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(54) **ABATEMENT OF FLUORINE GAS FROM EFFLUENT**

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(57) **ABSTRACT**

An effluent abatement system **200** that may be used to abate $F_2$ gas content of effluent exhausted from a process chamber **35,** such as effluent from a CVD chamber cleaning process, includes a catalytic reactor **250** to reduce the content of $F_2$ in the effluent **100.** The system may further include a prescrubber **230** to add reactive gases to the effluent **100** and/or to treat the effluent **100** prior to treatment in the catalytic reactor **250.** Alternatively reactive gases can be added to the effluent **100** by a gas source **220.**

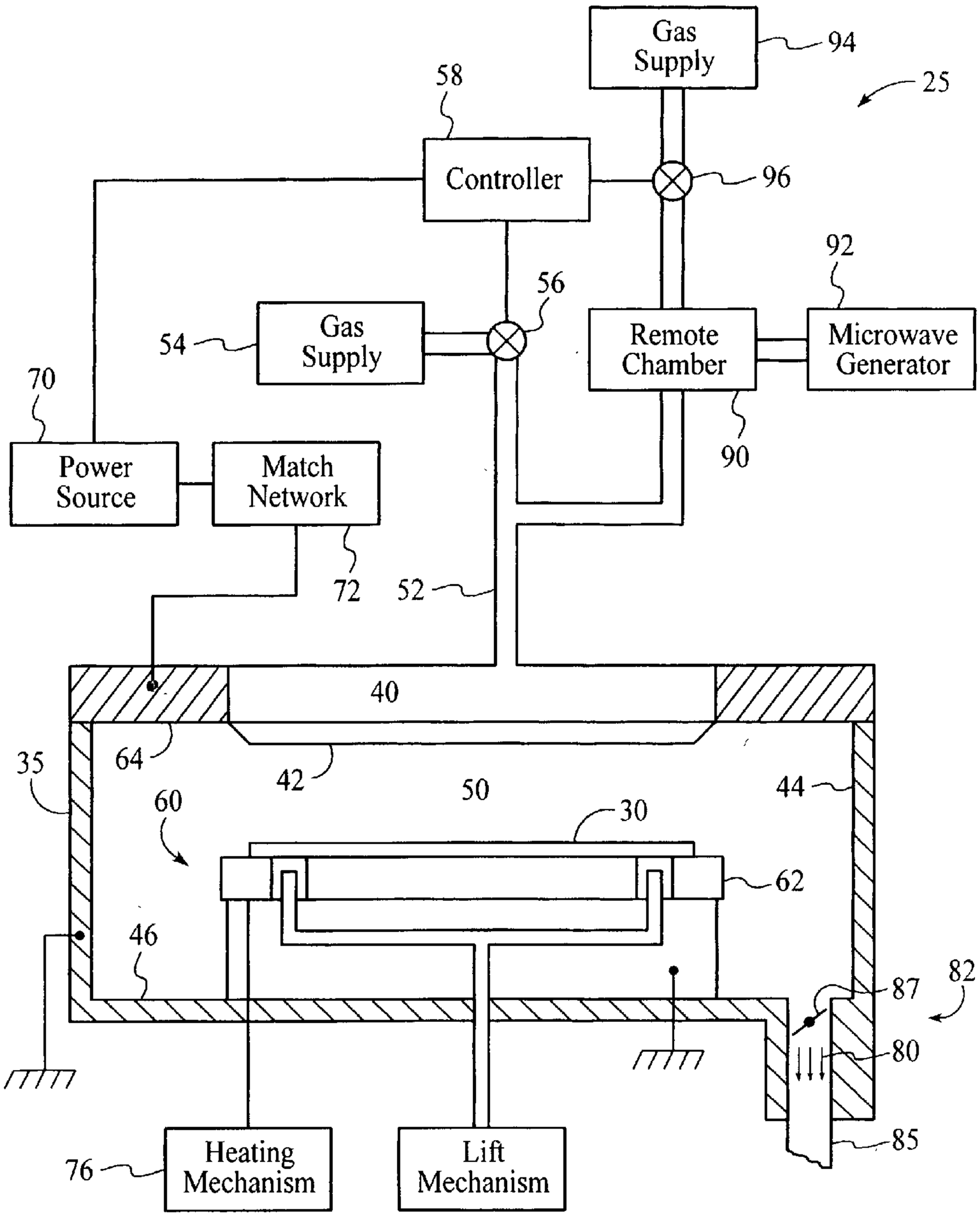

Gas Supply
94
25
58
Controller
96
92
56
54
Gas Supply
Remote Chamber
Microwave Generator
70
90
Power Source
Match Network
72
52
40
64
35
42
50
44
60
30
62
46
87
82
80
85
76
Heating Mechanism
Lift Mechanism

