US 20080102011A1

(19) **United States**

(12) **Patent Application Publication**

MOALEM et al.

(10) **Pub. No.: US 2008/0102011 A1**

(43) **Pub. Date: May 1, 2008**

(54) **TREATMENT OF EFFLUENT CONTAINING CHLORINE-CONTAINING GAS**

(75) Inventors: **Mehran MOALEM**, Cupertino, CA (US); **Morteza Frania**, Campbell, CA (US)

Correspondence Address:
JANAH & ASSOCIATES, P.C.
650 DELANCEY STREET, SUITE 106
SAN FRANCISCO, CA 94107

(73) Assignee: **Applied Materials, Inc.**

(21) Appl. No.: **11/553,894**

(22) Filed: **Oct. 27, 2006**

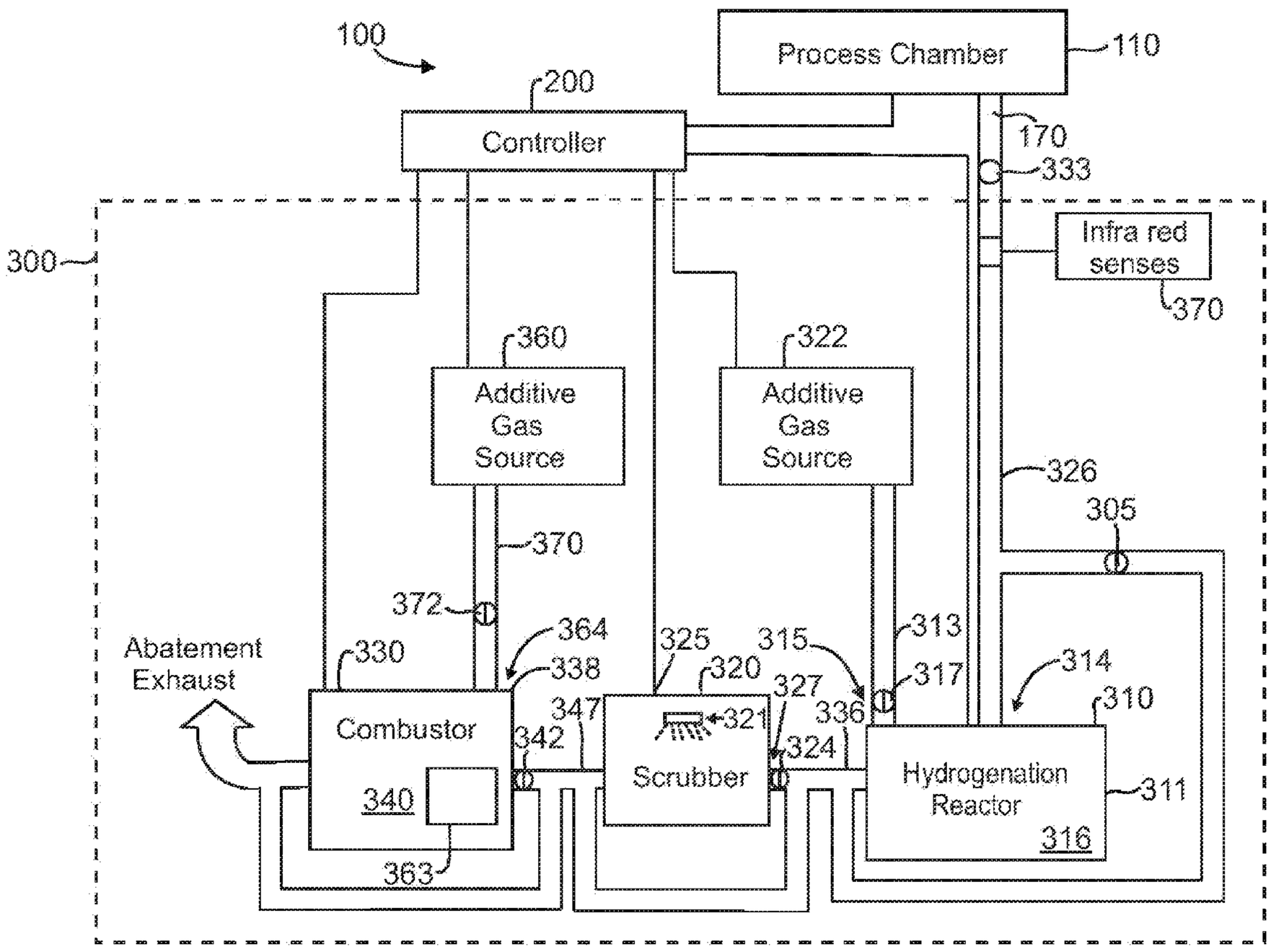
Publication Classification

(51) **Int. Cl.**
B01D 53/00 (2006.01)
B01J 8/00 (2006.01)

(52) **U.S. Cl.** ..... **423/240 R**; 423/245.3; 422/169; 422/173; 422/186

(57) **ABSTRACT**

A substrate processing apparatus comprises a process chamber and an effluent treatment apparatus comprising a hydrogenation reactor, scrubber, combustor, and a controller to operate the process chamber and effluent treatment apparatus. In the hydrogenation reactor, hydrogen-containing gas is used to treat chamber effluent to form a hydrogenated effluent comprising hydrogen chloride gas. A scrubber sprays water through the hydrogenated effluent to dissolve the hydrogen chloride gas. An oxygen-containing gas is added to the treated effluent during a combustion step to further abate the effluent.



