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(54) **TREATMENT OF EFFLUENT IN THE DEPOSITION OF CARBON-DOPED SILICON**

(75) Inventors: **Moretza Farnia**, Campbell, CA (US); **Mehran Moalem**, Cupertino, CA (US)

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

(73) Assignee: **Applied Materials, Inc.**, Santa Clara, CA (US)

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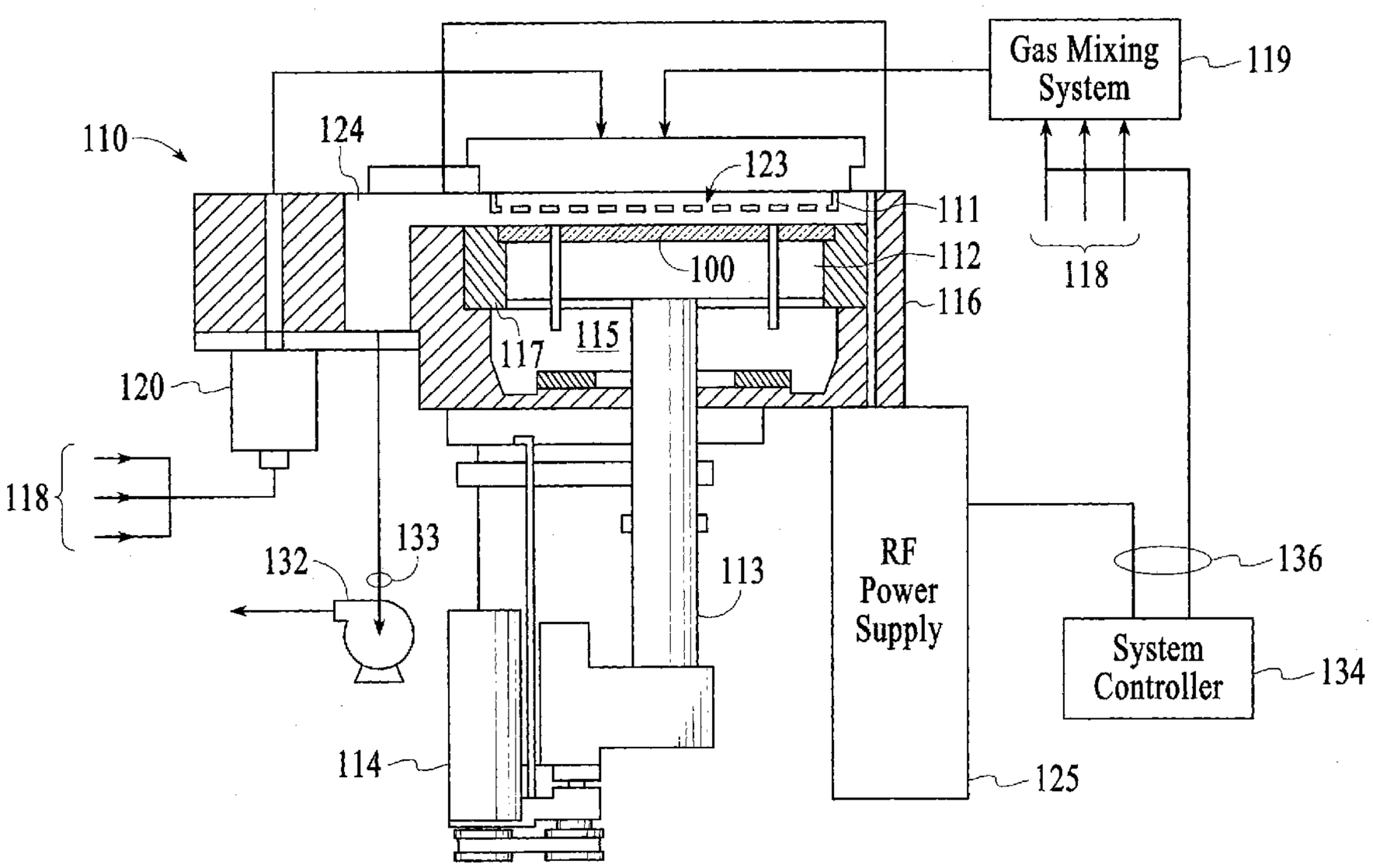
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(57) **ABSTRACT**

A substrate processing apparatus exposes a substrate in a process zone of a process chamber to a plasma of a precursor gas comprising a hydrocarbon gas to deposit carbon-doped silicon on the substrate. An effluent comprising unreacted precursor gas and byproducts from the carbon-doped silicon deposition process is exhausted from the process zone and passed into an effluent treatment zone of an effluent treatment reactor. An additive gas comprising an oxygen-containing gas is added to the effluent treatment zone and a plasma is formed of the effluent and additive gas to treat the effluent to reduce the content of unreacted precursor gas and byproduct in the effluent.