FIG. 1

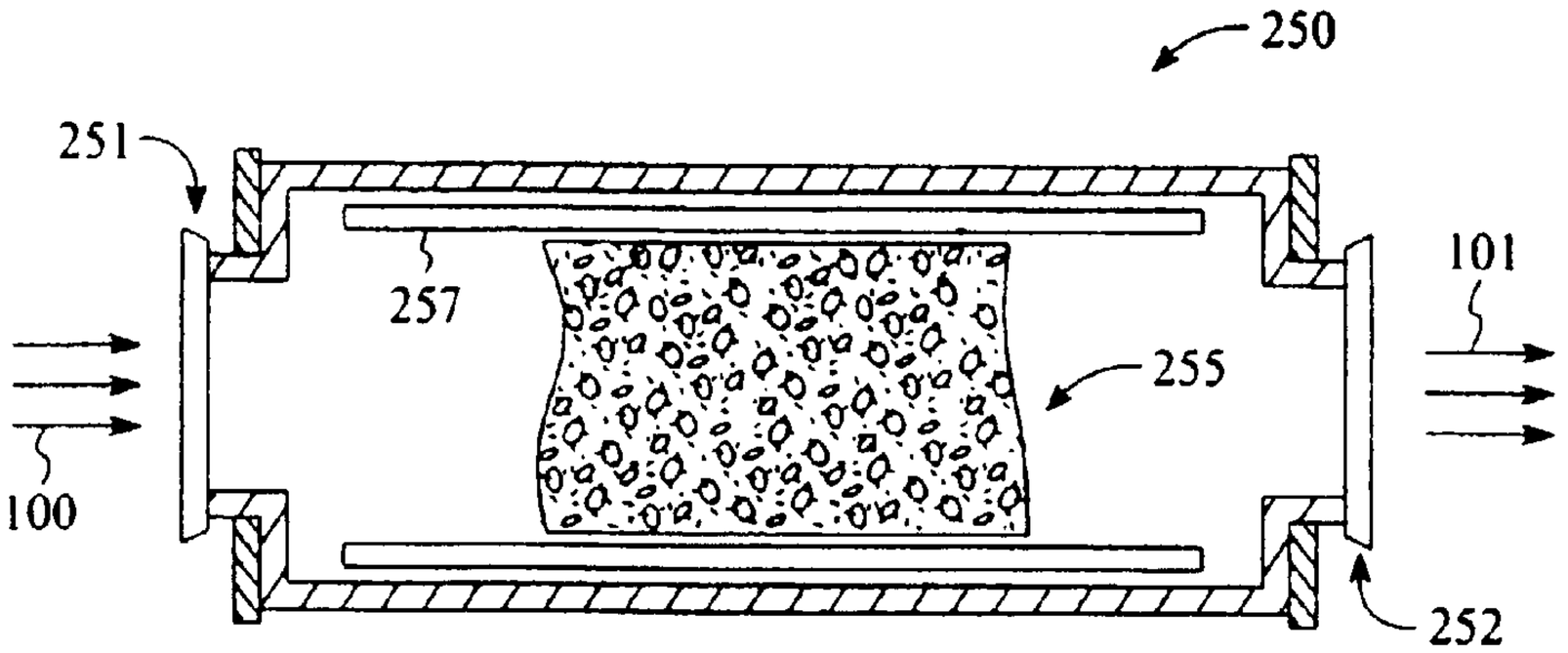

250
251
257
255
101
100
252

FIG. 2

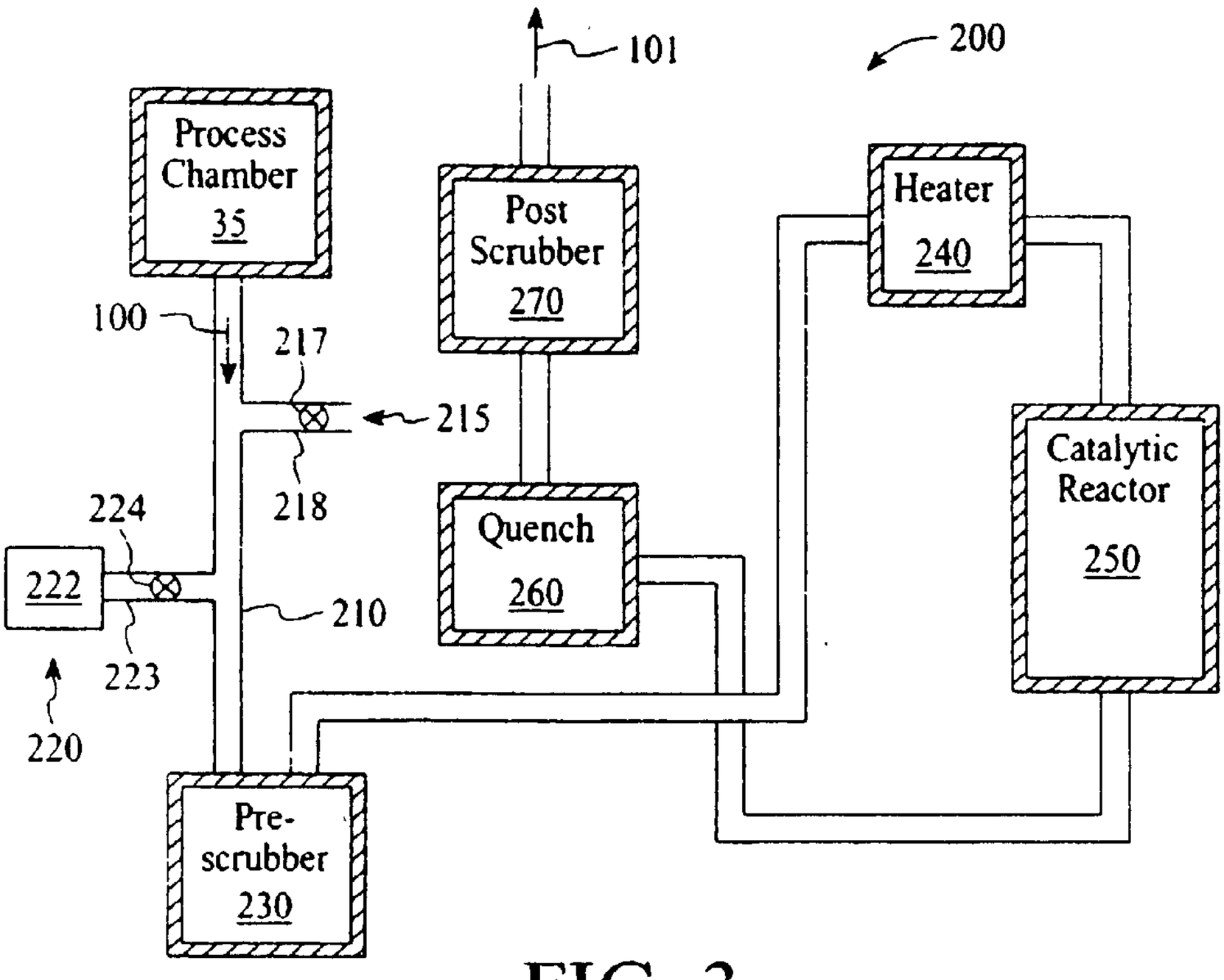

101
200
Process Chamber 35
Post Scrubber 270
Heater 240
100
217
215
218
224
222
210
223
220
Quench 260
Catalytic Reactor 250
Pre-scrubber 230

FIG. 3

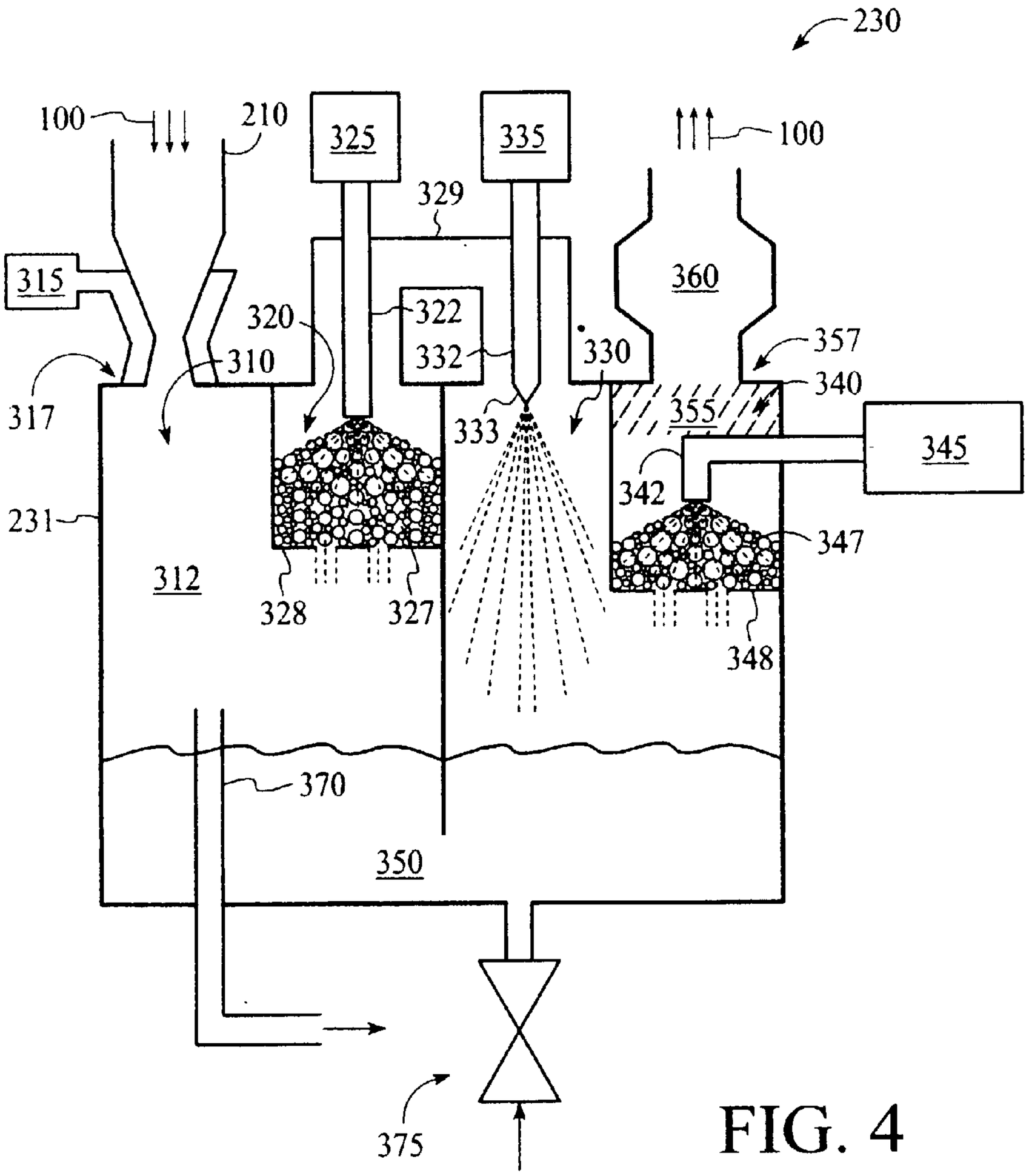

230
100
210
325
335
329
100
315
360
320
322
332
310
330
357
340
317
333
355
345
342
231
347
312
328
327
348
370
350
375