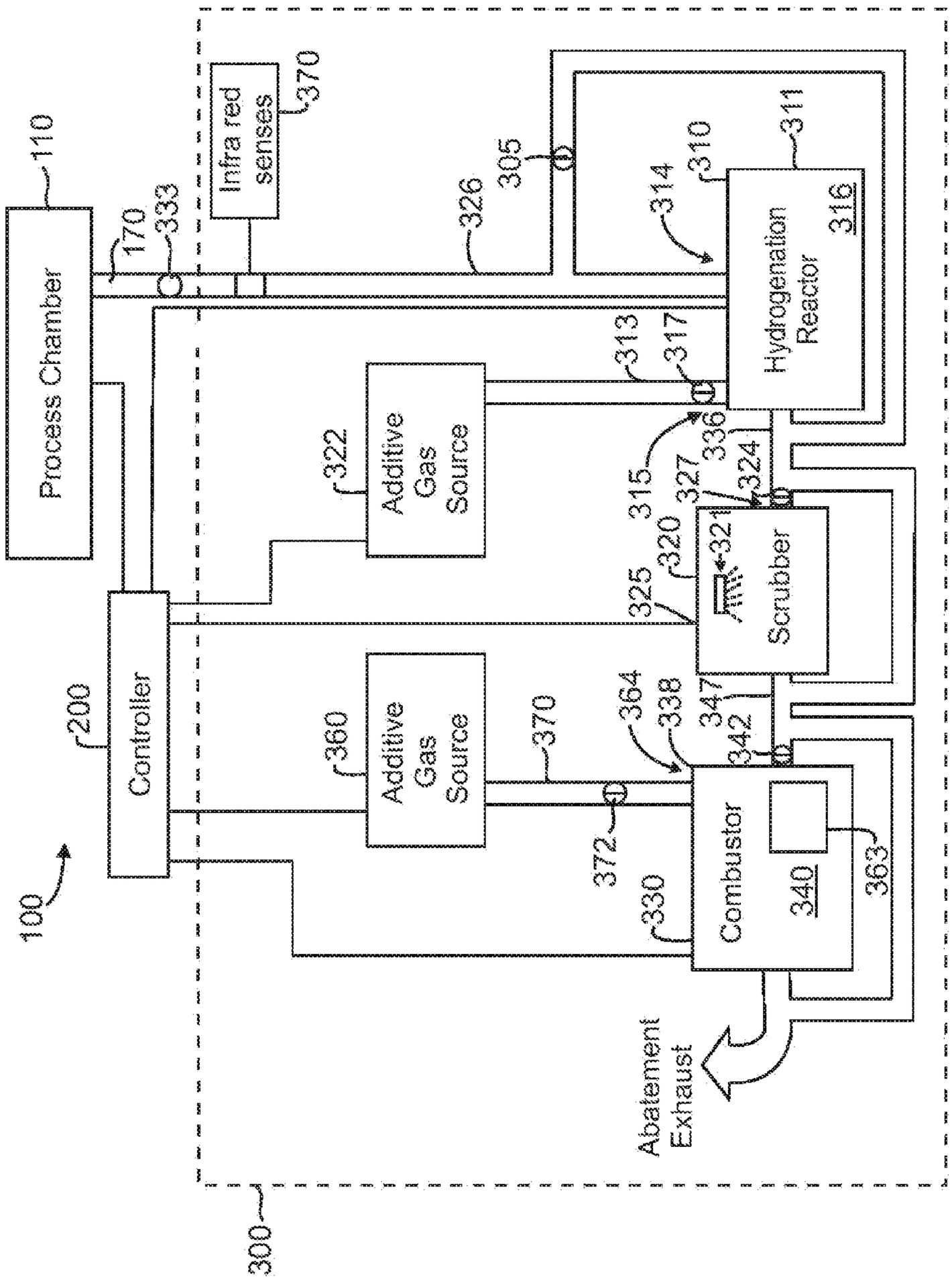

110
Process Chamber
170
333
Infra red senses
370
326
305
314
310
311
316
Hydrogenation Reactor
313
317
322
Additive Gas Source
315
336
327
324
320
325
Scrubber
200
Controller
360
Additive Gas Source
370
364
338
347
342
372
330
Combustor
340
363
100
Abatement Exhaust
300

FIG. 1

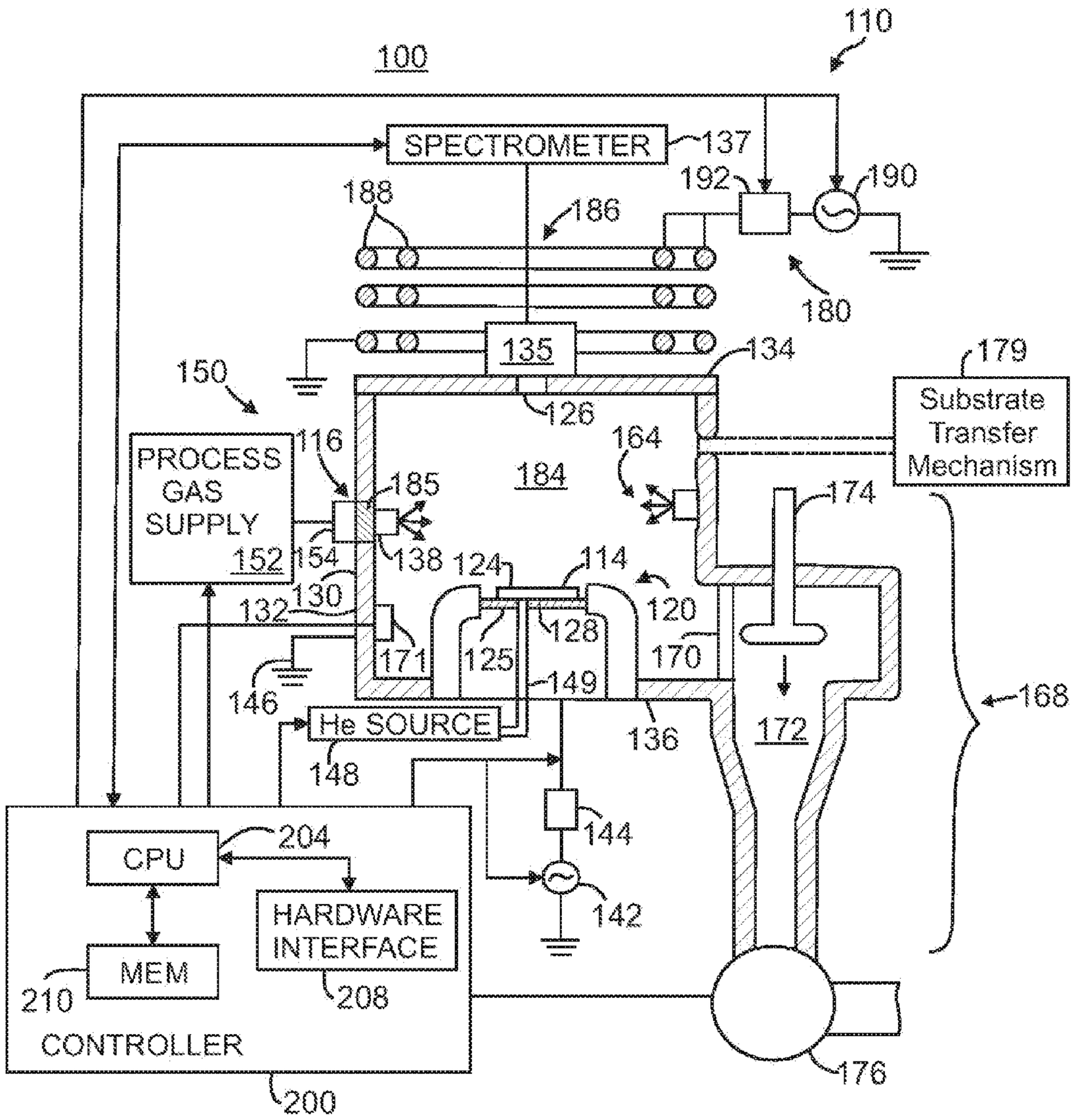

100
110
SPECTROMETER
137
192
190
188
186
180
135
134
179
150
126
Substrate Transfer Mechanism
116
PROCESS GAS SUPPLY
152
164
184
185
154
138
174
124
114
120
130
132
128
171
125
170
146
149
168
He SOURCE
148
136
172
144
142
204
CPU
HARDWARE INTERFACE
MEM
210
208
CONTROLLER
200
176

