen and nitrogen is preferably then routed to an ammonia synthesizer 100 which produces an ammonia rich stream in conduit 102. Ammonia in conduit 102 may be routed to a nitride process via line 104, or to an on-site or off-site HNO_3 generator 110, wherein the ammonia in stream 106 reacts with oxygen from stream 108 to produce an aqueous HNO_3 stream 112. Alternatively, ammonia may be sent via line 114 to an on-site NH_4OH generator 118 in which the ammonia in stream 114 reacts with ultra high purity water from stream 116 to generate ultra high purity NH_4OH in stream 120. The NH_4OH may be sent via conduit 122 to an on-site NH_4F generator 124 wherein the NH_4OH reacts with HF from stream 126 to generate a stream 128 comprising NH_4F . NH_4F may be routed via stream 130 to an on-site or off-site NF_3 generator 132, to generate a stream rich in NF_3 134. Aqueous NH_4F can either be used as a wafer cleaning solution (known in the art as buffered oxide etch BHF) or may be used as a reactant in the NF_3 electrolysis generator.

Example 4

Hydrogen recovery in epitaxial process.

During the epitaxy process, H_2 is introduced as a reduction agent for the deposition of a Si layer:



In CVD processes, this reaction does not have a high efficiency. Therefore, there are large amounts unreacted H_2 being vented from the process. By using this concepts of the present invention, this H_2 can be recovered from the exhaust lines and then purified, then fed back into the process. In this way, semiconductor manufacturers can reduce the total H_2 consumption via recovery and recycle of the unreacted H_2 . The current proposed process involves two steps: concentration and purification. During the concentration step, H_2 concentration at the exhaust line is concentrated from a few percentage up to 80 % using a membrane unit having a high selectivity of H_2/N_2 , i.e. the permeation rate for H_2 is much higher than that of N_2 . The output (permeate) of the membrane unit is fed to a purification unit, which may be a heat exchanger coupled with pressure swing adsorption unit, or a second membrane unit coupled with eat exchangers.

**What is claimed is:**

1. A waste recovery process characterized by the steps of:
 - a) providing a waste stream comprising halogenated gases;
 - b) wet scrubbing the waste stream using a composition comprising an inorganic hydroxide to generate a stream comprising an inorganic salt of F, Cl, and/or I; and
 - c) passing said stream comprising the inorganic salt through a generator with sulfuric acid to produce a stream comprising HX gas, wherein X is selected from the group consisting of F, Cl, and I.
2. A process in accordance with claim 1 further characterized by said waste stream being generated from a SACVD process.
3. A process in accordance with claim 1 further characterized by said halogenated gases are selected from the group consisting of COF_2 , HF, and the like.
4. A process in accordance with claim 1 further characterized by said stream comprising HX gases is routed to a wet chemical generator, wherein said HX gas is dissolved in ultra high purity water to form ultra high purity aqueous HX.
5. A process in accordance with claim 1 further characterized by step B also produces a gas stream comprising gases which are insoluble in water.
6. A process in accordance with claim 1 further characterized by said insoluble gases are routed to a recovery unit to separate useful gases from carrier gases.
7. A process in accordance with claim 6 further characterized by said insoluble gases comprise C_2F_6 and CF_4 , and said recovery unit is a membrane separator which separates substantially all of said C_2F_6 and CF_4 from said carrier gases.



8. A process for production of aqueous HNO_3 characterized by the steps of:
- providing a gas stream comprising at least one gas which, when combusted with oxygen, produces NO_x ;
 - routing said gas stream to a combustion process with an oxidant gas comprising oxygen;
 - combusting said at least one gas with said oxygen to form an NO_x -containing stream;
 - routing said NO_x containing stream to a separator and separating said NO_x from non- NO_x species; and
 - routing said NO_x to a chemical generator to generate aqueous HNO_3 .
9. A process in accordance with claim 8 further characterized by said gas stream being an affluent stream of a nitride process, said nitride process having a feed gas comprising SiH_4 , NF_3 , N_2 , N_2O and NH_3 .
10. A process in accordance with claim 8 further characterized by said at least one gas being selected from the group consisting of NF_3 , N_2 , N_2O , and NH_3 .
11. A process in accordance with claim 8 further characterized by said oxidant gas being an oxygen-rich stream emanating from a separation process selected from the group consisting of cryogenic air separation, VSA, PSA, and membrane separation.
12. A process in accordance with claim 8 further characterized by said separator being selected from the group consisting of cryogenic separation units and membrane separation units.
13. A process in accordance with claim 8 further characterized by said chemical generator being on-site of a semiconductor fabrication facility.
14. A process for simultaneous production of aqueous HCl and gaseous NH_3 , characterized by the steps of:
- providing a gas composition comprising SiCl_4 , H_2 , N_2 and HCl ;



b) wet scrubbing said gas composition with water to produce a wet HCl gas stream and a stream rich in N_2 and H_2 ;

c) routing said wet HCl gas stream to a chemical generator wherein water is admixed with the wet HCl to produce aqueous HCl; and

d) routing said stream rich in N_2 and H_2 to an ammonia NH_3 synthesizer.