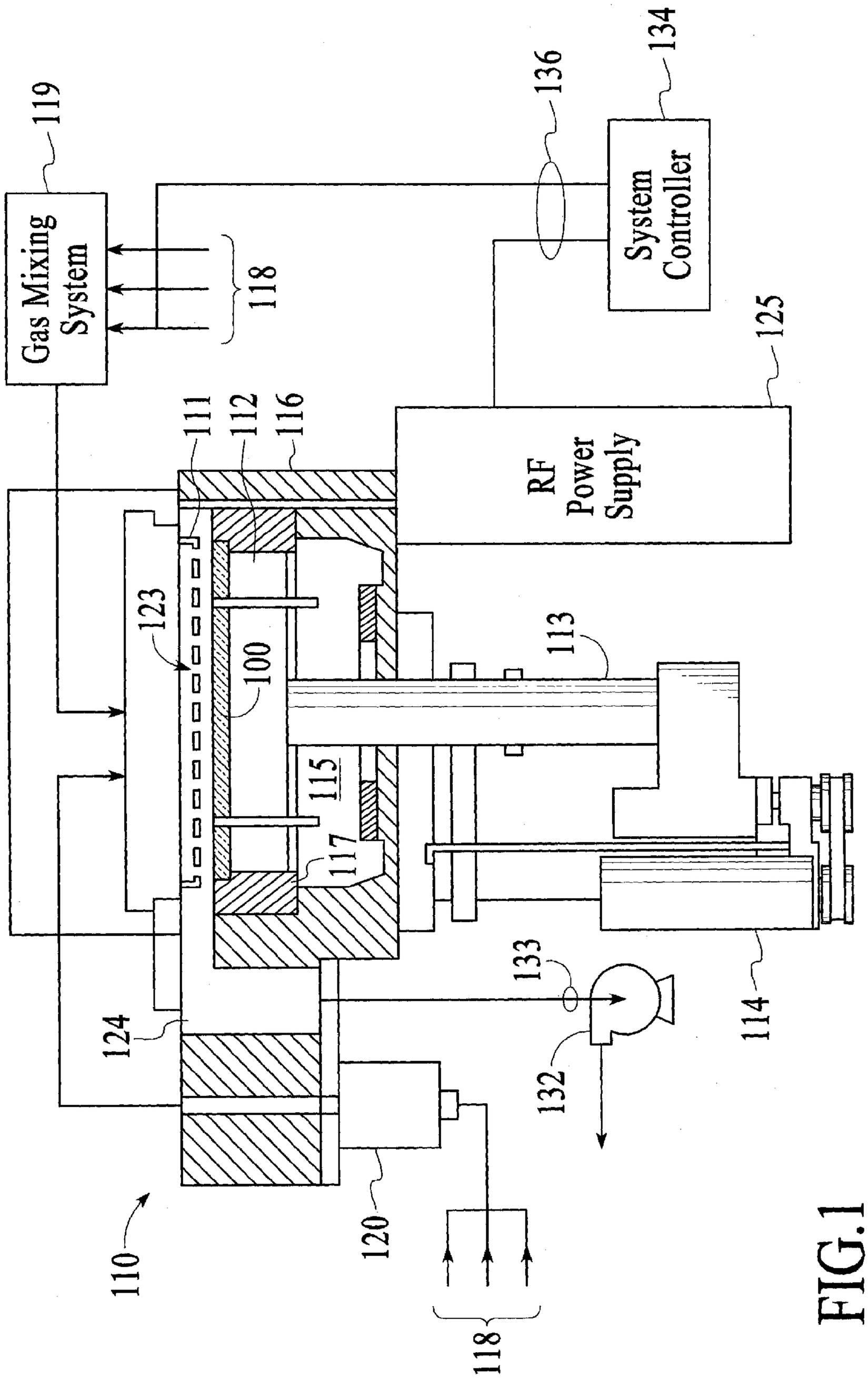

Gas Mixing System
119
118
136
System Controller
134
125
RF Power Supply
111
112
116
123
100
113
115
117
133
124
132
114
110
120
118

FIG.1

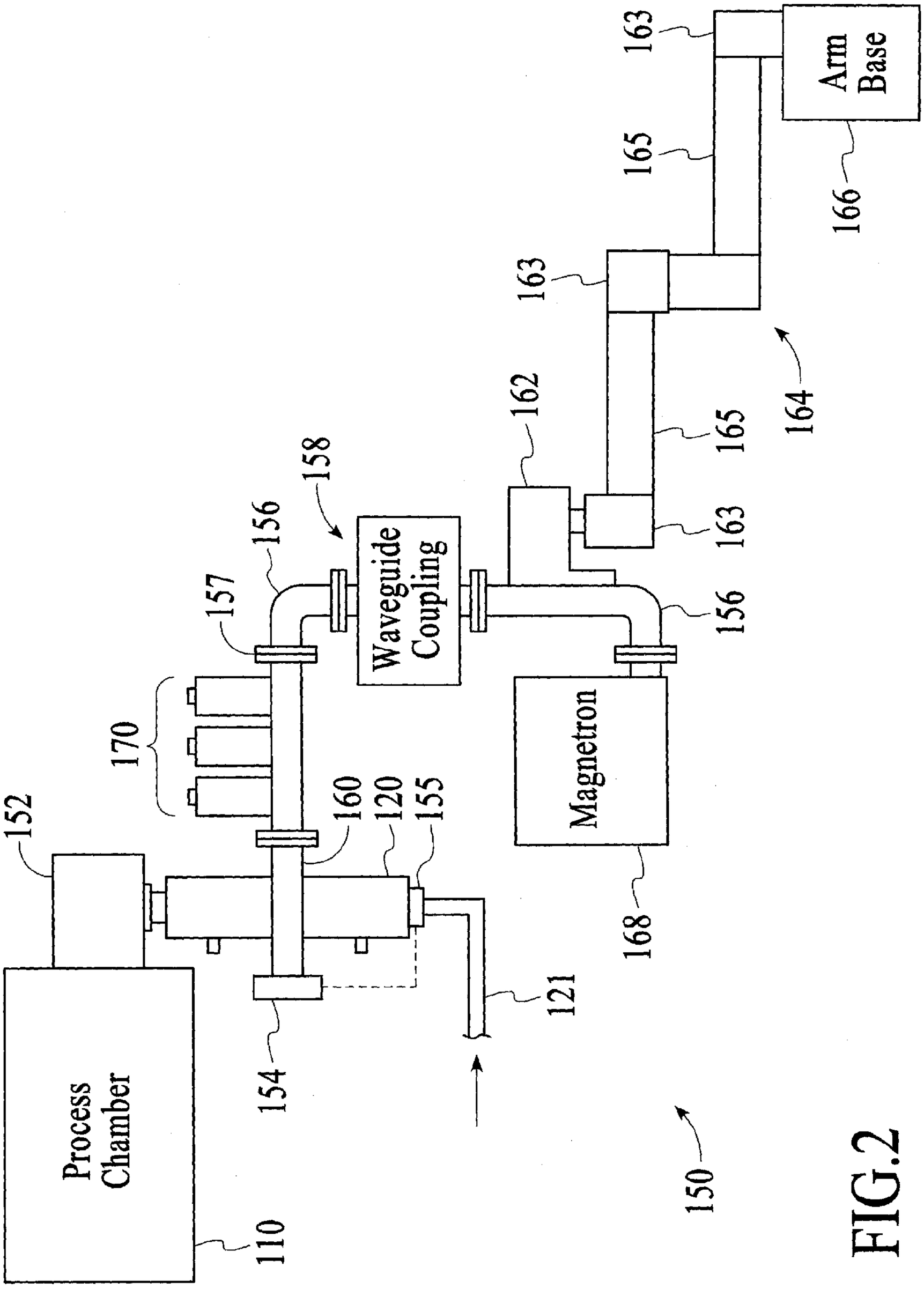
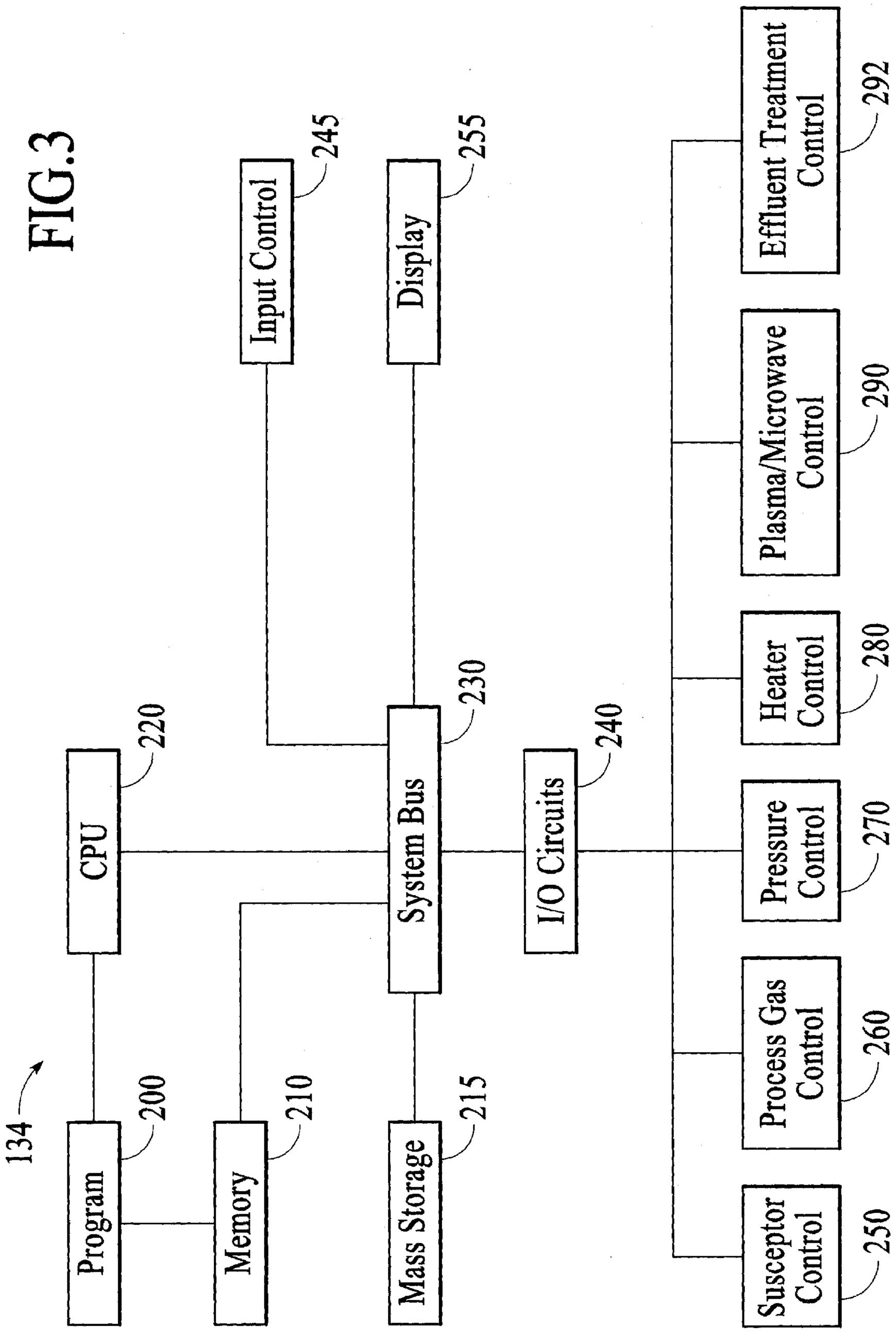