FIG. 2

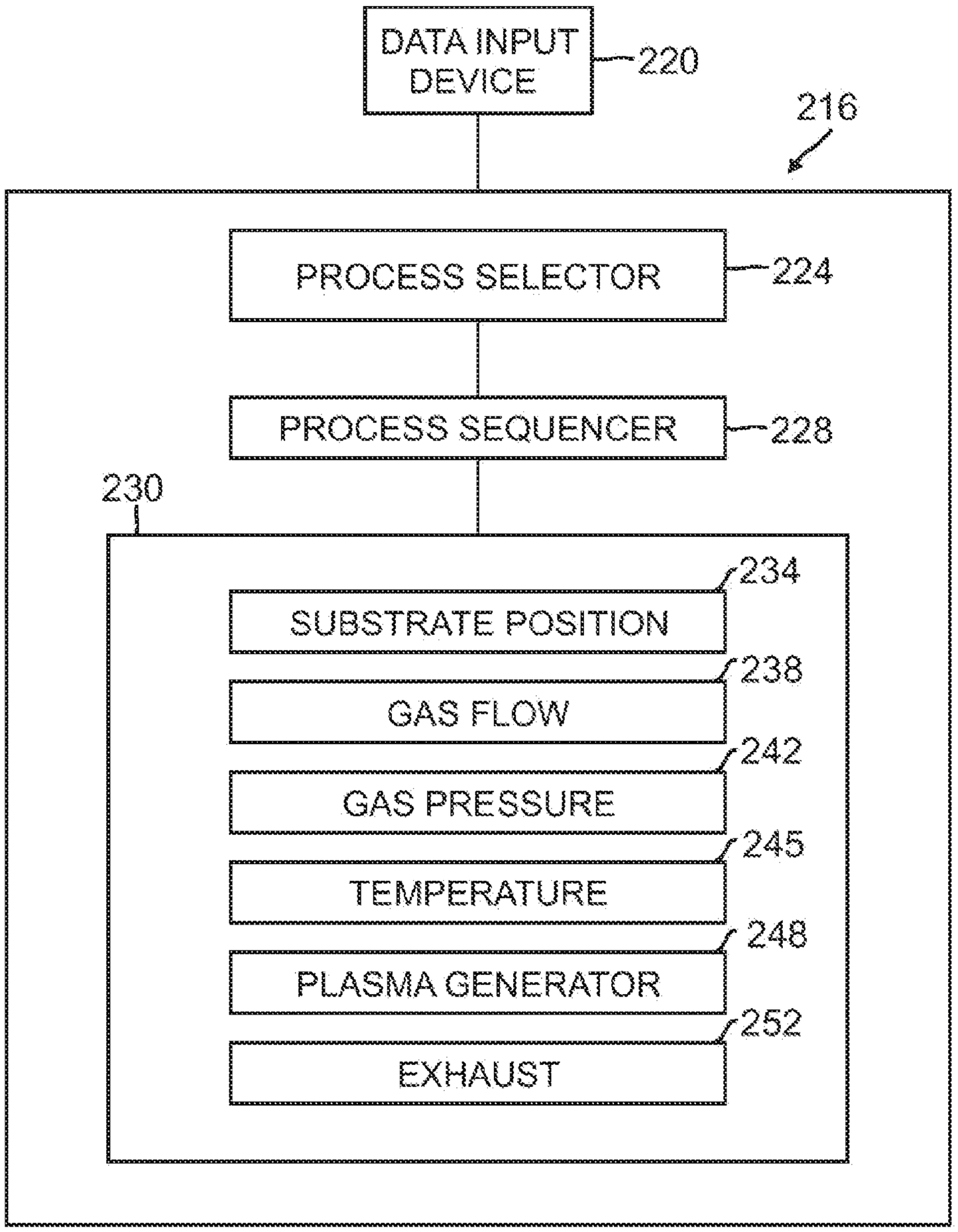

DATA INPUT DEVICE
220
216
PROCESS SELECTOR
224
PROCESS SEQUENCER
228
230
234
SUBSTRATE POSITION
238
GAS FLOW
242
GAS PRESSURE
245
TEMPERATURE
248
PLASMA GENERATOR
252
EXHAUST

FIG. 3

TREATMENT OF EFFLUENT CONTAINING CHLORINE-CONTAINING GAS

BACKGROUND

[0001] Embodiments of the present invention relate to the treatment of an effluent which is generated during substrate fabrication processes.

[0002] Chlorine-containing gases are used in, or formed as a byproduct of, substrate fabrication processes. For example, when depositing or etching materials on substrates such as semiconductor wafers and displays, various compositions of process gas comprising chlorine-containing gases can be used. For example, chlorine-containing gases such as Cl_2 and BCl_3 are often used to etch aluminum. As another example, chlorine-containing gases are added to fluorinated gases in the etching of oxide materials, such as silicon oxide. As yet another example, chlorine-containing gases such as aluminum chloride are used for the epitaxial deposition of aluminum. In these fabrication processes, the effluent gas released from the process chambers often contains high levels of chlorine-containing gases which have to be removed from the effluent gas before it is released to the environment.

[0003] Further problems arise when the effluent also contains other gases, such as hydrocarbon gases, which also have to be removed from the effluent. For example, next generation etching processes often use a process gas comprising chlorine-containing gases and hydrocarbon gases to etch features having smaller dimensions in the silicon dioxide material on a substrate. As another example, chlorine-containing gases and hydrocarbons such as Cl_2, BCl_3, CH_4, HCl, C_2H_2 and C_2H_6, are used as precursor gases in etching processes. The hydrocarbon gases can be removed by heating the effluent in an oxygen environment to temperatures of from about 600° C. to about 1100° C. to burn off the hydrocarbon precursors. However, these high temperatures are undesirable because they can result in the formation of toxic byproducts such as dioxins.

[0004] Several methods have been developed to reduce the concentration of chlorine-containing gases and other gases in the effluent. In one example, the effluent gas can be passed through a scrubber which sprays water through the effluent gas to dissolve the chlorine-containing gases to form water soluble chlorine acids. The acids are liquids that are more easily removed, and thus, the treated effluent has a reduced amount of chlorine and chlorine-containing compounds. However, the problem with scrubbing systems is that they do not sufficiently extract all of the chlorine-containing gases.

[0005] As another example, effluent is treated in a plasma to reduce the hazardous content of the effluent, for example, as described in U.S. Pat. No. 6,673,323 issued to Bhatnagar et al., entitled "Treatment of Hazardous Gases in Effluent", which is incorporated by reference herein in its entirety. However, heating or plasma treatment of effluent comprising hydrocarbon and chlorine-containing gases can cause the gases to react to form hazardous dioxin materials. Dioxin is the popular name for the family of halogenated organic compounds, the most common consisting of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs). The basic structure of PCDFs and PCDDs comprises two benzene rings joined by either a single (furan) or a double oxygen bridge (dioxin). Chlorine atoms are attached to the basic structure at any of 8 different places on the molecule, numbered from 1 to 8. Dioxins have serious adverse health effects on humans. In concentrations as low as a few parts per trillion, dioxins such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties.

[0006] Thus, it is desirable to treat effluent gas from a substrate processing chamber to reduce both chlorine-containing gases as well as hydrocarbon gases. It is further desirable to reduce or entirely eliminate the formation of dioxins in the treatment of effluent, before releasing the effluent into the environment.

DRAWINGS

[0007] 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:

[0008] FIG. **1** is a schematic block diagram of an embodiment of an effluent treatment apparatus;

[0009] FIG. **2** is a schematic diagram of an embodiment of a substrate processing chamber; and

[0010] FIG. **3** is an illustrative block diagram of a hierarchical control structure of a specific embodiment of a computer program according to the present invention.

DESCRIPTION

[0011] An effluent generated in the processing of a substrate, or the cleaning of a substrate processing chamber, is treated in an effluent treatment apparatus **300**. A simplified diagram of an exemplary embodiment of an effluent treatment apparatus, as shown in FIG. **1**, comprises a hydrogenation reactor **310**, a scrubber **320** and a combustor **330**. The hydrogenation reactor **310** comprises an enclosure **311** having a hydrogenation zone **316** and an inlet **314** to receive a chamber effluent from the gas exhaust port **170** of the process chamber **110**. The inlet **314** is connected to the gas exhaust port **170** of the process chamber **110** by a vacuum foreline **326**. Notably, the hydrogenation reactor **310** may be placed upstream or downstream of a process chamber pump (not shown) which is connected to the process chamber **110**. While a particular embodiment of an effluent treatment apparatus **300** is described to illustrate the effluent treatment process, it should be understood that the effluent treatment apparatus **300** can have other forms and configurations as would be apparent to one of ordinary skill in the art.