15. A process in accordance with claim 14 further characterized by said NH_3 being further routed to a nitride process.

16. A process in accordance with claim 14 further characterized by said NH_3 is routed to a HNO_3 generator.

17. A process in accordance with claim 14 further characterized by said NH_3 is routed to a NH_4HO generator to produce NH_4HO .

18. A process in accordance with claim 17 further characterized by said NH_4OH is routed to an NH_4F generator.

19. A process in accordance with claim 17 further characterized by said NH_4OH is routed to an NF_3 generator.

20. A process in accordance with claim 19 further characterized by said NF_3 is routed to a nitride process.

21. A system characterized by:

a) a source of a waste stream comprising halogenated gases;

b) a wet scrubber connected to the source by a conduit, the conduit adapted to carry the waste stream to the wet scrubber, the wet scrubber adapted to contact the waste stream with a composition comprising an inorganic hydroxide to generate a stream comprising a salt of the inorganic hydroxide and F, Cl, and/or I; and

c) a generator connected to the wet scrubber by a second conduit, the second conduit directing the stream comprising the inorganic salt to the generator, the generator adapted

to contact the stream comprising the inorganic salt with sulfuric acid to produce a stream comprising HX gas.

22. System in accordance with claim 21 further characterized by the source of the waste stream is a SACVD tool, and the halogenated gases are selected from the group consisting COF_2 , HF, and the like.

23. System in accordance with claim 21 further including a wet chemical generator, as described previously in the corresponding process embodiment of the invention.

24. A system adapted to produce aqueous HNO_3 , the system characterized by:

- a) a source of a gas stream comprising at least one gas which, when combusted with oxygen, produces NO_x species and non- NO_x species;
- b) a combustion unit connected to the source via a conduit, the conduit adapted to route the gas stream to the combustion unit, the combustion unit adapted to combust the at least one gas to form the NO_x species with an oxidant gas comprising oxygen;
- c) a separator connected to the combustion unit by a second conduit, the second conduit adapted to route the NO_x containing stream to the separator, the separator adapted to separate the NO_x species from the non- NO_x species; and
- e) an HNO_3 generator connected to the separator by a third conduit, the third conduit adapted route the NO_x species to the HNO_3 generator, the HNO_3 generator adapted to generate aqueous HNO_3 from the HNO_3 and water.

25. System in accordance with claim 24 further characterized by said source being a nitride process tool.

26. A system adapted to produce aqueous HCl and gaseous NH_3 , characterized by:

- a) a source of a gas composition comprising SiCl_4 , H_2 , N_2 and HCl;
- b) a wet scrubber connected to the source by a first conduit, the first conduit adapted to direct the gas composition to the wet scrubber in the presence of water to produce a wet HCl gas stream and a stream rich in N_2 and H_2 ;



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c) a chemical generator connected to the wet scrubber by a second conduit, the second conduit adapted to direct the wet HCl gas stream to the chemical generator wherein water is admixed with the wet HCl to produce aqueous HCl; and

d) an ammonia synthesizer connected to the wet scrubber by a third conduit, the third conduit routing the stream rich in N_2 and H_2 to the ammonia NH_3 synthesizer.

27. System in accordance with claim 26 further including an aqueous NH_4OH generator into which the NH_3 is directed

29. System in accordance with claim 26 further including a NH_4F generator into which the NH_4OH is directed.



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ON-SITE WASTE RECOVERY FOR SOLID STATE MANUFACTURING PROCESS**Abstract of the Disclosure**

Processes and systems are presented providing for a waste recovery of gases and liquids useful in a variety of processes. For example, a waste stream from a CVD chamber is wet scrubbed with calcium hydroxide to produce calcium fluoride, the calcium fluoride reacted with sulfuric acid to produce hydrogen fluoride (HF) gas which may then be routed either on-site or off-site to a liquid chemical generator wherein the gaseous HF is mixed with ultra-high purity water to form ultra-high purity aqueous hydrogen fluoride. The insoluble gases from the wet scrubber may be routed to a recovery unit where other useful gases may be separated from carrier gases.