FIG. 4

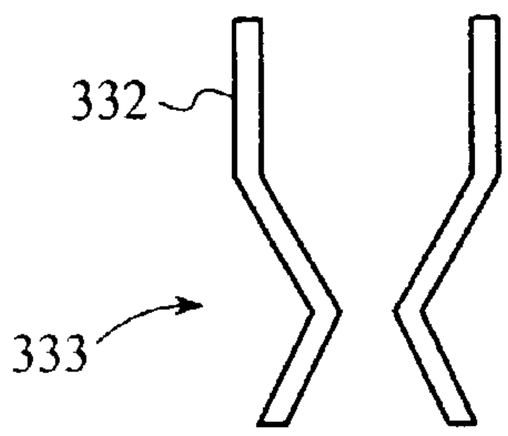

332
333

FIG. 5

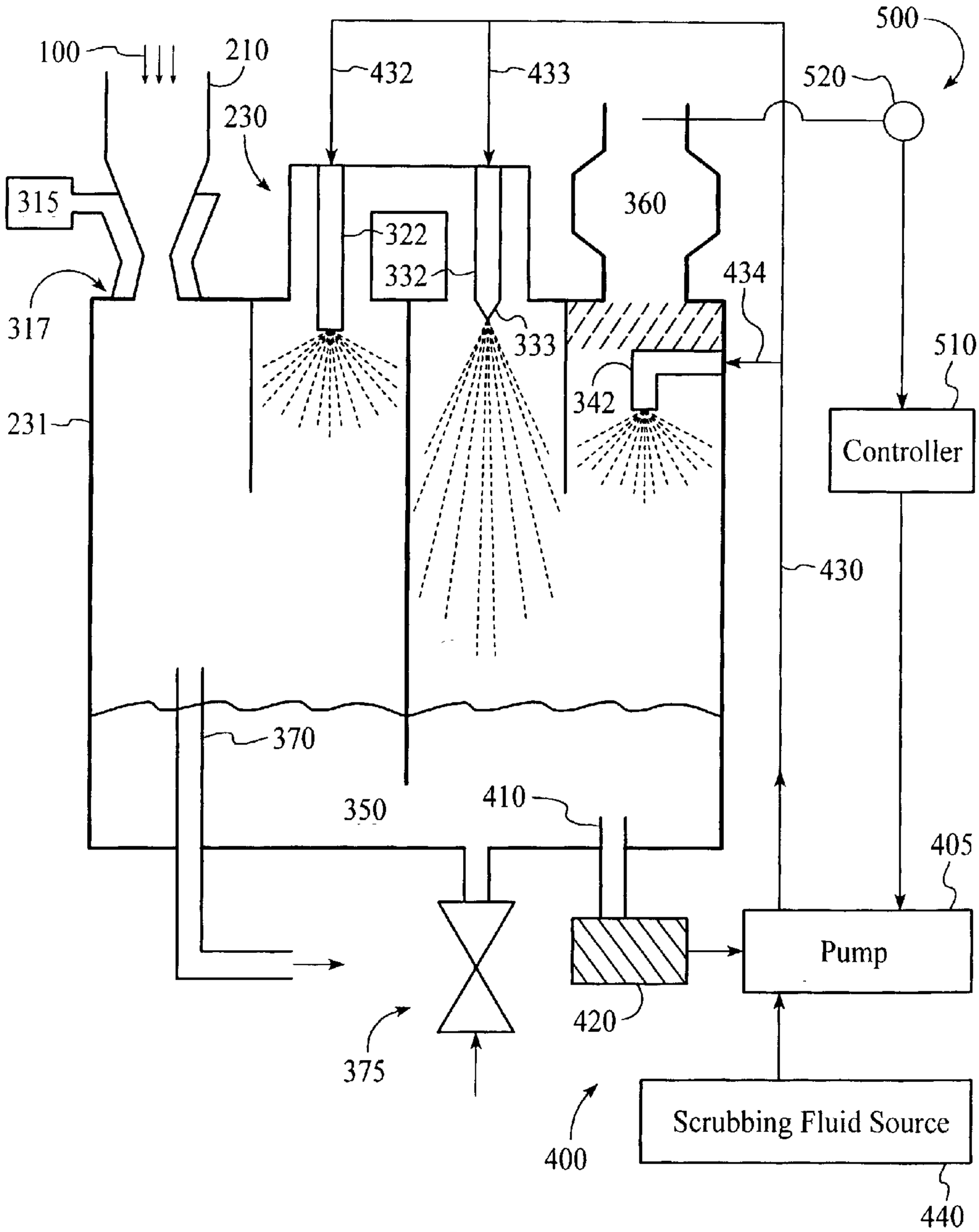

100
210
230
315
317
231
432
433
322
332
333
342
360
434
500
520
510
Controller
430
370
350
410
405
Pump
420
375
400
Scrubbing Fluid Source
440

FIG. 6

# ABATEMENT OF FLUORINE GAS FROM EFFLUENT

## CROSS-REFERENCE

[0001] This application is a divisional of U.S. patent application Ser. No. 09/607,918, filed on Jun. 29, 2000, entitled "ABATEMENT OF FLUORINE GAS FROM EFFLUENT" to Shamouilian et al., which is incorporated herein by reference in its entirety.

## BACKGROUND

[0002] The present invention is related to an apparatus and method for reducing a hazardous gas content of an effluent from a process chamber.

[0003] Fluorocarbon, chlorofluorocarbons, hydrocarbon, and other fluorine containing gases are used in, or formed as a byproduct during, the manufacture of active and passive electronic circuitry in process chambers. These gases are toxic to humans and hazardous to the environment. In addition, they may also strongly absorb infrared radiation and have high global warming potentials. Especially notorious are persistent fluorinated compounds or perfluorocompounds (PFCs) which are long-lived, chemically stable compounds that have lifetimes often exceeding thousands of years. Some examples of PFCs are carbon tetrafluoride ($CF_4$), hexafluoroethane ($C_2F_6$), perfluorocyclobutane ($C_4F_8$), difluoromethane ($CH_2F_2$), perfluorocyclobutene ($C_4F_6$), perafluoropropane ($C_3F_8$), trifluoromethane ($CHF_3$), sulfur hexafluoride ($SF_6$), nitrogen trifluoride ($NF_3$), carbonyl fluoride ($COF_2$) and the like. For example, $CF_4$ has a lifetime in the environment of about 50,000 years and can contribute to global warming for up to 6.5 million years.

[0004] Another hazardous gas is molecular fluorine, $F_2$. Extended exposure to as little as 1 ppm of $F_2$ can be hazardous, and $F_2$ is difficult to breakdown or reduce to non-toxic forms. Previously, effluents containing $F_2$ have been exhausted through exhaust stacks that are sufficiently tall that the concentration of $F_2$ in the air that descends to the ground is below regulatory levels. However, this technique is less than ideal from an environmental standpoint, and also undesirable from a manufacturing standpoint in that the volume of fluorinated gas processes that generate $F_2$ is limited by the height of the exhaust stack. Thus, it is desirable to have an apparatus or method that can reduce the hazardous gas content of effluents, especially effluents containing $F_2$, that may be released from process chambers.