[0012] The enclosure **311** of the hydrogenation reactor **310** is composed of a gas impermeable material, such as a ceramic or metal material. In one version, the enclosure **311** is a cylinder composed of a ceramic material such as Al_2O_3. The cylinder has sufficient strength to withstand operating vacuum type pressures of up to about 740 Torr. The cylinder can have a diameter of at least about 10 mm and more preferably, at least about 200 mm. Advantageously, the cylinder can be oriented linearly to the direction of flow of effluent through the reactor **310** to reduce possible backflow of effluent that can occur through obstructions of the effluent path through the reactor **310**. Thus, the cylinder has a longitudinal central axis that is oriented parallel to the direction of the flow path of effluent. The length of the

reactor **310** is sufficiently long to allow the effluent to remain resident in the cylinder for a time period that is sufficient to convert substantially all of the unreacted precursors and by-products in the effluent to soluble hydride species. The precise length of the reactor **310** depends on a combination of factors including the diameter of the exhaust tube (not shown), the composition and peak flow rate of the effluent, and the power level applied to the abatement plasma. For an effluent comprising Cl_2 at a total flow of about 100 sccm, a sufficient resident time is at least about 0.1 seconds, and more preferably about 2 seconds. A suitable length of reactor **310** that provides such a residence time, comprises a cylindrical tube **304** having a cross-sectional diameter of 200 mm, and a length of from about 10 cm to about 50 cm. In one version, a bypass valve **305** may be provided in or near the reactor to control the flow of effluent into, or to bypass, the hydrogenation reactor. The bypass valve **305** may optionally be under the control of the controller **200**.

[0013] The hydrogenation reactor **310** further comprises an additive gas port **315** to introduce an additive gas comprising a hydrogen-containing gas into the hydrogenation reactor **310**. The additive gas source **322** is connected to the reactor **310** via a conduit **313**. Optionally, the flow of gas could be controlled with a control valve **317**. The operation of the control valve may be under the control of a controller **200** or it may be operated by hand.

[0014] The additive gas source **322** provides an additive gas comprising a hydrogen-containing gas to the effluent gas, before or after the effluent is energized, to enhance the conversion of unreacted precursors and by-products to soluble hydride species. In one example, hydrogen-containing gas is introduced into the reactor in the absence of oxygen, to form a hydrogenated effluent comprising hydrogen chloride gas. The hydrogen chloride gas is removed by a wet scrubber **320** located downstream in the effluent treatment apparatus **300**. The addition of even a small amount of additive gas to the effluent gas can significantly improve abatement efficiency.

[0015] In one version, the additive gas comprises a hydrogen-containing additive gas comprising H_2. In the reactor **310**, the effluent and the additive gas are reacted as described above. Disassociated hazardous gases, such as Cl_2, are hydrogenated in the plasma and converted to reaction products, such as HCl, that are treatable for safe exhaustion. For example, the HCl can be scrubbed and then safely exhausted. It should be understood that other hydrogen-containing additive gases having various flow rates and energized at various powers, may also be used to effectively convert the unreacted precursors and by-products to soluble hydride species.

[0016] It has been discovered that by properly selecting the volumetric flow ratio of reactive gas to hazardous gas in the effluent, the hazardous gas reduction efficiency can be substantially and unexpectedly improved. For example, it has been discovered that when using an additive gas comprising a hydrogen-containing gas, the volumetric flow ratio of hydrogen atoms in the additive gas to chlorine atoms in the effluent **100** should be at least about 1:1.

[0017] A scrubber **320** comprising an enclosure **325** is provided in the effluent treatment apparatus **300**. The scrubber comprises an inlet **327** connected to a foreline **336** which passes the hydrogenated effluent through the inlet **327** and into the enclosure **325**. The scrubber **320** further comprises a water spray **321** to spray water through the hydrogenated effluent to dissolve the hydrogen chloride gas into the water to form a scrubbed effluent. In one version, a bypass valve **324** may be provided in or near the scrubber **320** to control the flow of effluent into, or to bypass, the scrubber **320**. The bypass valve may optionally be under the control of the controller.

[0018] The combustor **330** comprises an enclosure **338** having an oxygenating treatment zone **340**. The combustor **330** further comprises an inlet **344** connected to a foreline **347**, which passes the scrubbed effluent through the inlet **344** and into the oxygenating treatment zone **340** of the enclosure **338**. The combustor **330** also comprises an additive gas port **353** to introduce an additive gas comprising an oxygen-containing gas into the enclosure **338**. Additive gas comprising oxygen or oxygenated additives from the additive gas source **360** enters the combustor **330** through the additive gas port **364**. The additive gas source **360** is connected to the combustor **330** via foreline **370** and the flow of gas could be controlled with a control valve **372**. The operation of the control valve **372** may be under the control of a controller **200**, as will be described, or may be operated by hand.

[0019] The combustor **330** is composed of a gas impermeable material, such as a ceramic or metal material. For example, the enclosure **338** may be a cylinder composed of a ceramic material such as Al_2O_3. The cylinder has sufficient strength to withstand operating vacuum type pressures of up to 740 Torr. The cylinder can have a diameter of at least about 10 mm, and more preferably at least about 200 mm. Advantageously, the cylinder can be oriented linearly to the direction of flow of effluent through the scrubber **320** to reduce possible backflow of effluent that can occur through obstructions of the effluent path through the scrubber **320**. The cylinder has a longitudinal central axis that is oriented parallel to the direction of the flow path of effluent. The length of the combustor **330** is sufficiently long to allow the effluent to remain resident in the cylinder for a sufficient time to substantially oxidize all of the hazardous compounds that may not have been removed by the scrubber **320**. The exact length of the combustor **330** depends on a combination of factors including the diameter of the scrubber outlet and foreline **347**, the composition and peak flow rate of the effluent, and the power level applied to the abatement plasma. For an effluent comprising Cl_2 at total flow of about 100 sccm, a sufficient resident time is at least about 0.1 seconds, and more preferably about 2 seconds. A suitable length of the combustor **330** that provides such a residence time, comprises a cylindrical tube having a cross-sectional diameter of from about 100 to about 800 mm, and a length of from about 10 cm to about 20 cm.

[0020] In one version, a bypass valve **342** may be provided in or near the combustor **330** to control the flow of effluent into, or to bypass, the combustor **330**. The throttle valve **342** may optionally be under the control of the controller.

[0021] The combustor **330** further comprises a heater **363** to heat the reactant gases within the combustor **330**. The heater **363** comprises heating elements and control circuitry. The heater **363** is capable of heating the combustor **330** to a temperature of at least about 500° C. Examples of heaters which may be used to heat the combustor **330** include heaters available from BH Thermal Corporation, Columbus, Ohio. The heater is capable of supplying from about 5 to about 10 KW of heating power. The additive gas source **360** provides oxygen or oxygenated additives which when

heated or energized by the heater, react with the hazardous compounds which may remain in the effluent. The combustor **330** uses oxygen or oxygen additives to effectively oxidize unreacted compounds without concern for the formation of dioxins.

[0022] The effluent treatment apparatus **300** can comprise an infrared sensor **370** to generate a signal upon the detection of an infrared signature corresponding to carbon-hydrogen, carbon-halogen, or carbon-oxygen bonds, indicating the presence of carbon-containing gas in the effluent. This signal is then sent to the controller **200** which activates the hydrogenation reactor **310**. An infrared sensor **370** is described, for example, in U.S. Pat. No. 6,366,346 issued to Nowak et al., entitled "Method and Apparatus for Optical Detection of Effluent Composition", which is incorporated by reference herein in its entirety. The infrared sensor **370** is located in a gas line **326** between the gas exhaust port **170** of the process chamber **110** and the gas inlet **314** of the hydrogenation reactor **310**. Another infrared sensor **370** can be located in the foreline **347** between the scrubber **320** and the combustor **330**.