(Figure 2)

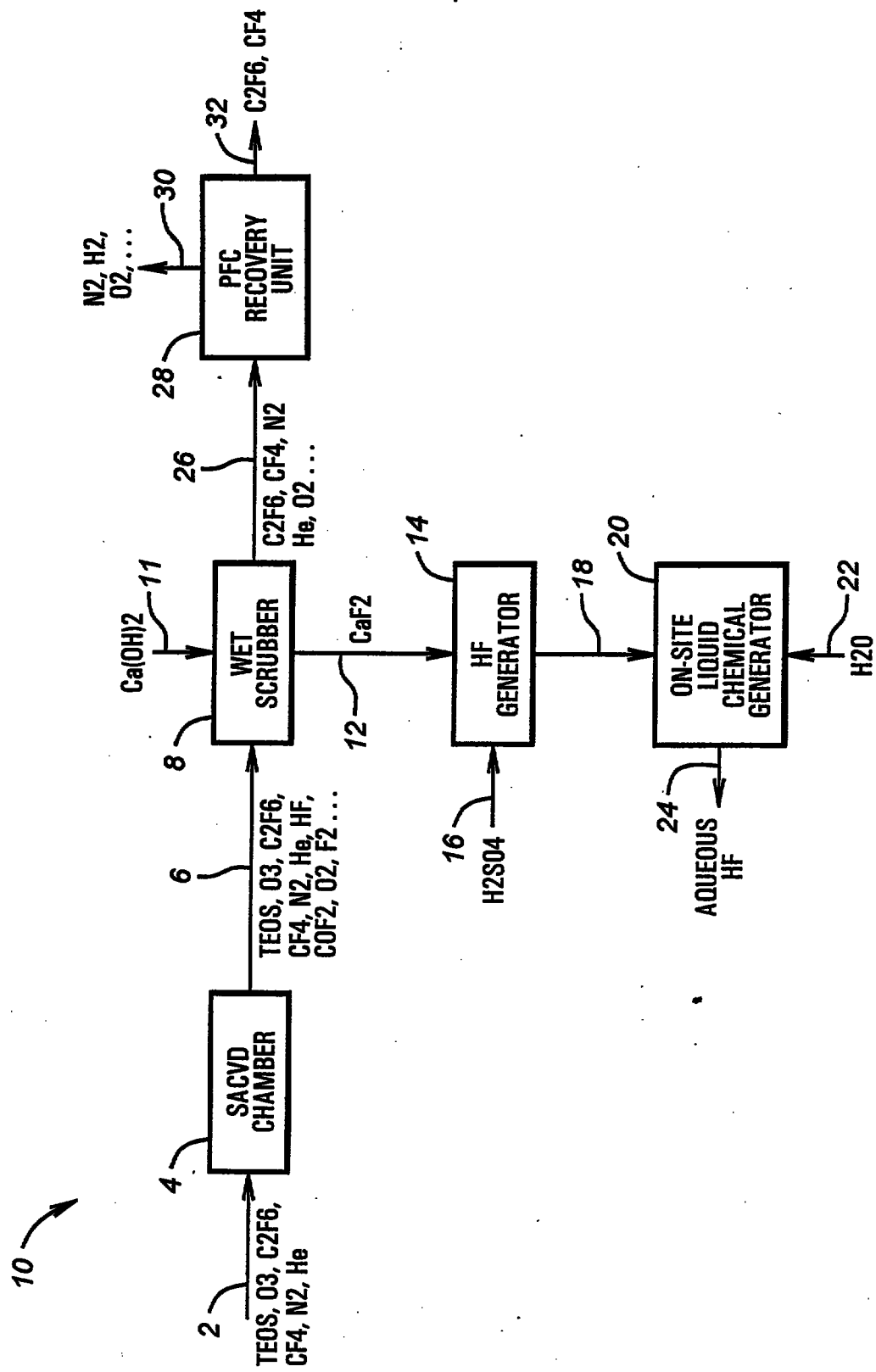


FIG. 1

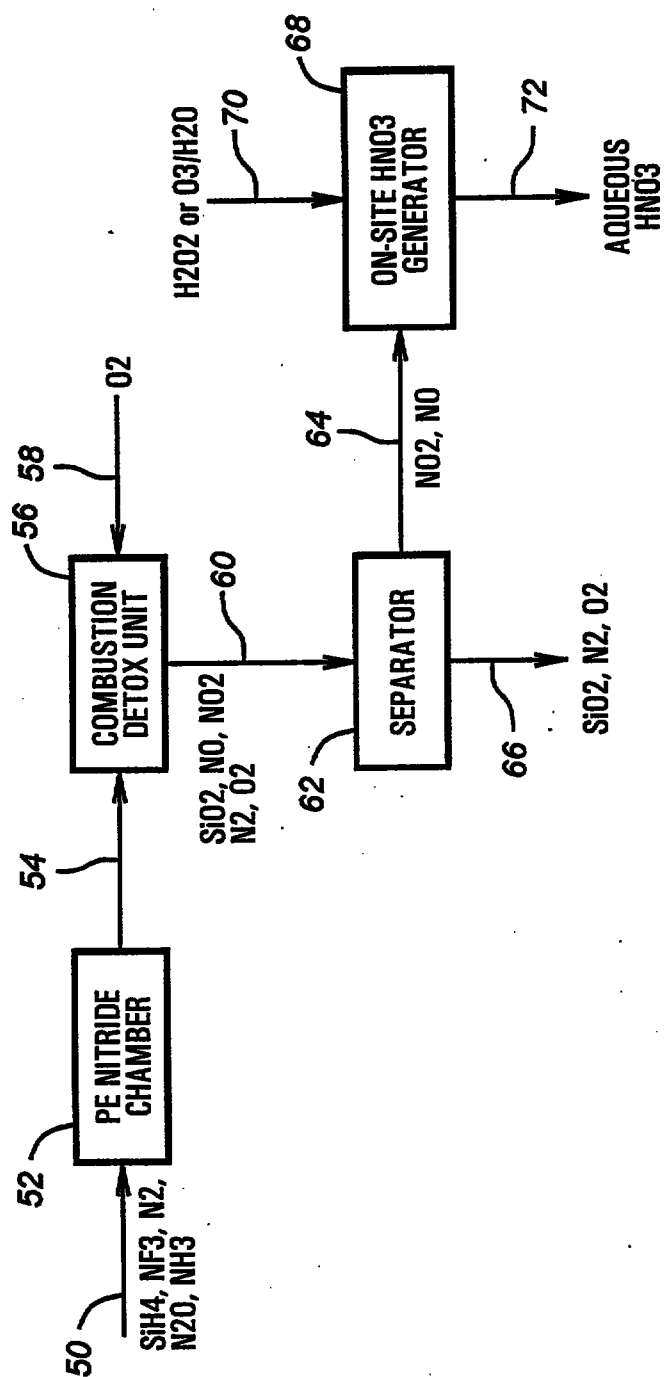


FIG. 2

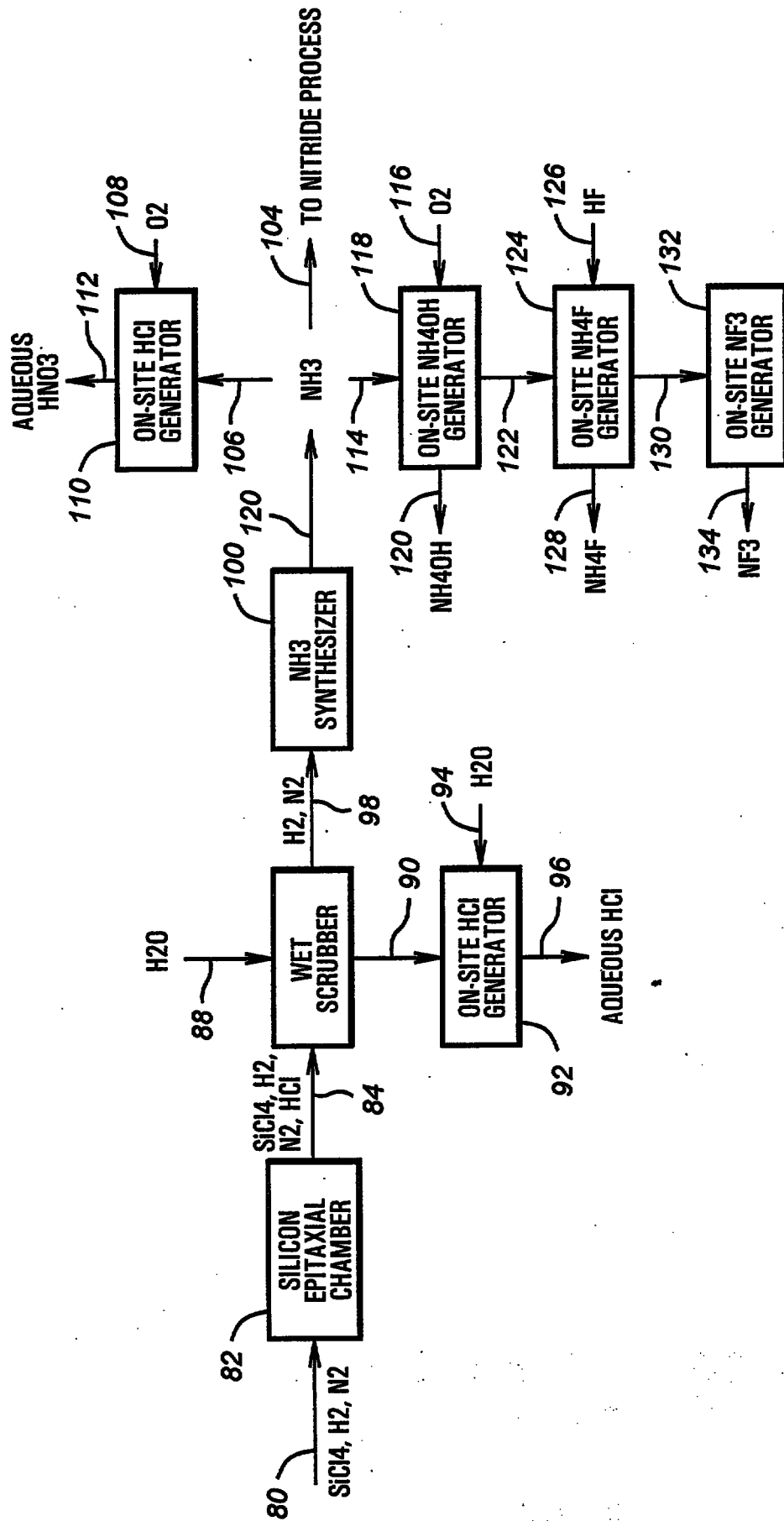


FIG. 3



to contact the stream comprising the inorganic salt with sulfuric acid to produce a stream comprising HX gas.

22. System in accordance with claim 21 further characterized by the source of the waste stream is a SACVD tool, and the halogenated gases are selected from the group consisting COF_2 , HF, and the like.

23. System in accordance with claim 21 further including a wet chemical generator into which the said stream comprising HX gas is directed.

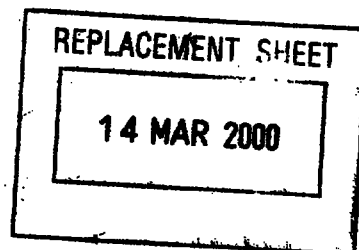
24. A system adapted to produce aqueous HNO_3 , the system characterized by:

- a) a source of a gas stream comprising at least one gas which, when combusted with oxygen, produces NO_x species and non- NO_x species;