[0005] One conventional $F_2$ abatement system uses a hydrogen burn box to reduce $F_2$. However, this system has several disadvantages. For example, a high temperature (generally above 850° C.) is necessary for the conversion of $F_2$ to HF in the presence of $H_2$. The heated HF is highly corrosive and hazardous, making its handling costly and dangerous. Additionally, the use of $H_2$ supply lines in a fabrication plant raises fire concerns that further add to the costs and danger of the system.

[0006] $F_2$ containing effluents are generated in numerous substrate fabrication processes, as well as in other processes. For example, process gases containing $F_2$, or that form $F_2$ as a byproduct of the process, are used in the etching of layers on substrates, such as oxide, metal and dielectric layers; during chemical vapor deposition processes; and to clean etchant or deposition residue in process chambers. These hazardous compounds may be exhausted from the chamber in the effluent gas stream.

[0007] It is desirable to minimize the introduction of such harmful gases and byproducts into the environment. There is also a need to minimize the harmful content of the effluent gas released into the atmosphere in an efficient and inexpensive manner. There is a further need to reduce $F_2$ emissions to the lowest possible levels especially for industries which widely use $F_2$ or $F_2$ producing gases, even though such use is a relatively small component of the overall consumption or release of $F_2$ in the world.

## SUMMARY

[0008] The present invention is useful for reducing a content of hazardous gases, such as $F_2$, in an effluent gas that results from processing of substrates. By hazardous gas it is meant any toxic, harmful or undesirable gas, including but not limited to $F_2$, PFCs, chlorofluorocarbons (CFCs), hydrocarbons, other fluorine containing gases, and other undesirable gases.

[0009] A substrate processing apparatus comprises a process chamber capable of performing a process with a process gas and thereby forming an effluent gas comprising $F_2$ gas. The chamber comprises a substrate support, a gas distributor, a gas energizer, and an exhaust. A catalytic reactor is provided to treat the effluent gas to reduce the $F_2$ content thereof.

[0010] In other versions, instead of, or in addition to the catalytic reactor, the apparatus may also comprise an additive source capable of introducing an additive into the effluent gas to reduce the $F_2$ content of the effluent gas, the additive comprising a hydrogen species and an oxygen species. For example, the additive may be a gas comprising a hydroxy species or $H_2O$.

[0011] In yet another version, the substrate processing apparatus comprises a process chamber capable of performing a process with a process gas and thereby forming an effluent gas comprising $F_2$ gas. The chamber comprises a substrate support, a gas distributor, a gas energizer, and an exhaust. A heater is provided to heat the effluent gas, and a catalytic reactor is provided to treat the effluent gas to reduce the $F_2$ content thereof.

## DRAWINGS

[0012] These features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings which illustrate exemplary features of the invention. However, it is to be understood that each of the features can be used in the invention in general, not merely in the context of the particular drawings, and the invention includes any combination of these features, where:

[0013] **FIG. 1** is a schematic sectional side view of an exemplary substrate processing apparatus which produces effluent containing hazardous gases;

[0014] **FIG. 2** is a schematic sectional side view of an exemplary catalytic reactor for use with a version of an abatement system;

[0015] **FIG. 3** is a schematic of a version of an abatement system with a catalytic reactor;

[0016] **FIG. 4** is a schematic sectional side view of a version of a prescrubber usable with an abatement system;

[0017] **FIG. 5** is a schematic sectional side view of an exemplary version of a venturi tube and venturi nozzle usable with a prescrubber; and

[0018] **FIG. 6** is a schematic sectional side view of a version of a prescrubber with a scrubbing fluid recirculation system.

## DESCRIPTION

[0019] The present invention relates to a gas treatment apparatus for use with a process chamber and a method of abating a hazardous gas content of effluent from the process chamber. The description and accompanying drawings represent illustrative embodiments of the invention and are not intended to limit the invention.

[0020] An exemplary substrate processing apparatus **25** for processing a substrate **30**, as illustrated in **FIG. 1**, comprises a chamber **35** such as for example, an chemical vapor deposition (CVD) chamber, such as an SACVD chamber or an HDP CVD chamber, both of which are commercially available from Applied Materials Inc., Santa Clara, Calif., and generally described in commonly assigned U.S. Pat. Nos. 5,207,836 to Chang; 5,788,778 to Shang et al.; 5,843,239 to Shrotriya; 6,009,827 to Robles et al.; and 6,013,584 to M'Saad, all of which are incorporated herein by reference in their entireties. Such chambers can be used in a multi-chamber integrated process system as for example, described in U.S. Pat. No. 4,951,601 to Maydan, et al., which is also incorporated herein by reference in its entirety. The particular version of the chamber **35** shown herein, is suitable for processing of substrates **30**, such as semiconductor wafers, for example silicon or gallium arsenide wafers or glass or ceramic substrates. The version is provided only to illustrate the invention, and should not be used to limit the scope of the invention.

[0021] The chamber **35** may be designed, for example, to deposit a silicon-containing layer, such as polysilicon, silicon nitride, silicon oxide, or metal silicide, or for depositing a metal layer or a metal-containing layer or any other type of layer on the substrate **30**. As shown in **FIG. 1**, the CVD system includes a deposition chamber **35**. Inside the chamber **35** is a gas distributor **40** for introducing process gas into the system. In the version shown in **FIG. 1**, the gas distributor **40** is a manifold or showerhead **42**. Alternatively, gas inlets extending from the walls **44** or floor **46** of the chamber **35** may be provided. The gas distribution system **40** distributes process gas into a process zone **50** in proximity to the substrate **30**. Process gas is delivered to the chamber **35** by supply line **52** from a process gas supply **54** when a gas flow valve **56** is opened under the control of a process controller **58**, for example a computer control system.

[0022] A support **60** in the chamber **35** supports the substrate **30** thereon. A support electrode **62** may be provided within the support **60**. The electrode **62** may be capacitively coupled with an upper electrode **64** above the substrate **30** to energize the process gas in the process zone **50** to form a plasma. In the version shown in **FIG. 1**, the upper electrode **64** is the ceiling of the chamber **35**. A power supply **70** supplies power to the upper electrode **64** through a match network **72** and the support electrode **62** is grounded, or vice versa. Typically, RF power is supplied to the electrodes **62**, **64**. The support **60** may include a heating mechanism **76** which may comprise a resistive heater or a heat transfer gas that circulates heat transfer gas in proximity to the substrate **30**. The support **60** may optionally comprise a mechanical or electrostatic chuck (not shown) having a surface adapted to receive the substrate **30**. The surface may have grooves in which a heat transfer gas, such as helium, is held to control the temperature of the substrate **30**.

[0023] During processing, the chamber **35** is evacuated to a low pressure, and a substrate **30** is transferred to the process zone **50** of the chamber **35** from a load lock transfer chamber (not shown) maintained at vacuum. Process gas is introduced into the chamber **35** through the gas supply **54** and gas distributer **40**. The gas in the chamber **35** is typically maintained at a low pressure. A plasma is formed in the process zone **50** from the gas. In the chamber **35**, the plasma is capacitively generated by applying an RF voltage to the electrode **64**. Alternatively, an RF current may be applied to an inductor coil (not shown) to inductively couple energy into the chamber **35** to generate the plasma in the plasma zone **35**. The frequency of the RF current applied to the electrode **64** or to the inductor coil (not shown) is typically from about 50 KHz to about 60 MHz, and more typically about 13.56 MHz. In another version, the capacitively generated plasma can also be enhanced by electron cyclotron resonance in a magnetically enhanced reactor in which a magnetic field generator, such as a permanent magnet or electromagnetic coils, that provide a magnetic field that may increase the density and uniformity of the plasma in the process zone **50**.