[0023] The sensor **370** detects the light emitted by the reactive species in the effluent and converts it into a voltage signal. The light emitted by the effluent indicates the types and concentrations of gases in the effluent because different gases will emit different wavelengths of light when excited in a plasma, and the amplitude of a detected wavelength provides an indication of the amount or concentration of a particular gas in the effluent stream. The sensor **370** can be any of a number of optical detectors, such as a phototransistor or photodiode. Although desirable in order to simplify data interpretation, it is not necessary for the sensor **370** response to be linear. The sensor **370** can also include various lens or filters as would be apparent to one of ordinary skill in the art. For example, a suitable filter is a band-pass filter centered at the infrared wavelength of interest. A suitable infrared sensor **370** is the model TPS434 NDIR gas analysis sensor available from Perkin Elmer, located in Fremont, Calif., in conjunction with an infrared filter, such a bandpass filter for wavelengths from 7.1 to 16.7 micrometers, or 3.0 to 3.6 micrometers, available from Barr Associates Inc., located in Westford, Mass.

[0024] A controller **200** can be used to operate a substrate processing apparatus **100** comprising both the process chamber **110** and the effluent treatment apparatus **300**, as shown in FIGS. **2** and **3**. The controller **200** comprises electronic hardware including integrated circuits that are suitable for operating both the process chamber **110** and the apparatus **300**. The controller **200** is adapted to accept data input, run algorithms, produce data output signals, detect data signals from sensors **370** and other chamber components, and monitor process conditions within the substrate processing apparatus **100**. The controller **200** comprises effluent treatment control instruction sets which comprise program code to receive a signal from the infrared sensor **370** upon detection of the presence of carbon-containing gas in the effluent. The controller **200** receives a signal from the infrared sensor **370** and adjusts operation of any one of the hydrogenation reactor **310**, scrubber **320** or combustor **330** in relation to the signal. The effluent treatment control also has safety code to turn off the effluent treatment apparatus **300** should unsafe conditions occur or be measured.

[0025] The controller **200** further comprises gas flow instruction sets which comprise program code to control a gas valve to distribute specific volumetric flow rates of particular gases. In one version, the controller **200** comprises program code to control a gas valve to set the volumetric flow rate of hydrogen-containing gas introduced into the additive gas port **315** of the hydrogenation reactor **310** such that the ratio of hydrogen to chlorine atoms in the hydrogenation reactor **310** is at least about 1:1. In another version, the controller **200** comprises program code to control a gas valve to set the volumetric flow rate of hydrogen-containing gas introduced into the additive gas port **315** of the hydrogenation reactor **310** such that the ratio of hydrogen to chlorine atoms in the hydrogenation zone **316** is from about 1.5:1 to about 3:1.

[0026] In the effluent treatment process, the effluent is passed from the exhaust port **170** of the process chamber **110** to the hydrogenation reactor **310** of the effluent treatment apparatus **300**. Notably, the methodology described here is applicable to all abatement apparatuses including plasma and thermal based technologies. In this reactor **310**, an additive gas comprising a hydrogen-containing gas is added to the effluent gas through the additive gas port **315**. The hydrogen-containing gas reacts with the unreacted chlorine-containing effluent gas to form soluble hydride species, such as hydrogen chloride gas. There should be little or no oxygen present in the effluent, otherwise the oxygen will react with the hydrogen-containing gas to form water. When the chlorine-containing gas reacts with hydrogen-containing gas, the formation of dioxins downstream of the hydrogenation reactor **310**, is minimized. Thus, the hydrogen-containing gases must be added in a sufficient quantity to substantially react with all the residual chlorine-containing gas. That is, the hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms in the hydrogenation zone **316** is sufficiently high to convert substantially all of the unsaturated hydrocarbon gases to saturated hydrocarbon gases. A suitable hydrogen-containing gas is H_2. A suitable ratio of hydrogen to chlorine atoms in the hydrogenation zone **316** is at least about 1.2:1, and even from about 1.5:1 to about 3:1.

[0027] The hydrogenation reactor **310** can also be used to convert unsaturated or complex hydrocarbon gases to fully saturated hydrocarbon gases, which are easier to abate in conventional downstream combustors **330** (as described below). For example, unsaturated hydrocarbon gases such as ethylene (C_2H_4) and propylene (C_3H_6) may be converted to saturated hydrocarbon gases such as CH_4, C_2H_6 and C_3H_8, in the hydrogenation reactor **310**. The hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms in the hydrogenation zone **316** is sufficiently high to convert substantially all of the unsaturated hydrocarbon gases to saturated hydrocarbon gases.

[0028] Thereafter, the hydrogenated effluent, now containing a soluble hydride species, such as hydrogen chloride gas, is passed through a scrubber **320** which removes the soluble hydrogen chloride gas by spraying water through the scrubbed effluent gas. The water dissolves the hydrogen chloride gas into the water, thus substantially removing the hydrogen chloride gas from the effluent.

[0029] If the scrubbed effluent is free of chlorine containing species, but still contains other hazardous or flammable gases, it can be further processed in a combustor **330**. For example, residual hydrocarbon by-products can be burned in a combustion zone **340** by heating the scrubbed effluent while adding an oxygen-containing gas into the combustion

zone **340** to form a treated effluent. Suitable oxygen-containing gases include oxygen and oxygenated additives such as H_2O. In the combustor **330**, the oxygen-containing gas effectively oxidizes unreacted gaseous compounds without the formation of dioxins. As another example, effluent comprising saturated hydrocarbon gases can be fully oxidized by combustion in the combustor **330** in an oxygen environment to form CO_2 and H_2O. Gases in the combustor **330** are processed by heating the combustion zone **340** to a temperature of at least about 500° C.

[0030] The novel solution provided above effectively abates the unreacted reactants and by-products produced by chlorine-based semiconductor manufacturing processes, while preventing or significantly reducing the formation of toxic dioxins. By separating the chamber effluent treatment processes for reacting the chlorine-containing species from the chamber, and for reacting other hydrocarbon-containing species, the reaction of hydrocarbon and chlorine to form toxic dioxins, is significantly reduced.

[0031] An embodiment of a substrate processing apparatus **100** capable of processing a substrate **114** and producing an effluent comprising hydrocarbon gas and chlorine-containing gas to be treated in the effluent treatment apparatus, is illustrated in FIG. **2**. The substrate processing apparatus **100** comprises a process chamber **110** for processing a substrate **114**. Such a process chamber **110**, may be, for example, a decoupled plasma source (DPS® II) type chamber commercially available from Applied Materials Inc., Santa Clara, Calif. A modified version of a DPS II chamber is described in U.S. Patent Application Publication No. 2006/0028646 A1 issued to Davis et al., which is incorporated by reference herein in its entirety. The chamber is generally used as a processing module of the CENTURA® processing system, also available from Applied Materials, Inc. of Santa Clara, Calif.

[0032] A typical process chamber **110** comprises a housing **116** comprising enclosure walls **130** that include sidewalls **132**, a bottom wall **136** and a ceiling **134**. The ceiling **134** may comprise a substantially arcuate shape, or in other versions, a dome shaped, substantially flat, or multi-radius shape. The walls **130** are typically fabricated from a metal, such as aluminum, or ceramic materials. The ceiling **134** and/or sidewalls **132** can also have a radiation permeable window **126** that allows radiation to pass through for monitoring processes being conducted in the chamber **110**, by, for example, beam forming optics **135** that collect the reflectance from the substrate **114**. The collected signals from the beam forming optics **135** are then sent to the spectrometer **137** for signal analysis.

[0033] The chamber **110** further comprises a substrate support **120** to support a substrate **114** in the chamber. The substrate support **120** typically comprises an electrostatic chuck, which comprises a dielectric which at least partially covers an electrode **125**, and which may include a substrate receiving surface **124**. The receiving surface **124** may have apertures or grooves (not shown) to provide a heat transfer gas, such as helium, from a helium gas source **148** through a conduit **149** through the substrate support **120** to control the temperature of the substrate **114**. The electrode **125** is capable of being electrically charged to generate an electrostatic charge for electrostatically holding the substrate **114** to the electrostatic chuck. The electrode **125** is also capable of serving as a process electrode **125**. The electrode **125** can be a single conductor or a plurality of conductors, and can be made from a metal such as tungsten, tantalum or molybdenum. The substrate support or cathode **120** is coupled through a second matching network **144** to a biasing power source **142**. The biasing power source **142** generally is capable of producing up to 10 kW at a frequency of approximately 13.56 MHz. The biasing power may be either continuous or pulsed power. In other embodiments, the biasing power source **142** may be a DC or pulsed DC source.