Arm Base
Waveguide Coupling
Magnetron
Process Chamber
150
152
154
155
156
157
158
160
162
163
164
165
166
168
170
120
121
110

FIG.2

FIG.3


134
CPU
220
Program
200
System Bus
230
Memory
210
Mass Storage
215
I/O Circuits
240
Input Control
245
Display
255
Effluent Treatment Control
292
Plasma/Microwave Control
290
Heater Control
280
Pressure Control
270
Process Gas Control
260
Susceptor Control
250

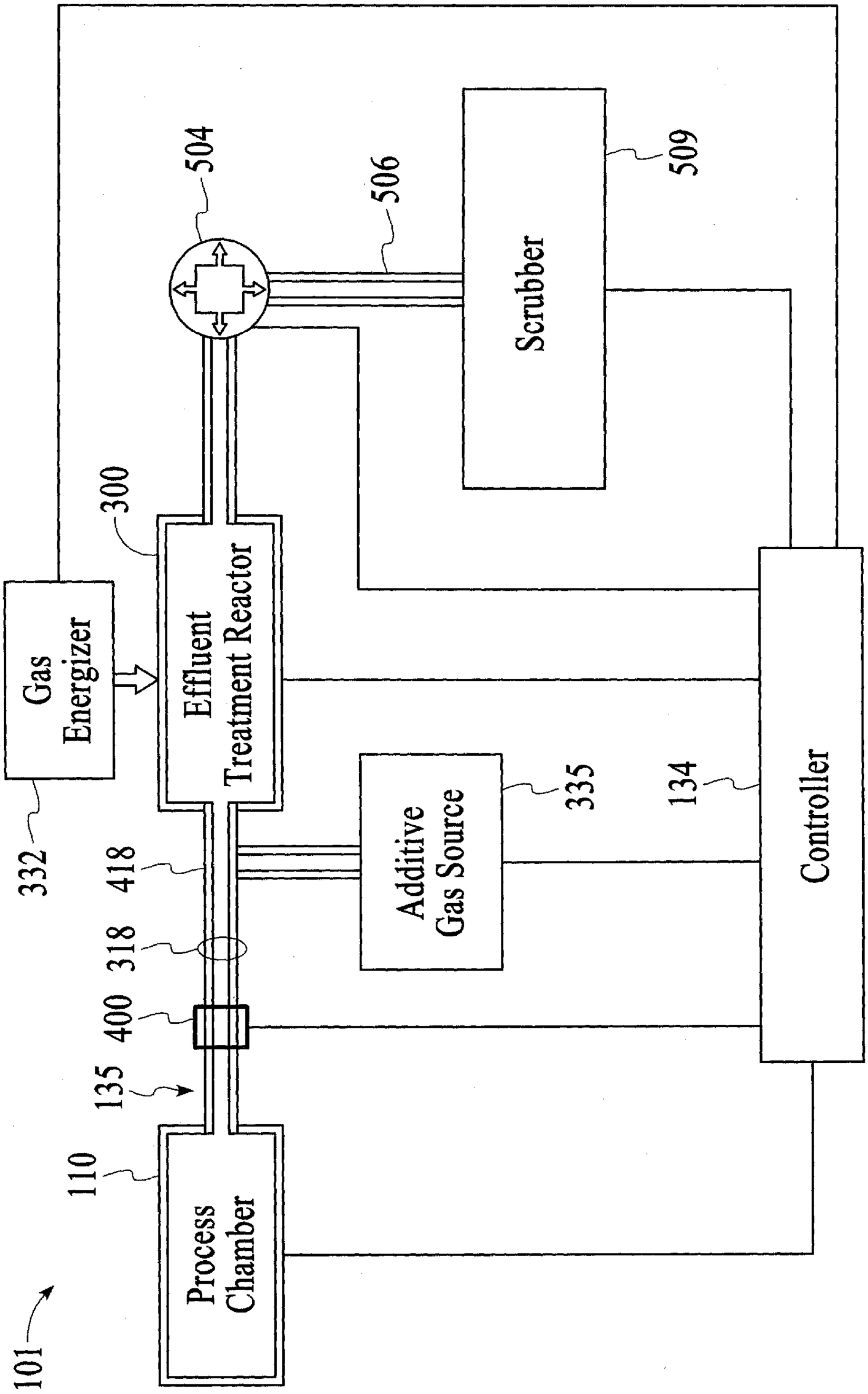

504
506
509
Scrubber
Gas Energizer
300
Effluent Treatment Reactor
332
418
318
400
135
110
Process Chamber
101
Additive Gas Source
335
134
Controller