[0024] Effluent **80** comprising process gas and process byproducts is exhausted from the chamber **35** through an exhaust system **82** capable of achieving a minimum pressure of about $10^{-3}$ mTorr in the chamber **35**. The exhaust system **82** comprises an exhaust tube **85** that leads to one or a plurality of pumps, such as roughing and high vacuum pumps, that evacuate the gas in the chamber **25**. A throttle valve **87** is provided in the exhaust tube **85** for controlling the pressure of the gas in the chamber **25**. Also, an optical endpoint measurement technique is often used to determine completion of the etching process by measuring a change in light emission intensity of a gas species in the chamber **35** or measuring the intensity of light reflected from a layer being processed on the substrate **30**.

[0025] During operation of the chamber **35** in a typical substrate process, a substrate **30** is placed on the support **60** in the process chamber **35**, and a process gas comprising reactive gas is introduced into the process zone **50** through the process gas distributor **40**. For example, an insulator or dielectric material such as, for example, $SiO_2$ or $Si_3N_4$, may be formed in a chemical vapor deposition (CVD) process using a process gas comprising one or more of $SiH_4$, $SiClH_2$, $CO_2$, $H_2$, $N_2O$, $Si(OC_2H_5)_4$, $NH_3$ and $N_2$. Additionally or alternatively, a metal-containing material which may comprise an elemental metal, a metal compound or a metal alloy, may be formed in the deposition chamber. For example, a tungsten-containing material may be deposited using a process gas comprising one or more of $WF_6$, $H_2$, and $SiH_4$; a molybdenum-containing material may be formed using, for example, a process gas comprising $MoCl_5$ and $H_2$ or equiva-

lents; or an aluminum-containing material may be formed using, for example, $AlCl_3$ or $Al(CH_3)_3$ mixed with Ar or $H_2$ or both. The process gas may be energized in the process chamber **35** as described above, or alternatively may be energized in a remote chamber to, for example, process the substrate **30** in an energized plasma gas or a microwave energized gas. The energized reactive gas decomposes and deposits material onto the surface of the substrate **30**. During and after processing, an effluent gas stream **100** of spent process gas and gaseous byproducts is exhausted from the process chamber **25**.

[**0026**] Although the deposition process is designed to preferentially deposit material onto the substrate **30**, material is also deposited onto the surfaces in the chamber **35**. To clean the chamber **35** an in situ dry clean process may be periodically performed to clean or etch away the deposition residue from these surfaces. In one version, this cleaning process is carried out by remotely activating or energizing a cleaning gas in a remote chamber **90**. A microwave generator **92**, as described in U.S. Pat. No. 5,788,778, activates the cleaning gas which is delivered to the remote chamber **90** from a cleaning gas supply **94** when a valve **96** is opened under the control of controller **58**. Alternatively, the cleaning gas could be energized inductively or capacitively or could be energized within the process chamber **35**. The activated cleaning gas is delivered to the chamber **35** through the gas distributer **40** to clean or etch away the deposition residue in the chamber **35**. A flow restrictor may be provided to allow a pressure differential to be provided between the process chamber **35** and the remote chamber **90**.

[**0027**] In one version, the cleaning gas may comprise $NF_3$ at a flow of from about 1 to about 2 liters/minute. It is believed that the $NF_3$ breaks down in the remote chamber **90** (or in the process chamber if activated therein) to provide fluorine radicals that etch the silicon containing residues in the chamber **35**. A significant percentage, approximately 90% or more of the fluorine, however, combines to form $F_2$ gas that is exhausted in an $F_2$ containing effluent **100**. Effluent **100** is compositionally quite different that effluent **80** which is composed primarily of spent process gas and process byproducts. $F_2$ containing effluent **100**, on the other hand, contains a significant percentage of $F_2$. For example, depending on the process conditions, the $F_2$ concentration in effluent **100** can be more than about 90%. Other processes and/or process conditions can produce effluents **100** having more than about 50% $F_2$, and others can produce effluents **100** having more than about 10% $F_2$. Alternatively, the $F_2$ may be generated when using process gas comprising other fluorine-containing gases, such as $CF_4$, $C_2F_6$, $C_3F_8$, $CHF_3$, $SF_6$, $COF_2$, $CH_3F$, $C_4F_8$, $CH_2F_2$, $C_4F_6$ and the like. Furthermore, the $F_2$ effluent may be generated in a process chamber **35** capable of performing other substrate fabrication processes, such as etching or post etch treatment processes. The effluent may be formed either before, during, or after processing of a substrate. In one version, the effluent is formed after the processing of a substrate or a set of substrates during a chamber cleaning process.

[**0028**] It is desirable to reduce the amounts of $F_2$ present in the effluent **100** before the effluent **100** is exhausted. It has been discovered that passing the effluent **100** over a catalyst reduces the $F_2$-content of the effluent **100**. The catalytic abatement may be conducted in the presence of an additive. In one version, the additive comprises hydrogen species and oxygen species, such as, for example, $H_2O$, $H_2O_2$, alcohols, hydroxyl containing gases, $H_2$ and $O_2$ and the like. In the presence of a catalyst, the water and $F_2$ convert the easily scrubbable and/or exhaustible HF and oxygen. It is believed that the one reaction is:

$$2F_2+2H_2O+\text{catalyst}\rightarrow 4HF+O_2$$

[**0029**] The $O_2$ may be exhausted, and the HF may be easily disposed of by dissolving it in water. Thus, it has been discovered that $F_2$ containing effluent **100** may be abated with an additive comprising hydrogen species and oxygen species.

[**0030**] That the addition of an additive, such as water, to effluent containing $F_2$ provides abatement of the effluent **100** is unexpected. Typically, water, or other oxygen species containing additive, contact with $F_2$ gas is specifically avoided because water reacts with the $F_2$ to form $OF_2$ which is an undesirable gas that needs to be reduced to concentrations less than 50 ppb before it can be released into the environment. However, it has been unexpectedly discovered that in the presence of the catalyst, the $OF_2$ formation is replaced by the HF and $O_2$ formation.

[**0031**] In one version, the present catalyst may be housed in a catalytic reactor **250** through which the $F_2$ containing effluent **100** with additive gas is passed, an example of which is shown in **FIG. 2**. A vacuum pump draws the effluent **100** through the catalytic reactor **250**, and optionally, flow controllers such as throttle valves may be used to regulate the flow of effluent through the catalytic reactor **250**. In addition, the effluent gas **100** may be mixed upstream with a reactant such as an additive gas or liquid, and the mixture of gases passed through the catalytic reactor **250** through the inlet **251** and out of the outlet **252** to provide abated gas **101** exiting the catalytic reactor that may be exhausted to the atmosphere or easily treated for safe exhaustion.

[**0032**] The catalytic reactor **250** may comprise a catalytic surface **257** that catalyzes a reaction for reducing the hazardous gas content in the effluent. The catalytic surface **257** may be in the form of a structure made from catalytic material or supporting a finely divided catalyst, a bed of foam or pellets, or a coating on a wall or component of the catalytic reactor **250**. For example, the catalytic surfaces **257** may comprise surfaces of a support structure comprising a honeycomb member with the catalyst embedded therein to form a high surface area member **255** over and through which the effluent **100** passes as it flows from the inlet **251** to the outlet **252**. The catalytic surfaces **257** may be on, for example, a structure comprising a ceramic material, such as cordierite, $Al_2O_3$, alumina-silica, mullite, silicon carbide, silicon nitride, zeolite, and their equivalents; or may comprise a coating of materials, such as $ZrO_2$, $Al_2O_3$, $TiO_2$ or combinations of these and other oxides. The catalytic surfaces **257** may also be impregnated with catalytic metals, such as Pt, Pd, Rh, Cu, Ni, Co, Ag, Mo, W, V, La or combinations thereof or other materials known to enhance catalytic activity.