[0034] The gas distributor **138** enclosed within the process chamber **110** serves to introduce a process gas into the housing **116** to process a substrate **114** placed on the substrate support **120**. The process gas is provided by a gas delivery system **150** that includes a process gas supply **152** comprising sources for various gases. Each gas source has a conduit with a gas flow control valve such as a mass flow controller, to pass a set flow rate of the gas therethrough. The conduits feed the gases to a mixing manifold **154** in which the gases are mixed to form a desired process gas composition. The mixing manifold **154** feeds the gas distributor **138** having gas outlets **164** in the chamber **106**. The gas outlets **164** may pass through the chamber sidewalls **132** proximate to a periphery of the substrate support **120** or may pass through the ceiling **134**, terminating above the substrate **114**.

[0035] Spent process gas and byproducts are exhausted from the chamber **110** through an exhaust system **168** which includes one or more exhaust ports **170**. The exhaust ports **170** receive spent process gas and chamber effluent comprising unreacted process gas, passing the spent gas and chamber effluent to an exhaust conduit **172**, in which there is a throttle valve **174** to control the pressure of the gas in the chamber **110**. The exhaust conduit **172** feeds one or more exhaust pumps **176**, used to remove the chamber effluent from the chamber **110**. The vacuum pump **176** may have a throttle valve **174** to control the exhaust rate of gases from the chamber **110**.

[0036] The process gas is energized to process the substrate **114** by a plasma generator **180**. The plasma generator **180** couples energy to the process gas in a process zone **184** of the chamber **110** (as shown) or in a remote zone upstream from the chamber **110** (not shown). By "energized process gas," it is meant that the process gas is activated or energized to form one or more dissociated gas species, non-dissociated gas species, ionic gas species and neutral gas species. In one version, the plasma generator **180** comprises an antenna **186** comprising at least one inductor coil **188** which has a circular symmetry about the center of the chamber **106**. Typically, the antenna **186** comprises solenoids having from about 1 to about 20 turns with a central axis coincident with the longitudinal vertical axis that extends through the process chamber **110**. When the antenna **186** is positioned near the ceiling **134** of the chamber **110**, the adjacent portion of the ceiling **134** may be made from a dielectric material, such as silicon dioxide, which is transparent to RF or electromagnetic fields. The antenna **186** is powered by an antenna current supply **190** and the applied power is tuned by an RF match network **192**. The antenna current supply **190** provides, for example, RF power to the antenna **186** at a frequency of typically about 50 KHz to about 60 MHz, and more typically about 13.56 MHz, and does so at a power level of from about 100 to about 5000 Watts.

[0037] When an antenna **186** is used in the chamber **110**, the walls **130** include a ceiling **134** made from an induction field permeable material, such as aluminum oxide or silicon

dioxide, to allow the inductive energy from the antenna **186** to permeate through the walls **130** or ceiling **134**. A suitable semiconductor material which may also be used is doped silicon. For doped silicon semiconducting ceilings, the temperature of the ceiling is preferably held in a range at which the material provides semiconducting properties, for example, from about 100 K to about 600 K. The temperature of the ceiling **134** can be controlled using a plurality of radiant heaters such as tungsten halogen lamps and a thermal transfer plate in contact with the ceiling **134**. The thermal transfer plate may be made of aluminum or copper, with passages (for a heat transfer fluid to flow therethrough. A heat transfer fluid source supplies heat transfer fluid to the passages to heat or cool the thermal transfer plate as needed to maintain the chamber **110** at a constant temperature. The thermal transfer plate may be supported at a distance above the antenna **186** of at least one half the overall height of the antenna **186** to reduce inductive coupling between the antenna **186** and the plasma, which would otherwise result from their close proximity to the conductive plate.

[0038] In one version, the plasma generator **180** is also a pair of electrodes **128** that may be capacitively coupled to provide a plasma initiating energy to the process gas or to impart a kinetic energy to energize the gas species. Typically, one electrode **128** is in the support **120** below the substrate **114** and the other electrode **128** is a wall, for example, the sidewall **130** or ceiling **134** of the chamber **110**. For example, the electrode **128** may be a ceiling **134** made of a semiconductor that is sufficiently electrically conductive to be biased or grounded to form an electric field in the chamber **110**, while still providing low impedance to an RF induction field transmitted by the antenna **186** above the ceiling **134**. A suitable semiconductor comprises silicon doped to have an electrical resistivity of, for example, less than about 500 Ω-cm at room temperature. Generally, the electrodes **128** may be electrically biased relative to one another by a biasing voltage supply **142** that provides an RF bias voltage to the electrodes **128** to capacitively couple the electrodes **128** to one another. The applied RF voltage is tuned by an RF match network **144**. The RF bias voltage may have frequencies of about 50 kHz to about 60 MHz, or as in one version, about 13.56 MHz. The power level of the RF bias current is typically from about 50 to about 3000 Watts.

[0039] The chamber **110** may be operated by a controller **200** comprising a computer **204** that sends instructions via a hardware interface **208** to operate the chamber components, including the substrate support **120**, the gas flow control valves, the gas distributor **138**, the plasma generator **180**, the gas exhaust port **170** and the throttle valve **174**. The process conditions and parameters measured by the different detectors in the chamber **110** are sent as feedback signals by control devices such as the gas flow control valves, pressure monitor **171**, throttle valve **174**, and other such devices, and are transmitted as electrical signals to the controller **200**.

[0040] The controller **200** comprises electronic hardware including electrical circuitry comprising integrated circuits that are suitable for operating the chamber **110** and its peripheral components. Generally, the controller **200** is adapted to accept data input, run algorithms, produce useful output signals, detect data signals from the detectors and other chamber components, and to monitor or control the process conditions in the chamber **110**. For example, the controller **200** may comprise a computer **204** comprising (i) a central processing unit (CPU), such as for example, a conventional microprocessor from the INTEL Corporation, that is coupled to a memory **210** that includes a removable storage medium, such as a CD or floppy drive, a non-removable storage medium, such as a hard drive, ROM, and RAM; (ii) application specific integrated circuits (ASICs) that are designed and preprogrammed for particular tasks, such as retrieval of data and other information from the chamber **110** or operation of particular chamber components; and (iii) interface boards that are used in specific signal processing tasks, comprising, for example, analog and digital input and output boards, communication interface boards and motor controller boards. The user interface between an operator and the controller **200** can be, for example, via a display and a data input device **220**, such as a keyboard or light pen. To select a particular screen or function, the operator enters the selection using the data input device **220** and can review the selection on the display.

[0041] In one version, the controller **200** comprises a computer program **216** that is readable by the computer **204** and may be stored in the memory **210**. The computer program **216** generally comprises process control software comprising program code to operate the chamber **110** and its components, process monitoring software to monitor the processes being performed in the chamber **110**, safety systems software and other control software. The computer program may be written in any conventional programming language, such as for example, assembly language, C++, Pascal, or Fortran. Suitable program code is entered into a single file or multiple files using a conventional text editor and stored or embodied in computer-usable medium of the memory **210**. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of pre-compiled library routines. To execute the linked, compiled object code, the user invokes the object code, causing the CPU to read and execute the code to perform the tasks identified in the program.