FIG.4

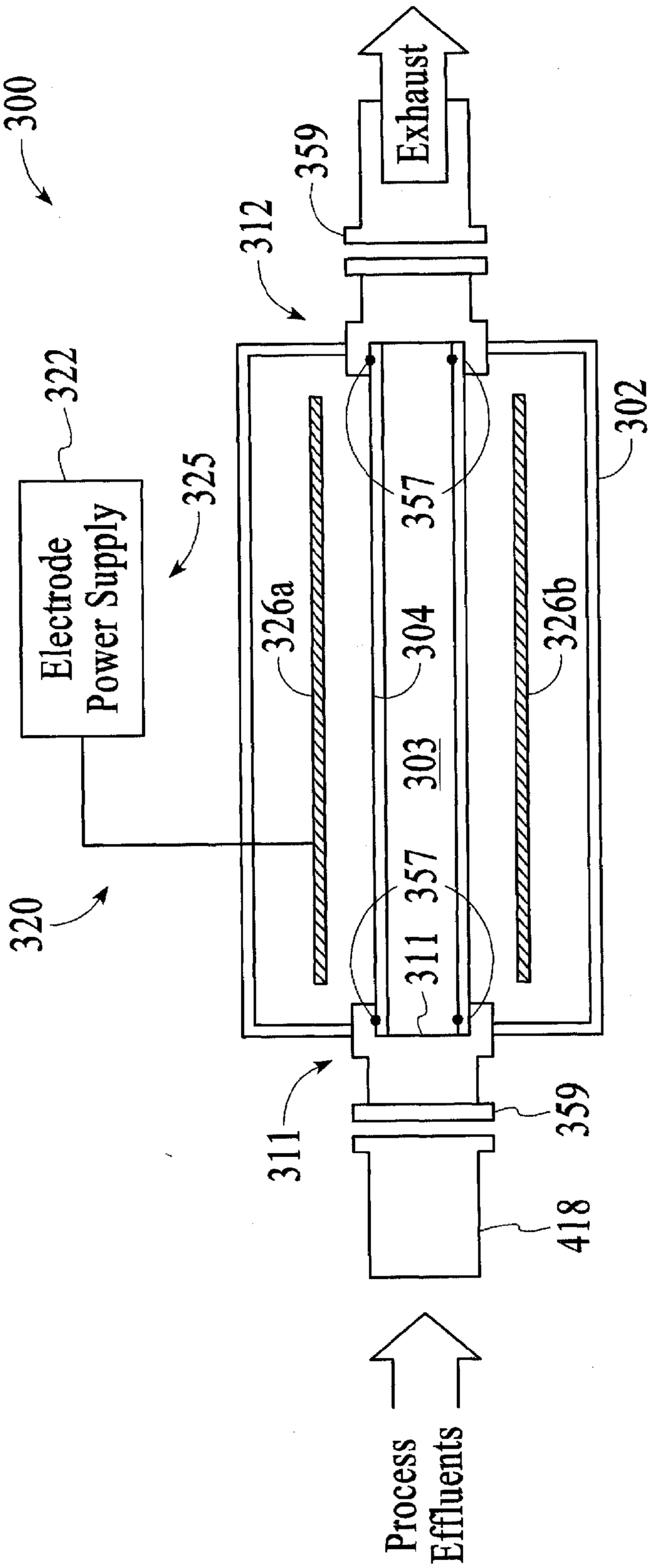

300
Exhaust
359
312
322
Electrode Power Supply
325
326a
304
326b
302
357
303
357
320
311
359
418
311
Process Effluents

FIG.5

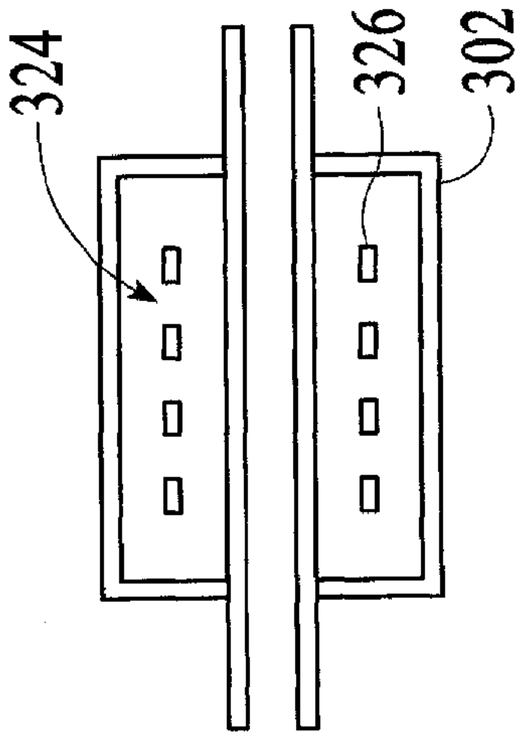

324
326
302

FIG.5A

# TREATMENT OF EFFLUENT IN THE DEPOSITION OF CARBON-DOPED SILICON

## BACKGROUND

**[0001]** Embodiments of the present invention relate to treatment of an effluent generated in the deposition of carbon-doped silicon.

**[0002]** In the manufacture of electronic circuits and displays in substrate processing chambers, a carbon-doped silicon layer which can be a low k dielectric layer having a dielectric constant of less than 3, is deposited on the substrate. The carbon-doped silicon layer is typically an amorphous and porous silicon-oxy-carbide material which may also include organic molecules. The low k dielectric deposition process uses precursor gases that include silicon-containing gases and hydrocarbon gases. The hydrocarbon precursors, include for example, polycyclic hydrocarbons, polycyclic unsaturated hydrocarbons, alkenes, alkynes arenes and arylenes. The hydrocarbons are typically not fully decomposed in the chamber and these hydrocarbons, as well as their by-products, deposit as greasy liquids and solids in the gas exhaust components of the process chamber. The deposits are especially a problem when the precursor gas contains high boiling point precursors such as terpenes, terpenenes, norbornenes, oligomeric hydrocarbons and particularly unsaturated polycyclic hydrocarbons and their fluorinated counterparts which have boiling points higher than 100° C. The exhaust deposits adversely affect the low k deposition process, degrade the components of the exhaust apparatus, and can also pose serious safety issues. Thus, it is desirable to prevent the buildup of such deposits in the exhaust system.

**[0003]** Several methods have been developed to treat the effluents of substrate processing chambers. For example, the effluent can be treated by heating the effluent gas outside the chamber to burn off undesirable gases. For example, the exhaust lines can be heated to temperatures of up to 150° C., or even to temperatures of 800 to 1100° C. Oxygen can also be added to the effluent to further react with and remove undesirable gases. However, such heating processes only partially alleviate the deposition problem, and may even cause the composition of the unreacted precursor gases and process byproducts to combine into other undesirable hazardous gases. Also, it is often difficult to heat the exhaust systems or lines to high temperatures without significant chamber modifications to maintain operator safety. Furthermore, even these high temperatures are often not effective at cleaning the deposits and leave significant amounts of deposits on the walls of the exhaust lines.