[**0033**] In one version, the catalytic reactor **250** is part of a catalytic abatement system **200**. One version of the catalytic abatement system is shown in **FIG. 3**. A conduit **210** is sealingly engaged to the exhaust system **80** of chamber **35** so that effluent gas **100** comprising hazardous PFC gases

from process chamber **35** flows into conduit **210**. The conduit **210** delivers the effluent **100** through the catalytic abatement system **200**. The catalytic abatement system may comprise, in general, one or more of a flow regulating system **215**, an additive gas supply **220**, a prescrubber **230**, a heater **240**, a catalytic reactor **250**, a cooling system **260** and a postscrubber **270**.

[**0034**] The flow regulating system **215** comprises a valve **217** on an inlet tube **218** in communication with the conduit **210** to allow air or other non-reactive gases to be introduced into the effluent stream **100** and to allow adjustment of the pressure within the conduit **210**. Appropriate additive gases, such as $H_2O$ and $O_2$, may be introduced into the effluent **100** by any one of the flow regulating system **215**, the additive gas supply **220**, and/or the prescrubber **230**. For example, a suitable additive gas supply **220** includes a tube **223** for communicating additive gas or fluid from a gas source **222** to the conduit **210** under the control of a valve **224**. Additives that react with the hazardous gases in the effluent **100** to abate the hazardous gases are added. For example, in one version, $F_2$ is chemically broken down by adding $H_2O$ to the effluent **100** in a volumetric concentration of from about 0.2% to about 20%, preferably from about 3.5% to about 10%, and more preferably from about 4% to about 5%. Other additive gases, such as oxygen, may also be added to the effluent either as $O_2$ or by adding air or other additives that release oxygen containing species or compounds in the hazardous gas. Alternatively or additionally, a non-reactive gas such as $N_2$ can be added, for example as a purge gas to purge the system.

[**0035**] A scrubber or prescrubber **230** is provided to add the additives in conjunction with or as an alternative to the additive gas supply **220**. The prescrubber **230** may also be used to treat the effluent **100** before it is introduced into the catalytic reactor **250** to remove gaseous or particulate components of the effluent **100** that can damage the catalytic reactor **250** or make it less effective. For example, when $SiF_4$ is present in the effluent **100**, the $SiF_4$ can potentially deactivate the catalyst or form deposits on the catalyst by breaking up in the presence of moisture and depositing silicon. The $SiF_4$ vapor is often generated, for example, during etching and cleaning processes in the chamber **35**. The prescrubber **230** reacts $SiF_4$ with a scrubbing fluid, for example water, to reduce the content thereof in the effluent **100**. It is believed that water reacts with the $SiF_4$ vapor as follows:

$$2H_2O+SiF_4 \rightarrow SiO_2+4HF$$

[**0036**] The resultant $SiO_2$ and HF products are more easily removable from the effluent **100**. The HF may be dissolved in water and the $SiO_2$ may be removed by filtering. The removal of $SiF_4$ extends the life of the catalytic material in the catalytic reactor **250**. Preferably, the size and process conditions in the prescrubber **230** are selected to remove substantially all of the $SiF_4$ from the effluent. One version of a prescrubber **230** is disclosed in U.S. patent application Ser. No. 09/435,119, filed on Nov. 5, 1999 and entitled "Process Gas Effluent Scrubber," which is incorporated herein by reference in its entirety. The prescrubber **230** may also allow $H_2O$ or other such additive gases to be added to the effluent **100** in sufficient quantities to complete the hazardous gas reaction in the catalytic reactor **250**. When the system is used to abate effluent **100** that does not contain significant quantities of catalyst contaminants such as $SiF_4$, the prescrubber **230** may be removed from the system.

[**0037**] Downstream, a heating system, for example a heater **240** and/or a cross flow heat exchanger (not shown), optionally heats the effluent **100** and additives within conduit **210** to temperatures sufficient to promote the catalytic reaction and abate the hazardous gases in the catalytic reactor **250**. The effluent **100** is passed through the catalytic reactor **250** to abate the content of hazardous gases in the effluent. If the effluent **100** is heated, the abated effluent **101** may also be cooled before it is scrubbed and exhausted. In one version, the cooling system **260** comprises a fluid cooling system such as a cold water quenching system that sprays cold water to cool the abated effluent **101**. The abated effluent **101** is then introduced into a scrubber **270** having a reactor where the acidic materials in the abated effluent **101** are dissolved in a solvent, such as for example water, to form an acidic solution that is more easily exhausted or disposed. Although heating the $F_2$ containing effluent is not required to reduce the $F_2$ concentration in the catalytic reactor, it has been further discovered that heat improves the abatement efficiency and extends the life of the catalyst. Temperatures at or less than about 700° C., or in the range from about 50° C. to about 300° C., depending on the composition and concentration of the effluent **100** have been discovered to be particularly effective.

[**0038**] It should be noted that HF is produced both in the prescrubber **230** and in the catalytic reactor **250**. The presence of HF in the effluents **100,101** may pose safety concerns and handling difficulties because HF is toxic and should not come into contact with skin. Additionally, HF is highly corrosive, particularly at elevated temperatures and in the presence of moisture and oxygen. It has been discovered that nickel-based alloys, for example Inconel 600 or 625 (TM) available from Inco Corporation in Huntington, W. V. , provide excellent corrosion resistance in the catalytic abatement system **200** environment and may be reliably sealable and gas tight to prevent unwanted HF escape from the system. Additionally, this system provides sufficiently sealed system protecting against $OF_2$ if any $OF_2$ is formed between the prescrubber **230** and the catalytic reactor **250**. It is believed that if any $OF_2$ is formed before the catalysis reactor **250**, the catalytic reactor encourages the breakdown of the $OF_2$ and the subsequent formation of HF and $O_2$. It has been determined from gas analysis that the abated effluent **101** is absent dangerous levels of $OF_2$.

[**0039**] It has been discovered that it may be desirable to introduce a high percentage of water into the $F_2$ containing effluent **100**. An exemplary prescrubber for adding $H_2O$ to $F_2$ containing effluent is shown in **FIG. 4**. The prescrubber **230** includes a reactor **231** for receiving the $F_2$ (and potentially $SiF_4$) containing effluent **100** and reacting the effluent **100** with a scrubbing fluid, such as water. A hydrolyzer column or channel **310** receives effluent **100** from the conduit **210**. The effluent **100** may have been previously mixed with an additive, as discussed above. The hydrolyzer column **310** presents a hydrolytic or humid environment **312** to the effluent **100**. This initial exposure to moisture, or other scrubbing fluid, begins the breakdown of the desired component in the effluent **100**, for example $SiF_4$. The hydrolyzer column **310** allows for the removal of large scrubbed particles before these large scrubbed particles can clog or deposit in subsequent columns in the prescrubber **230**. The

combination of the initial moisture exposure, the substantially vertical nature of the column and the downward flow of effluent **100** allows for the removal of these large particles. A hydrolyzer column or channel downstream of a scrubbing fluid dispenser or other direct source of scrubbing fluid would not be effective at removing a substantial amount of, for example, $SiF_4$. A purge gas supply **315** may be provided at or near an inlet **317** to introduce a purge gas, for example air, $O_2$, or $N_2$, to purge the system and/or to prevent upstream hydrolyzation. The inlet may be of a venturi type.