[0042] An illustrative block diagram of a hierarchical control structure of a specific embodiment of a computer program **216** according to the present invention is shown in FIG. **3**. Using a data input device **220**, for example, a user enters a process set and chamber number into the computer program **216** in response to menus or screens on the display that are generated by a process selector **224**. The computer program **216** includes instruction sets to control the substrate position, gas flow, gas pressure, temperature, RF power levels and other parameters of a particular process, as well as instructions sets to monitor the chamber process. The process sets are predetermined groups of process parameters necessary to carry out specified processes. The process parameters are process conditions, including gas composition, gas flow rates, temperature, pressure, and gas energizer settings such as RF or microwave power levels. The chamber number reflects the identity of a particular chamber when there are a set of interconnected chambers on a platform.

[0043] A process sequencer **228** comprises instruction sets to accept a chamber number and set of process parameters from the computer program **216** or the process selector **224**, and to control its operation. The process sequencer **228** initiates execution of the process set by passing the particular process parameters to a chamber manager **230** that controls multiple tasks in a chamber **110**. The chamber

manager **230** may include instruction sets, such as, for example, substrate positioning instruction sets **234**, gas flow control instruction sets **238**, gas pressure control instruction sets **242**, temperature control instruction sets **245**, plasma generator control instruction sets **248**, and exhaust control instruction sets **252**.

[0044] The substrate positioning instruction sets **234** comprise code for controlling chamber components that are used to load a substrate **114** onto the substrate support **120**, and optionally, to lift a substrate **114** to a desired height in the chamber **110**.

[0045] The gas flow control instruction sets **238** comprise code for controlling the flow rates of different constituent gases that make up the process gas. For example, the gas flow control instruction sets **238** may regulate the opening size of the gas flow control valves to obtain the desired gas flow rates from the gas outlets **164** into the chamber **110**.

[0046] The gas pressure control instruction sets **242** comprise program code for controlling the pressure in the chamber **110**, for example, by regulating the open/close position of the throttle valve **174**.

[0047] The temperature control instruction sets **245** may comprise, for example, code for controlling the temperature of the substrate **114** during etching and/or code for controlling the temperature of walls **130** of the chamber **110**, such as the temperature of the ceiling **134**.

[0048] The plasma generator control instruction sets **248** comprise code for setting, for example, the RF power level applied to the electrodes **128** or to the antenna **186**; the power applied to energize the process gas into a plasma.

[0049] The exhaust control instruction sets **252** comprise code for controlling the opening of the throttle valve **174** to exhaust effluent from the chamber **110** through the gas exhaust port **170**.

[0050] While described as separate instruction sets for performing a set of tasks, it should be understood that each of these instruction sets can be integrated with one another, or the tasks of one set of program code integrated with the tasks of another to perform the desired set of tasks. Thus, the controller **200** and the computer program **216** described herein should not be limited to the specific version of the functional routines described herein; any other set of routines or merged program code that perform equivalent sets of functions are also in the scope of the present invention. Also, while the controller **200** is illustrated with respect to one version of the chamber **110**, it may be used for any chamber compatible for executing the invention described herein.

[0051] The apparatus **100** illustrated herein can be used to process material on a substrate **114**, for example, to etch material from the substrate **114**, remove contaminant deposits or residues deposited on surfaces in the chamber **110**, such as on the surfaces of walls **130** of the chamber **110** and the surfaces of components in the chamber **110**, and perform post processing treatment of a substrate **114** or the like. For example, in one version, the apparatus **100** may be used to etch a substrate **114** comprising one or more layers of material. Such layers are often superimposed on one another and may comprise dielectric layers comprising, for example, silicon dioxide, undoped silicate glass, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), carbon-doped silicate glass (CSG), silicon nitride or TEOS deposited glass; semiconducting layers comprising, for example, silicon-containing layers such as polysilicon or a silicon compound; and conductive layers such as metal-containing layers comprising, for example, aluminum, copper, or metal silicide such as tungsten silicide and cobalt silicide. Suitable etchant gases for etching layers on the substrate **105**, include for example, HCl, BCl_3, $CHCl_3$, C_nH_n, C_nH_{n+2}, C_nH_{2n+2} (where "n" is any integer from 1 to 4), Cl_xBr_y, Cl_xF_y (where "x" and "y" are any combination of integers from 0 to 3), $XeCl_2$, $BiCl_xF_y$, NCl_3, NCl_xF_y, NCl_xBr_y, $NO_2Cl_xF_y$, $NOCl_xF_y$ (where "x" and "y" are any combination of integers from 0 to 3), $C_nH_yCl_x$, $C_nH_yCl_xF_z$, $C_nH_yCl_xBr_zF_v$ (where "x", "y", "z" and "v" are any combination of integers from 0 to 3 and "n" is any integer from 1 to 4), CCl_3OCCl_3, $AlCl_3$, HBr, Br_2, Cl_2, CCl_4, $SiCl_4$, SF_6, F, NF_3, HF, CF_3, CF_4, CH_3F, CHF_3, $C_2H_2F_2$, $C_2H_4F_6$, C_2F_6, C_3F_8, C_4F_8, C_2HF_5, C_4F_{10}, CF_2Cl_2, $CFCl_3$, O_2, N_2, He and mixtures thereof. The etchant gas is selected to provide high etch rates and highly selective etching of the particular layers or materials that are being etched. When multiple layers are sequentially etched, etchant gas compositions may be sequentially introduced into the chamber **110** to etch each particular layer. Further, while the effluent treatment apparatus **300** is illustrated in the context of an etching process, it should be understood that the effluent treatment apparatus **300** can be used with other substrate fabrication processes and chambers.

[0052] A substrate **114** is placed by a substrate transfer mechanism **179**, such as a wafer blade, onto the substrate support **120** in the process zone **184** of the process chamber **110**. To etch one or more of the layers on the substrate **114** in the process chamber **110**, process gas comprising etchant gas comprising a hydrocarbon gas and a chlorine-containing gas is introduced from the gas supply **152** into the process zone **184**. In one version, the hydrocarbon gas comprises one or more of C_nH_n, C_nH_{n+2}, C_nH_{2n+2}, where n is any integer from 1 to 4. In one version, the chlorine-containing gas comprises one or more of Cl_2, CCl_4, $SiCl_4$, HCl, BCl_3, $CHCl_3$, Cl_xBr_y, Cl_xF_y, $XeCl_2$, $BiCl_xF_y$, NCl_3, NCl_xF_y, NCl_xBr_y, $NO_2Cl_xF_y$, $NOCl_xF_y$, $C_nH_yCl_x$, $C_nH_yCl_xF_z$, $C_nH_yCl_xBr_zF_v$, CCl_3OCCl_3, $AlCl_3$, CF_2Cl_2, and $CFCl_3$, where x, y, z and v are any integers from 0 to 3 and n is any integer from 1 to 4.

[0053] Process gases are supplied to the process zone **184** from a gas panel **185** having entry ports leading to a gas distributor **138**. The orifices of the gas distributor **138** release the various gases to form a gaseous mixture. The gaseous mixture is ignited into a plasma in the chamber **110** by a plasma generator **180** comprising radical species such as atomic chlorine and other etchant species, as well as hydrocarbon or boron-containing species that polymerize to enhance the anisotropic etch process. The gas may be energized by inductively and/or capacitively coupling energy into the process zone **184** of the chamber **110**, or by applying microwaves thereto or to an etchant gas in a remote zone of a remote chamber (not shown), that is at a location remote from the process zone **184**. By "energized process gas" it is meant that the process gas is activated or energized so that one or more dissociated species, non-dissociated species, ionic species and neutral species are excited to higher energy states, in which they are more chemically reactive. In one version, the plasma generator **180** applies power from the biasing source power **142** to the inductive coil element **188** and the cathode **128**, respectively. The pressure within the interior of the chamber **110** is controlled using a throttle valve **174** and a vacuum pump **176**. Typically, the chamber wall **130** is coupled to an electrical

ground **146**. The temperature of the wall **130** is controlled using liquid-containing conduits that run through the wall.