**[0004]** The substrate processing effluent can also be treated in a plasma to reduce the hazardous content of the effluent. For example, 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, discloses a gaseous treatment apparatus for treating effluent gases which uses a plasma reactor and adds inert gases and oxygen to the effluent in the reactor. However, such plasma effluent gas treatment processes are designed for treating effluent containing perfluorocarbons gases or other halogen gases and not polycyclic hydrocarbons or polymeric and oligomeric byproducts. The plasma effluent treatment processes for fluorocarbon gases are ineffective when used for unsaturated hydrocarbons and liquids and can even cause further polymerization and clogging of the exhaust lines and poses significant safety threat in operation of tools and abatement units.

**[0005]** Thus it is desirable to have an effluent treatment apparatus capable of treating effluent containing hydrocarbon gases, especially high boiling point hydrocarbon liquids and solids. It is desirable to reduce the level of hazardous and toxic materials in the effluent before releasing it to the environment.

## DRAWINGS

**[0006]** 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:

**[0007]** FIG. **1** is a schematic partial sectional side view of a processing chamber for the deposition of carbon doped silicon;

**[0008]** FIG. **2** is a schematic diagram of a remote microwave chamber for dissociation of precursor gases prior to entering the chamber of FIG. **1**;

**[0009]** FIG. **3** is a flowchart of a process control computer program product used in conjunction with the processing chamber of FIG. **1**;

**[0010]** FIG. **4** is a simplified diagram of a substrate processing apparatus comprising the process chamber of FIG. **1** and an effluent treatment reactor;

**[0011]** FIG. **5** is a schematic of an embodiment of an effluent treatment reactor with electrodes; and

**[0012]** FIG. **5**A is a schematic of another embodiment of an effluent treatment reactor with an inductor antenna.

## DESCRIPTION

**[0013]** An effluent treatment apparatus can be used to abate effluents formed in the manufacture of electronic circuits and displays in substrate processing chambers, especially when the effluent contains hydrocarbon gases, liquids and solids and halogen-containing oligomers. For example, a substrate fabrication process that generates such effluent is the deposition of carbon-doped silicon material on a substrate. An exemplary process chamber **110** capable of depositing a carbon-doped silicon, such as BLACK DIAMOND™ material, is a CVD plasma chamber such as a "DLK" chamber available from Applied Materials of Santa Clara, Calif. As shown in FIG. **1**, the chamber **110** comprises a housing **116** enclosing a process zone **115** capable of maintaining a precursor gas at a low pressure. Typically, any or all of the chamber housing **116** and components in the chamber **110** can be made out of material such as aluminum or anodized aluminum. The particular embodiment of the chamber **110** shown herein, is suitable for processing of substrates **100**, such as semiconductor wafers. An example of such a CVD processing chamber is described in U.S. Pat. No. 5,000,113, entitled "Thermal CVD/PECVD Reactor and Use for Thermal Chemical Vapor Deposition of Silicon Dioxide and In-situ Multi-step Planarized Process," issued to Wang et al. and assigned to Applied Materials, Inc., the assignee of the present invention, which is incorporated by reference herein in its entirety. Another example of such a

CVD processing chamber is described in U.S. Pat. No. 6,541,367, entitled "Very Low Dielectric Constant Plasma-Enhanced CVD Films," issued to Mandal and also assigned to Applied Materials, Inc., the assignee of the present invention, which is also incorporated by reference herein in its entirety. However, it should be noted that the effluent treatment process can be used in any other process chamber as would be apparent to one of ordinary skill in the art.

**[0014]** Referring to FIG. **1**, the housing **116** encloses a gas distributor **111** for dispersing precursor gases through perforated holes **123** into the process zone **115**. Before reaching the distributor **111**, deposition and carrier gases are input through gas lines **118** into a mixing system **119** where they are combined and then sent to manifold **111**. A liquid injection system (not shown), such as that typically used for liquid injection of TEOS, may also be provided for injecting a liquid reactant. Preferred liquid injection systems include the AMAT Gas Precision Liquid Injection System (GFLIS) and the AMAT Extended Precision Liquid Injection System (EPLIS), both available from Applied Materials, Inc. Generally, the precursor gases supply lines **118** for each of the precursor gases include (i) safety shut-off valves (not shown) that can be used to automatically or manually shut off the flow of precursor gas into the chamber **110**, and (ii) mass flow controllers (also not shown) that measure the flow of gas through the gas supply lines **118**. When toxic gases are used in the process, several safety shut-off valves are positioned on each gas supply line **118** in conventional configurations.

**[0015]** An optional remote microwave system **150**, as shown in FIG. **2**, having an applicator tube **120** may be located on the input gas line **121** for the oxidizing gas to provide additional energy that dissociates only the oxidizing gas prior to entry to the chamber **110**. The microwave applicator **120** provides power from between about 0 and about 6000 W, or even from about 0 to about 3000 W. Separate coupling of the microwave power to activate the gas avoids excessive dissociation of the silicon compounds prior to reaction with the oxidizing gas. Also, a gas distribution plate (not shown) having separate passages for the silicon compound and the oxidizing gas can also be used when microwave power is added to the oxidizing gas.

**[0016]** The microwave system **150** includes an applicator tube **120**, a plasma ignition system including an ultraviolet (UV) lamp **154** and a UV power supply **155**, a microwave waveguide system that includes various lengths of straight and curved waveguide sections **156**, waveguide coupling **158**, which may be connected together at joints **157**, an output waveguide section **160**, and a magnetron **168**. The waveguide section **156** may further have an arm support **162** formed therein for attachment to an pivoting arm **164** mounted on an arm base **166**. The pivoting arm comprises arm pieces **165** coupled to arm joints **163** that provide vertical separation of the arm pieces and allow rotational movement of the arm **164** around the arm joints **163**. The arm joints **163**, are vertically disposed cylinders coupled to one arm piece **165** at the bottom of the arm joint **163** and coupled to a second arm piece **165** at the top of the arm joint **165**. The arm pieces **165** and arm joint **163** allow vertical separation of the arm pieces and flexibility in positioning arm **164**, and thus the microwave system **150**, during operation and maintenance of the processing reactor **110**.

**[0017]** Magnetron **168** is a typical magnetron source capable of operating between about 0 and about 3000 Watts for continuous wave (CW) or pulsed output of microwaves of about 2.45 Gigahertz (GHz) frequency. Of course, other magnetrons may be utilized as well. A circulator (not shown) allows only forward microwave transmission from magnetron **168** toward applicator tube **120**. Tuning system **170**, which may use stub tuners or other tuning elements allows matching the load at waveguide section **160** to the characteristic impedance of the waveguides. Tuning system **170** may provide fixed tuning, manual tuning, or automated tuning. In the specific embodiment, the waveguide sections have rectangular cross-sections, but other types of waveguide also may be used.