[**0040**] The effluent **100** then passes through a first scrubber column or channel **320**. A nozzle **322** dispenses scrubbing fluid, for example water, from a source **325** into the stream of effluent **100**. In one version, as shown, the fluid dispensing is done by spraying water is in a direction which is countercurrent to the flow of gas. By "countercurrent" it is meant that at least a portion of the flow is in a direction substantially opposing the general direction of the flow of the gas. This arrangement allows for gravity and the flow of water to encourage transport of reactant products, for example silicon dioxide particles and HF, into a reservoir **350**. Column **320** may optionally be provided with surface area increasing material **327**, for example plastic or ceramic pellets or granules of differing sizes, such as for example PVC balls, for increasing the surface area of water/gas contact in the column and thereby encouraging $SiF_4$ destruction reactions. A platform **328** that is readily permeable to the effluent **100** and the reaction products but impermeable to the surface area increasing material **327** may be provided to contain the surface area increasing material **327** within the first column **320**.

[**0041**] The effluent **100** then flows though a conduit **329** to a venturi column or channel **330**. A venturi tube **332** dispenses fluid, for example water, from a source **335** into the column **330**. A venturi nozzle **333** is located at the end of the venturi tube **332** to inject the water into the venturi column. By "venturi" it is meant a tube with a constricted, throatlike passage that increases the velocity and lowers the pressure of a fluid conveyed through it. By "inject" it is meant that the scrubbing fluid is dispensed through a "venturi." The venturi **332**, **333** of the present invention provides a constriction with a small opening that breaks the water down into small droplets. In one version, the opening of the venturi nozzle is sized from about 0.1 inch to about 1.4 inches, more preferably from about 0.25 inches to about 1.25 inches, and most preferably from about 0.5 inches to about 1 inch for a tube **332** having a 1.5 inch diameter. In the version shown, the flow of water is in the direction of the flow of effluent **100**. The venturi column **330** serves to (i) further scrub the effluent by increasing the surface area of water/gas contact by the generation of the droplets, (ii) further transport reaction products to the reservoir **350** by the high speed bombardment of water from the venturi nozzle **333**, (iii) provide the additive $H_2O$ for destroying PFC's, as discussed above, in the catalytic reactor **250**, and (iv) generate negative pressure and thereby effectively supply positive pressure to the effluent **100** to compensate for pressure drops through the prescrubber **230**. The resulting net pressure drop through the prescrubber **230** is approximately zero. Optionally, a pressure gain can even be generated. **FIG. 5** shows an exemplary version of the venturi tube **332** and venturi nozzle which is not intended to limit the invention. For example, the relative sizes and angles of the tube and the opening of the constriction can be modified to adjust or optimize the flow for a desired purpose.

[**0042**] Referring again to **FIG. 4, a** second scrubber column or channel **340** receives the effluent from the venturi column **330**. The second scrubber column may include a second spray nozzle **342** for dispensing scrubbing fluid, for example by spraying water, from a source **345** countercurrently into the effluent **100**. The second scrubber column **340** may further have surface area increasing material **347** contained on platform **348** which may be similar to surface area increasing material **327** and platform **328** of the first scrubbing column **320**. The second scrubbing column **340** provides yet another level of scrubbing the effluent **100** and further serves to transport the reaction products to the reservoir **350**. A mist eliminator **355** may be positioned near outlet **357** to remove water droplets from the effluent **100**. While about 4% to about 5% percent moisture content in the effluent **100** is desired for catalytic treatment, droplets are not desired because they can carry scrubbing product particles that can contaminate the catalyst within the catalytic reactor **250**. The mist eliminator **355** removes the droplets, but passes the desired moisture. Mist eliminator **355** may comprise, for example, packed material or a mesh such as a wire mesh.

[**0043**] The prescrubber **230** may be designed in one version so that a sufficient amount of water and/or pressure is introduced into the effluent **100** to make the $H_2O$ content of the effluent **100** from about 4 to about 5 percent. Each column or channel **310**, **320**, **330**, **340** is designed for about 80 percent to about 90 percent destruction of $SiF_4$. Therefore, if two columns were provided and the effluent **100** passed through two columns, from about 96 percent to about 99 percent of the $SiF_4$ would be removed. Passage through three columns provides from about 99.2 percent to about 99.9 percent removal. Passage through all four columns provides from about 99.8 percent to about 99.99 percent removal. Qualitative measurements carried out by EPA Method 5 "Determination of Particulate Emissions from Stationary Sources" techniques indicates consistent $SiF_4$ removal efficiency of 99.97 percent or better. Particle measurement determinations indicate that about 80 percent of the particles in the treated effluent **100** range in size from about 1 to about 2.5 $\mu$m. Therefore, another level of particle removal may be provided by filter **360**, for example a hepa filter, which may be positioned near outlet **357**. The hepa filter **360** removes a substantial amount of the reaction product particles that have not been transported into the reservoir **350**. The hepa filter **360** is effective for filtering particles greater than about 0.3 $\mu$m and is therefore ideal for removing these reaction product particles. It should be appreciated that the prescrubber **230** may be provided with any number of columns. Furthermore, it should be appreciated that the "columns" need not necessarily be vertically oriented, but may be channels oriented horizontally, vertically or at any orientation therebetween. Furthermore, the channels need not be parallel. Adjacent channels may be angularly oriented at any angle from zero degrees (i.e., substantially parallel and with the effluent flow **100** in opposite directions, as shown in **FIG. 4**) to 180 degrees (i.e., parallel and with the effluent flow in the same direction). In one arrangement, the channels have a relative orientation of less than 90 degrees. An overflow drain **370** and a filling unit **375** maintain the reservoir **350** at a desired level.

[0044] Another version of the prescrubber **230** is shown in **FIG. 6**. In this version a recirculation system **400** recirculates the scrubbing fluid, for example water with reaction products, through the prescrubber **230**. The reservoir **350** is first filled to a desired level by filling unit **375** which is connected to a source of scrubbing fluid, for example a water source. The desired level corresponds with a height of overflow drain **370**. Pump **405** is then turned on. Pump **405** withdraws fluid from reservoir **350**. In the version shown, the fluid in the reservoir is a mixture of water and scrubber reaction products such as silicon dioxide and HF. The fluid passes through outlet **410** under the influence of negative pressure generated by the pump **405** and through particulate filter **420** which removes reaction product particles. Particulate filter **420** may comprise filter which is capable of removing particles above from about 2 microns to about 1 mm in diameter. In one version, the particulate filter **420** removes particles sized greater than about 70 microns. The filtered fluid is then pumped via line **430** to fluid nozzles **322**, **342** and to venturi tube **332** by lines **432**, **434**, **433**, respectively. The pump **405** also withdraws fresh scrubbing fluid, water in the version shown, from a scrubbing fluid source **440** (i.e., a water source) at a predetermined rate. The addition of fresh water results in an overflow of reservoir **350** into overflow drain **370** which transports the overflow to an acid drain. The addition of fresh water allows for the maintenance of a predetermined or adjustable pH of reservoir **350**. In one version, fresh water is introduced at a rate of from about 0.25 gallons per minute to about 1 gallon per minute. In one version, fresh water is introduced at about 0.5 gallons per minute, or at a rate sufficient to maintain the pH of the scrubbing fluid at a level of about 2 to about 3. Alternatively, a pH meter can be provided and a controller can adjust the amount of fresh water introduced in accordance with the measured pH.