[0054] During the etching process, the temperature of the substrate **114** is controlled by stabilizing a temperature of the substrate support **120**. Helium gas from a gas source **148** can be provided via a gas conduit **149** to channels formed in the substrate support surface **124** under the substrate **114**. The helium gas is used to facilitate heat transfer between the support **120** and the substrate **114**. During processing, the substrate support **120** may be heated by a resistive heater within the substrate support **120**, to a steady state temperature, and then the helium gas may be utilized to facilitate uniform heating of the substrate **114**. Using such thermal control, the substrate **114** is maintained at a temperature of from about 20° C. to 350° C.

[0055] The energized etchant gas etches one or more layers on the substrate **114** to form volatile gaseous species that are exhausted from the chamber **110** by exhaust system **168**. After processing, an effluent comprising unreacted process gas comprising the hydrocarbon species and the chlorine-containing gas is exhausted from the process zone **184** through the gas exhaust port **170**. The effluent can now be treated in the effluent treatment apparatus **300** to remove remaining hazardous gases and by-products resulting from the etch process.

[0056] Those skilled in the art will understand that other process chambers may be used to practice the invention, including chambers with remote plasma sources, electron cyclotron resonance (ECR) plasma chambers, and the like.

[0057] Although the present invention has been described in considerable detail with regard to certain preferred versions thereof, other versions are possible. For example, the scrubber **320** that sprays water to remove the HCl from the effluent gas may be interchangeable with a resin bed scrubber performing the same function. Also, the apparatus **100** of the present invention can be used in and/or with other chambers and for other processes, such as, for example, physical vapor deposition and chemical vapor deposition. Therefore, the appended claims should not be limited to the description of the preferred versions contained herein.

What is claimed is:

1. A method of processing a substrate and treating an effluent comprising hydrocarbon gas and chlorine-containing gas, the method comprising:

(a) exposing a substrate to a plasma of a process gas comprising a hydrocarbon gas and a chlorine-containing gas;

(b) exhausting from the process zone, a chamber effluent comprising unreacted process gas comprising the hydrocarbon gas and the chlorine-containing gas;

(c) exposing the chamber effluent to hydrogen-containing gas to form a hydrogenated effluent comprising hydrogen chloride gas;

(d) scrubbing the hydrogenated effluent with water to dissolve the hydrogen chloride gas in the water to form a scrubbed effluent that is substantially absent hydrogen chloride gas; and

(e) combusting the scrubbed effluent by heating the scrubbed effluent while adding an oxygen-containing gas to form a treated effluent.

2. A method according to claim **1** wherein in (b), the hydrocarbon gas comprises one or more of C_nH_n, C_nH_{n+2}, C_nH_{2n+2}, where n is any integer from 1 to 4.

3. A method according to claim **1** wherein in (b), the chlorine-containing gas comprises one or more of Cl_2, CCl_4, $SiCl_4$, HCl, BCl_3, $CHCl_3$, Cl_xBr_y, Cl_xF_y, $XeCl_2$, $BiCl_xF_y$, NCl_3, NCl_xF_y, NCl_xBr_y, $NO_2Cl_xF_y$, $NOCl_xF_y$, $C_nH_yCl_x$, $C_nH_yCl_xF_z$, $C_nH_yCl_xBr_zF_v$, CCl_3OCCl_3, $AlCl_3$, CF_2Cl_2, and $CFCl_3$, where x, y, z and v are any integers from 0 to 3 and n is any integer from 1 to 4.

4. A method according to claim **1** wherein in (c), the hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms is at least about 1:1.

5. A method according to claim **4** wherein the hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms is from about 1.2:1 to about 3:1.

6. A method according to claim **1** wherein the hydrogen-containing gas comprises H_2.

7. A method according to claim **4** wherein the hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms is sufficiently high to convert substantially all of the unsaturated hydrocarbon gases to saturated hydrocarbon gases.

8. A method according to claim **1** wherein in (c), the hydrogen-containing gas is added in a sufficient quantity that the ratio of hydrogen to chlorine atoms in the hydrogenation zone is at least about 1:1.

9. A method according to claim **1** wherein (d) comprises spraying water through the scrubbed effluent gas.

10. A method according to claim **1** wherein (e) comprises adding an oxygen-containing gas comprising oxygen or H_2O.

11. A method according to claim **1** wherein (e) comprises heating the combustion zone to a temperature of at least about 500° C.

12. A substrate processing apparatus capable of processing a substrate and treating an effluent comprising hydrocarbon gas and chlorine-containing gas, the apparatus comprising:

(a) the process chamber comprising

(i) a housing enclosing a substrate support;

(ii) a gas distributor to introduce a process gas into the housing, the process gas comprising a hydrocarbon gas and a chlorine-containing gas,

(iii) a plasma generator to form a plasma of the process gas, and

(iv) a gas exhaust port to remove chamber effluent comprising unreacted process gas from the housing;

(b) an effluent treatment apparatus comprising:

(i) a hydrogenation reactor comprising an enclosure, an inlet to receive the chamber effluent from the gas exhaust port of the process chamber, and an additive gas port to introduce a hydrogen-containing gas into the hydrogenation reactor to form a hydrogenated effluent comprising hydrogen chloride gas;

(ii) a scrubber comprising an enclosure, an inlet to receive the hydrogenated effluent, and a water spray to spray water through the hydrogenated effluent to dissolve the hydrogen chloride gas into the water to form a scrubbed effluent; and

(iii) the combustor comprising an enclosure, an inlet to receive the scrubbed effluent, an additive gas port to introduce an oxygen-containing gas into the combustor, and a heater to heat the combustor; and

(c) a controller to operate the process chamber and effluent treatment apparatus to process a substrate and treat the chamber effluent.

13. An apparatus according to claim **12** wherein the controller comprises program code to control a gas valve to set the volumetric flow rate of hydrogen-containing gas introduced into the additive gas port of the hydrogenation reactor such that the ratio of hydrogen to chlorine atoms in the hydrogenation reactor is at least about 1:1.

14. An apparatus according to claim **13** wherein the controller comprises program code to control a gas valve to set the volumetric flow rate of hydrogen-containing gas introduced into the additive gas port of the hydrogenation reactor such that the ratio of hydrogen to chlorine atoms in the hydrogenation zone is from about 1.2:1 to about 3:1.

15. An apparatus according to claim **12** wherein the heater is capable of heating the combustor to a temperature of at least about 500° C.

16. An apparatus according to claim **12** wherein the heater is capable of supplying from about 5 to about 10 KW of heating power.

17. An apparatus according to claim **12** further comprising an infrared sensor to generate a signal upon detection of an infrared signature.

18. The apparatus according to claim **17** wherein the sensor detects light emitted by reactive species in the effluent and converts it into a voltage signal, wherein the light indicates the types and concentrations of gases in the effluent.

19. An apparatus according to claim **17** comprising an infrared sensor to generate a signal upon detection of an infrared signature indicating the presence of hydrocarbon gas in the effluent.

20. An apparatus according to claim **17** wherein the infrared sensor is capable of detecting an infrared signature corresponding to carbon.

21. An apparatus according to claim **17** wherein the controller receives a signal from the infrared sensor and adjusts operation of any one off the hydrogenation reactor, scrubber or combustor in relation to the signal.

22. An apparatus according to claim **12** wherein the plasma generator comprises an antenna.

23. An apparatus according to claim **12** wherein the plasma generator comprises a pair of electrodes which are capacitively coupled to provide energy to the process gas to form a plasma.

* * * * *