**[0018]** Applicator tube **120** is a circular (or other cross-section) tube made of a composite or ceramic material, preferably alumina, or other material resistant to etching by radicals. In a specific embodiment, applicator tube **120** has a length of about 18 to 24 inches and a cross-sectional diameter of about 3 to 4 inches. Applicator tube **120** is disposed through a waveguide section **160**, which is open at one end for transmitting microwaves and is terminated at the other end with a metal wall. Microwaves are transmitted through the open end of waveguide section **160** to gases inside applicator tube **120**, which is transparent to microwaves. Of course, other materials such as sapphire also may be used for the interior of applicator tube **120**. In other embodiments, applicator tube **120** may have a metal exterior and an interior made of a composite or ceramic material wherein microwaves in waveguide section **160** enter a window through the exterior of applicator tube **120** to the exposed interior of tube **120** to energize the gases.

**[0019]** The processing that occurs in the chamber **110** includes heating the precursor gases and substrate **100**, such as by resistive heating coils (not shown) or external lamps (not shown). Referring back to FIG. **1**, substrate support **112** is mounted on a pedestal **113** so that the substrate **100**, which is seated within a pocket on the upper surface of the substrate support **112** can be controllably moved between a lower loading/off-loading position and an upper processing position which is closely adjacent to gas distributor **111**. The substrate support **112** is raised or lowered by a lift motor **114**. The lift motor **114** raises and lowers substrate support **112** between a processing position and a lower, substrate-loading position. The motor **114**, the gas mixing system **119**, and the RF power supply **125** are controlled by a system controller **134** over control lines **136**. The chamber **110** includes analog assemblies, such as mass flow controllers (MFCs) and standard or pulsed RF generators, that are controlled by the system controller **134** which executes system control software stored in a memory **210**, which in the preferred embodiment is a hard disk drive. Motors and optical sensors are used to move and determine the position of movable mechanical assemblies such as the throttle valve **133** of the vacuum pump **132** and motor **114** for positioning the substrate support **112**. When substrate support **112** and the substrate **100** are in the processing position, they are surrounded by an insulator **117** and precursor gases exhaust into a manifold **124**.

**[0020]** The deposition process performed in chamber **110** can be either a non-plasma process on a cooled substrate support **112** or a plasma enhanced process. In a plasma process, a controlled plasma is typically formed adjacent to the substrate **100** by RF energy applied to a plasma generator (not shown) from RF power supply **125** while the substrate support **112** is grounded. Alternatively, RF power can be

provided to the substrate support **112** or RF power can be provided to different components at different frequencies. RF power supply **125** can supply either single or mixed frequency RF power to enhance the decomposition of reactive species introduced into the high vacuum region. A mixed frequency RF power supply **125** typically supplies power at a high RF frequency (RF**1**) of about 13.56 MHz to the distribution manifold **111** and at a low RF frequency (RF**2**) of about 360 KHz to the substrate support **112**. The silicon oxide layers of the present invention are most preferably produced using low levels or pulsed levels of high frequency RF power. Pulsed RF power preferably provides 13.56 MHz RF power at about 20 to about 200 W during about 10% to about 30% of the duty cycle. Non-pulsed RF power preferably provides 13.56 MHz RF power at about 10 to about 150 W as described in more detail below. Low power deposition preferably occurs at a temperature range from about −20 to about 40° C. At the preferred temperature range, the deposited film is partially polymerized during deposition and polymerization is completed during subsequent curing of the film.

**[0021]** The chamber **110** also includes a gas exhaust port **135** to remove the effluent comprising unreacted processing gas and byproducts. A vacuum pump **132** having a throttle valve **133** controls the exhaust rate of gases from the chamber **110**.

**[0022]** The system controller **134** controls all of the activities of the CVD chamber and a preferred embodiment of the controller **134** includes a hard disk drive, a floppy disk drive, and a card rack. The card rack contains a single board computer (SBC), analog and digital input/output boards, interface boards and stepper motor controller boards. The system controller **134** conforms to the Versa Modular Europeans (VME) standard which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure having a 16-bit data bus and 24-bit address bus.

**[0023]** To facilitate control of the chamber **110** as described above, the controller **134** embodied in a CPU **220** may be one of any form of general purpose computer processor that can be used in an industrial setting for controlling various chambers and subprocessors. The memory **210** is coupled to the CPU **220**, and is accessible to the system bus **230**. The memory **210**, or mass storage device **215**, may be one or more of readily available memory such as random access memory (RAM), read only memory (ROM), floppy disk drive, hard disk, or any other form of digital storage, local or remote. The support circuits (not shown) are coupled to the CPU **220** for supporting the processor **220** in a conventional manner. The deposition process is generally stored in the memory **210**, typically as a software routine. The software routine may also be stored and/or executed by a second CPU (not shown) that is remotely located from the hardware being controlled by the CPU **220**.

**[0024]** The memory **210** contains instructions that the CPU **220** executes to facilitate the performance of the processing system **10**. The instructions in the memory **210** are in the form of program code such as a program **200** that implements the method of the present invention. The program code may conform to any one of a number of different programming languages. For example, the program code can be written in C, C++, BASIC, Pascal, or a number of other languages.

**[0025]** The mass storage device **215** stores data and instructions and retrieves data and program code instructions from a processor readable storage medium, such as a magnetic disk or magnetic tape. For example, the mass storage device **215** can be a hard disk drive, floppy disk drive, tape drive, or optical disk drive. The mass storage device **215** stores and retrieves the instructions in response to directions that it receives from the CPU **220**. Data and program code instructions that are stored and retrieved by the mass storage device **215** are employed by the processor unit **220** for operating the processing system. The data and program code instructions are first retrieved by the mass storage device **215** from a medium and then transferred to the memory **210** for use by the CPU **220**.

**[0026]** The input control unit **245** couples a data input device, such as a keyboard, mouse, or light pen, to the processor unit **220** via the system bus **230** to provide for the receipt of a chamber operator's inputs. The display unit **255** provides information to a chamber operator in the form of graphical displays and alphanumeric characters under control of the CPU **220**.

**[0027]** The control system bus **230** provides for the transfer of data and control signals between all of the devices that are coupled to the control system bus **230**. Although the control system bus **230** is displayed as a single bus that directly connects the devices in the CPU **220**, the control system bus **230** can also be a collection of busses. For example, the display unit **255**, input control unit **245** (with input device), and mass storage device **215** can be coupled to an input-output peripheral bus, while the CPU **220** and memory **210** are coupled to a local processor bus. The local processor bus and input-output peripheral bus are coupled together to form the control system bus **230**.

**[0028]** The system controller **134** is coupled to the elements of the processing system **220**, employed in dielectric deposition processes in accordance with the present invention via the system bus **230** and the I/O circuits **240**. The I/O circuits **240** receive instructions from the program **200** stored in memory **210** via the CPU **220** and system bus **230**. The program **200** provides program subroutines that enable the I/O circuits **240** to provide for substrate positioning control **250**, precursor gas control **260**, pressure control **270**, heater control **280**, and plasma/microwave control **290**, of the chamber **110**, and effluent treatment control **292** which controls the effluent treatment apparatus described below.