[0045] A control system **500** including a programmable controller **510** may be provided to control the operation of the pump **405**. The controller **510**, which may be in the form of a central processing unit (CPU), operates the pump **405** in accordance with a set of programmed instructions designed to introduce a predetermined amount of water into the effluent **100**. For example, when $F_2$ containing effluent **100** is to be abated, the pumping rate necessary to provide greater than about 2% or from about 2% to about 20% or from about 4% to about 5% water concentration in the effluent **100** can be selected (as empirically determined). In another version, a gas analyzer **520** may be provided at the outlet of the prescrubber **230**. The controller **510** can be responsive to the output signal from the analyzer **520** and can adjust the operation of the pump **405** in accordance with the output signal to maintain the water concentration at a predetermined level. For example, when the percentage of moisture, or other additive gas, falls below a predetermined level, as determined by analyzer **520**, the controller **510** can automatically adjust the operating speed or the fresh water intake of the pump **405**. Alternatively, a gas analyzer (not shown) can be located downstream of the catalytic reactor **250**, and the controller **510** can be responsive to an $F_2$ concentration signal from the gas analyzer. For example, the amount of water introduced into the effluent **100** can be increased when the $F_2$ concentration exceeds a predetermined level.

[0046] The controller **510** comprises a computer readable medium having computer readable program code embodied therein that monitors the output signal(s) from the gas analyzer **520**. The controller **510** may be incorporated into a system controller, such as the system controller described in U.S. patent application Ser. No. 09/363,302, filed on Jul. 28, 1999, and entitled "Treatment of Process Gas Effluent," which is incorporated herein by reference in its entirety. The controller **510** may comprise a computer program code product that controls a computer comprising one or more central processor units (CPUs) interconnected to a memory system with peripheral control components, such as for example, a PENTIUM microprocessor, commercially available from Intel Corporation, Santa Clara, Calif. The CPUs of the controller **510** can also comprise ASIC (application specific integrated circuits) that operate a particular component of the system. An interface between an operator and the controller **510** may be a CRT monitor and a light with a light sensor in the tip of the pen. To select a particular screen or function, the operator touches a designated area of the CRT monitor and pushes a button on the pen. The area touched changes its color or a new menu or screen is displayed to confirm the communication between the light pen and the CRT monitor. Other devices, such as a keyboard, mouse or pointing communication device can also be used to communicate with the controller **510**. An operator may be able thereby to input ranges of pH values or flow rates of the scrubbing fluid.

[0047] The computer program code operating the CPU(s) and other devices of the computer can be written in any conventional computer readable programming language, such as for example, assembly language, C, $C^{++}$, or Pascal. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-usable medium, such as a memory system of the computer. If the entered code text is in a high level language, the code is compiled to a compiler code which is linked with an object code of precompiled windows library routines. To execute the linked and compiled object code, the system user invokes the object code, causing the computer to load the code in memory to perform the tasks identified in the computer program. The software may include code to evaluate the pH of the scrubbing fluid and to accordingly adjust the amount of fresh water added to the scrubbing fluid, for example.

[0048] The $F_2$ catalytic abatement system **200** may be a self-contained and integrated unit that is compatible with various process chambers **25**. The catalytic abatement system **200** can be used to destroy a large variety of hazardous gases, including substantially all types of PFCs. The catalytic abatement system **200** has no impact on process chamber **25** operation and may be used with any process chamber that exhausts hazardous gases. The catalytic abatement system is convenient to handle and occupies less than 40 cubic feet.

[0049] Although the present invention has been described in considerable detail with regard to certain preferred versions thereof, other versions are possible. For example, the described system could be used to abate other undesirable gases from the effluent. Therefore, the appended claims should not be limited to the description of the preferred versions contained herein.

What is claimed is:

**1**. A substrate processing apparatus comprising:

(a) a process chamber capable of performing a process with a process gas and thereby forming an effluent gas comprising $F_2$ gas, the chamber comprising:

(i) a substrate support;

(ii) a gas distributor;

(iii) a gas energizer; and

(iv) an exhaust; and

(b) a catalytic reactor to treat the effluent gas to reduce the $F_2$ content thereof.

**2**. An apparatus according to claim 1 comprising a source of additive capable of introducing an additive comprising a hydrogen species and an oxygen species, into the effluent gas.

**3**. An apparatus according to claim 2 wherein the additive comprises $H_2O$.

**4**. An apparatus according to claim 2 wherein the source of additive is downstream of the catalytic reactor.

**5**. An apparatus according to claim 2 further comprising a controller to control the addition of the additive into the effluent gas.

**6**. An apparatus according to claim 1 further comprising a scrubber capable of scrubbing the effluent gas before treatment in the catalytic reactor.

**7**. An apparatus according to claim 1 wherein the process chamber is a chemical vapor deposition chamber.

**8**. An apparatus according to claim 1 wherein the catalytic reactor comprises a catalyst comprising a ceramic impregnated with a metal.

**9**. An apparatus according to claim 8 wherein the ceramic comprises one or more of $Al_2O_3$, $ZrO_2$, and $TiO_2$.

**10**. An apparatus according to claim 8 wherein the metal comprises one or more of Pt, Pd, Rh, Cu, Ni, Co, Ag, Mo, W, V, and La.

**11**. An apparatus according to claim 1 wherein the apparatus comprises a process gas source that is a source of a gas capable of cleaning the chamber.

**12**. A substrate processing apparatus comprising:

(a) a process chamber capable of performing a process with process gas and thereby forming an effluent gas comprising $F_2$ gas, the chamber comprising:

(i) a substrate support;

(ii) a gas distributor;

(iii) a gas energizer; and

(iv) an exhaust;

(b) an additive source capable of introducing an additive into the effluent gas to reduce the $F_2$ content of the effluent gas, the additive comprising a hydrogen species and an oxygen species; and

(c) a catalytic reactor to treat the effluent gas to reduce the $F_2$ content thereof.

**13**. An apparatus according to claim 12 wherein the hydrogen and oxygen species comprises a hydroxy species.

**14**. An apparatus according to claim 12 wherein the additive comprises $H_2O$.

**15**. An apparatus according to claim 12 comprising a controller adapted to control the addition of the additive into the effluent gas to maintain a volume percent of additive in the effluent gas of at least about 2%.

**16**. An apparatus according to claim 12 wherein the process chamber is a chemical vapor deposition chamber.

**17**. An apparatus according to claim 12 comprising a scrubber to scrub the effluent gas before passing the effluent gas into the catalytic reactor.

**18**. An apparatus according to claim 17 wherein the source of additive introduces the additive into the effluent gas while the effluent gas is in the scrubber.

**19**. An apparatus according to claim 12 wherein the source of additive introduces the additive into the effluent gas after the effluent gas is passed through the catalytic reactor.

**20**. An apparatus according to claim 12 comprising wherein the source of additive comprises a source of an acid dissolving additive.

**21**. An apparatus according to claim 12 wherein the catalytic reactor comprises a catalyst comprising a ceramic impregnated with a metal.

**22**. A substrate processing apparatus comprising:

(a) a process chamber capable of performing a process with the process gas and thereby forming an effluent gas comprising $F_2$ gas, the chamber comprising:

(i) a substrate support;

(ii) a gas distributor;

(iii) a gas energizer; and

(iv) an exhaust; and

(b) a source of additive capable of introducing additive into the effluent gas, the additive comprising $H_2O$; and

(c) a catalytic reactor to treat the resulting effluent gas to reduce the $F_2$ content thereof.

**23**. An apparatus according to claim 22 wherein the process chamber comprises a chemical vapor deposition chamber.

**24**. An apparatus according to claim 22 wherein the catalytic reactor comprises a catalyst comprising a ceramic impregnated with a metal.

**25**. A substrate processing apparatus comprising:

(a) a process chamber capable of performing a process with the process gas and thereby forming an effluent gas comprising $F_2$ gas, the chamber comprises a substrate support, a gas distributor, a gas energizer and an exhaust;

(b) a heater to heating the effluent gas; and

(c) a catalytic reactor to treat the resulting effluent gas to reduce the $F_2$ content thereof.

**26**. An apparatus according to claim 25 comprising a source of additive capable of introducing additive into the effluent gas, the additive comprising a hydrogen species and an oxygen species.

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