- b) a combustion unit connected to the source via a conduit, the conduit adapted to route the gas stream to the combustion unit, the combustion unit adapted to combust the at least one gas to form the NO_x species with an oxidant gas comprising oxygen;
- c) a separator connected to the combustion unit by a second conduit, the second conduit adapted to route the NO_x containing stream to the separator, the separator adapted to separate the NO_x species from the non- NO_x species; and
- e) an HNO_3 generator connected to the separator by a third conduit, the third conduit adapted route the NO_x species to the HNO_3 generator, the HNO_3 generator adapted to generate aqueous HNO_3 from the HNO_3 and water.

25. System in accordance with claim 24 further characterized by said source being a nitride process tool.

26. A system adapted to produce aqueous HCl and gaseous NH_3 , characterized by:

- a) a source of a gas composition comprising SiCl_4 , H_2 , N_2 and HCl;
- b) a wet scrubber connected to the source by a first conduit, the first conduit adapted to direct the gas composition to the wet scrubber in the presence of water to produce a wet HCl gas stream and a stream rich in N_2 and H_2 ;



c) a chemical generator connected to the wet scrubber by a second conduit, the second conduit adapted to direct the wet HCl gas stream to the chemical generator wherein water is admixed with the wet HCl to produce aqueous HCl; and

d) an ammonia synthesizer connected to the wet scrubber by a third conduit, the third conduit routing the stream rich in N_2 and H_2 to the ammonia NH_3 synthesizer.

27. System in accordance with claim 26 further including an aqueous NH_4OH generator into which the NH_3 is directed

28. System in accordance with claim 26 further including a NH_4F generator into which the NH_4OH is directed.



REPLACEMENT SHEET

14 MAR 2000