**[0029]** The CPU **220** forms a general purpose computer that becomes a specific purpose computer when executing programs such as the program **200** of the embodiment of the method of the present invention depicted in the flow diagram of FIG. **3**. Although the invention is described herein as being implemented in software and executed upon a general-purpose computer, those skilled in the art will realize that the invention could be implemented using hardware such as an application specific integrated circuit (ASIC) or other hardware circuitry. As such, it should be understood that the invention can be implemented, in whole or in part, in software, hardware or both.

**[0030]** The processing chamber **110** as described above is provided only to illustrate the invention, and should not be used to limit the scope of the invention. It will be appreciated that other suitable processing chambers can be used as well. The above CVD processing chamber description is mainly for illustrative purposes, and other plasma CVD equipment such as electrode cyclotron resonance (ECR) plasma CVD

devices, induction-coupled RF high density plasma CVD devices, or the like may be employed. Additionally, variations of the above described system such as variations in substrate support design, heater design, location of RF power connections and others are possible. For example, the substrate could be supported and heated by a resistively heated substrate support. The pretreatment and method for forming a pretreated layer of the present invention is not limited to any specific apparatus or plasma excitation method. The use of other apparatuses may be utilized while remaining within the scope of the invention.

**[0031]** Depositing a layer of carbon-doped silicon on a substrate **100** is described, for example, in U.S. Pat. No. 6,610,354 issued to Law et al., entitled "Plasma Display Panel with a Low k Dielectric Layer", which is incorporated by reference herein in its entirety. A carbon-doped silicon layer is deposited on a substrate by first loading a substrate **100** into the processing chamber **110** through a vacuum interlock (not shown) and placing the substrate **100** onto a substrate support **112** in the chamber **110**. Once the substrate **100** is properly positioned, the temperature of the substrate **100** and chamber **110** are controlled so as to maintain a processing temperature of for example, from about 0° C. to about 250° C.

**[0032]** Next, a precursor gas is introduced into the chamber **110** and then an RF power component (not shown) is applied to the precursor gas to form a plasma. The precursor gas is introduced into the processing chamber **110** from a gas distributor **111**. The precursor gases include trimethylsiliane (TMS) or methylsilane (MS) or a combination of these precursors, along with an oxygen precursor gas. In some embodiments, the precursor gas also includes an inert gas such as a gaseous source of helium (He) or argon (Ar). TMS or MS or a combination of TMS and MS is introduced into the processing chamber **110** at a flow rate of about 30-150 sccm and either $O_2$, $O_3$, $N_2O$ or some combination thereof is introduced at a flow rate of about 300-1500 sccm. Those skilled in the art recognize that the gases can be flowed sequentially or simultaneously and that the flow rates scale with the size of the chamber being used and the surface area of the substrate upon which the film is to be deposited. In addition, helium (He) may be may be introduced as a carrier gas. If used, He will be introduced into the processing chamber **110** at a rate of about 1500-8000 sccm. Generally, the gas flow rates are set such that a ratio of the sum of the flow rates of the gaseous sources of oxygen divided by the sum of the flow rates of TMS and MS will be about 2 to 50, usually about 5 to 40. If used, the ratio of He flow to the sum of the flow rates of TMS and MS will be about 10 to 260, usually about 30 to 75.

**[0033]** The chamber **110** is maintained at a pressure of about 1-15 Torr and the precursor gas is excited into a plasma state through the use of an RF power source **125** which generates a power density of about 0.10 to 0.25 $W/cm^2$. The deposition rate of the process will be at least about 350 nanometers per minute, for a flow ratio, defined by the flow rate of gaseous sources of oxygen divided by the sum of the flow rates of TMS and MS of about 10. The duration of the flow of precursor gases will be determined by the desired thickness of the layer to be deposited. After deposition of the layer, the RF power **125** is turned off, the gas flow into the chamber **110** is stopped and the gases in the chamber **110** are pumped out of the chamber **110** to form an effluent gas. The result of this process is a stable carbon-doped silicon layer having a thickness of about 10 to 15 microns having a dielectric constant of less than about 3.5, and usually between about 2.6 to 3.4. It is understood that the processing gases can be flowed concurrently or serially. It is noted that a capping layer may be omitted for a carbon-doped silicon dielectric layer.

**[0034]** In one example, the chamber **110** is used to deposit a carbon-doped silicon layer on a substrate **100** while the chamber **110** is maintained at a temperature of about 25° C. after loading the substrate. Methylsilane is flowed into the chamber **110** at about 117 sccm, $N_2O$ at about 1,235 sccm, and He gas at about 6,800 sccm. The pressure in the chamber **110** is controlled to about 3 Torr and an RF power of about 275 W used to generate the plasma for forming the carbon-doped silicon deposition layer. Processing will proceed for about 25 to 45 minutes to form a deposition layer of about 10 to 15 microns in thickness.

**[0035]** The effluent generated by the carbon-doped silicon process is treated in an effluent treatment reactor **300**. While the effluent treatment reactor **300** is described in the context of the deposition of carbon-doped silicon, it should be understood that the effluent treatment reactor **300** can be used with other substrate fabrication processes and chambers. An exemplary effluent treatment reactor **300**, as illustrated in FIG. **5**, comprises an enclosure **302** having an inlet **311** connected to an exhaust port **135** of the process chamber **110** to pass effluent generated in the process chamber **110** to the reactor **300** through gas line **418**. Gas line **418** connects to and inlet **311** and an outlet **312** of the reactor **300** with O-rings **357**. A vacuum flange **359** is located in the forline **418** before the inlet **311** and after the outlet **312**.

**[0036]** The enclosure **302** has an effluent treatment zone **303**, which is composed of a gas impermeable material, such as a ceramic or metal material. In one version, the enclosure **302** is a cylinder **304** comprising a ceramic material such as quartz (silicon dioxide) or polycrystalline aluminum oxide ($Al_2O_3$). The cylinder **304** has sufficient strength to withstand operating vacuum type pressures of $10^{-5}$ Torr. The cylinder **304** can have a diameter of at least about 5 mm, or even at least about 35 mm. Advantageously, the cylinder **304** can be linearly oriented to the direction of flow of effluent through the reactor **300** to reduce possible backflow of effluent that can occur through obstructions of the effluent path through the reactor **300**. Thus, the cylinder **304** has a longitudinal central axis that is oriented parallel to the direction of the flow path of effluent. The length of the reactor **300** is sufficiently long to allow the effluent to remain resident in the cylinder **304** for a sufficient time to abate substantially all of the hazardous gas content of the effluent. The precise length of the reactor **300** 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 aromatic hydrocarbons oligomers such as terpenenes at total flow of about 1000 sccm, a sufficient resident time is at least about 0.01 seconds, or even about 0.1 seconds. A suitable length of reactor **300** that provides such a residence time, comprises a cylindrical tube **304** having a cross-sectional diameter of 35 mm, and a length of from about 20 cm to about 50 cm.

**[0037]** In one version, a bypass valve **318** may be provided in or near the reactor **300** to control the flow of effluent into, or to bypass, the reactor **300**. The throttle valve **318** may optionally be under the control of the controller **134**. The

bypass valve **318** is a safety feature and can also be used to redirect the effluent gas flow to avoid the reactor **300**.

**[0038]** The reactor **300** receives additive gas from additive gas source **335**. The additive gas source **335** is connected to the reactor **300** via gas line **418**. Optionally, the reactor **300** may include the additive gas source **335** connected directly to reactor **300** by a conduit (not shown) and the flow of gas could be controlled with a control valve (not shown). The operation of the control valve may be under the control of a controller **134**, as will be described, or may be operated by hand.

**[0039]** The additive gas source **335** provides an additive gas to the effluent gas, before, or as after the effluent is energized, to enhance abatement of the hazardous gas emissions. When energized, the additive gas dissociates or forms energized species that react with the energized hazardous gas species to create gaseous compounds that are non-toxic, or soluble and easily removed by a wet scrubber located downstream in the exhaust apparatus **300**. The addition of even a small amount of additive gas to the effluent gas can significantly improve abatement efficiency.

**[0040]** In one example, the additive gas comprises an oxygen-containing gas, such as $O_2$ and $O_3$. The oxygen-containing gas combines with the effluent in the exhaust tube (not shown) or in the reactor **300**. In the reactor **300**, the effluent and the additive gas are energized as described above. Disassociated hazardous gases, such as terpenenes and their oligomers are oxidized in the plasma and converted to reaction products, such as $CO_2$, $CH_4$, HF, $C_3H_6$ and $H_20$, that are exhaustible or are treatable for safe exhaustion. For example, $CO_2$ can be safely exhausted and HF can be scrubbed and dissolves in water. It should be understood the other additive gases such as oxygen plasma, hydrogen plasma and water plasma having various plasma powers and flow rates may also be used to effectively break down the energized hazardous gas species.

**[0041]** 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 improved by an unexpected amount. For example, it has been discovered that when using an additive gas comprising an oxygen-containing gas the volumetric flow ratio of oxygen atoms in the additive gas to carbon atoms in the effluent **100** should be at least about 1.8:1. In one version, the volumetric flow rate of the oxygen-containing gas may be determined by comparing the stoichiometric formula of the oxygen-containing gas to the stoichiometric formula or formulae of the hydrocarbon gas or gases. A factor can be calculated by dividing the sum of the number of carbon atoms and ½ of hydrogen atoms in the hydrocarbon formula by the number of oxygen atoms in the oxygen-containing gas formula and multiplying the result by 2. This factor can then be used to determine the minimum oxygen-containing gas volumetric flow rate by multiplying the volumetric flow rate of the hydrocarbon gas by the factor.

**[0042]** For example, when the additive gas comprises $O_2$, the volumetric flow rate of the $O_2$ is determined by multiplying the volumetric flow rate of the hydrocarbon gas by the appropriate factor to reach an oxygen atom to carbon atom in the effluent ratio of at least about 1.8:1. For example, for single-carbon hydrocarbons, such as $CH_4$, the volumetric flow rate of $O_2$ is at least about 2 times the volumetric flow rate of the $CH_4$. For hydrocarbons containing two carbon atoms, such as $C_2H_6$, the volumetric flow rate of $O_2$ is at least about 2.5:1. In another version, the reactive gas in the additive gas comprises ozone, $O_3$. Since ozone contains three oxygen atoms, the minimum volumetric flow ratio of ozone to carbon atoms in the effluent for the case of $CH_4$ is 1.33:1.

**[0043]** In instances when the effluent gas comprises more than one type of hydrocarbon gas, the minimum flow rate of the reactive gas is determined by summing the minimum flow rates of reactive gas associated with each constituent of hydrocarbon gas. For example, in an effluent comprising 100 sccm of Alpha-Terpenene and 50 sccm of mDEOS, the additive comprising $O_2$ can be introduced at a flow rate of at most about (14)(100 sccm)+(8.5)(50 sscm), or about 1825 sccm oxygen or 912.5 sccm O2. At the optimum condition, at least 730 sccm O2 can be used because about half the carbon is partially oxidized to CO instead of $CO_2$.

**[0044]** The effluent treatment apparatus **300** further comprises a gas energizer **322**. The gas energizer **322** may, in one version, inductively or capacitively couple RF energy to the effluent to form charged ionized species in the reactor **300**. In the embodiment shown in FIGS. **5** and **5**A, the gas energizing system **320** comprises a gas energizer power supply **325** and an inductor antenna **324** around or adjacent to the reactor **300**. The power supply **325** may comprise an RF energy coupling system including RF source and RF match network circuits that supplies a gas energizing RF voltage to the antenna **324** to form an energized gas or plasma in the reactor chamber **300**. In an alternative arrangement, such as the one shown in FIG. **5**A, a pair of electrodes **326***a,b* can be positioned in the reactor **300** (as shown) or outside the reactor **300** (not shown) and acting on gas through a dielectric barrier. The gas energizing system **320** in this embodiment comprises a gas energizer power supply **325** that applies an RF bias voltage to one of the electrodes **326***a* and the other electrode **326***b* is maintained at a different potential, such as ground, in order to capacitively couple the electrodes **326***a,b*. The gas energizer **322** can also be a microwave coupling system similar to the one used on the process chamber **110**, or an adaptation of the same.

**[0045]** The energy applied to the effluent and additive gas is carefully controlled so that the RF radiation raises the energy of some electrons of the atoms of the effluent gas molecules to energies from 1 to 10 eV, thereby freeing electrons and breaking the bonds of the gas molecules to form dissociated atomic gaseous species. In an energized plasma gas, avalanche breakdown occurs in the gaseous stream when the individual charged species electrons and charged nuclei are accelerated in the prevalent electric and magnetic fields to collide with other gas molecules causing further dissociation and ionization of the effluent gas. The ionized or dissociated gaseous species of the energized effluent react with each other, or with other non-dissociated gaseous species, to form non-toxic gases or gases that are highly soluble in conventional gas scrubbers. For example, hydrocarbon containing effluent may be mixed with an oxygen-containing gas, such as $O_2$ gas, and passed through the reactor **215**. The gas **101** exiting the gas energizing reactor **210** has been determined to have a greater than about a 95 percent reduction of the hydrocarbon gases from the effluent **100**. Preferably, the effluent and additive gas are energized at a plasma power level of at least about 1200 watts, or even from about 100 to about 3000 watts.

**[0046]** Substrate processing apparatus **101** further comprises an infrared sensor **400** which is capable of generating

a signal upon detection of an infrared signature of a hydrocarbon gas in the effluent **400**. An infrared sensor 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 **400** is located outside of a window in the gas line **418** between the gas exhaust port **135** of the process chamber **110** and the gas inlet **311** of the effluent treatment reactor **300**. The infrared sensor **400** is capable of generating a signal upon detection of an infrared signature of a hydrocarbon gas in the effluent. This signal is then sent to the controller **134** which activates the gas energizer **322**. In one version, the infrared sensor **400** is capable of detecting an infrared signature corresponding to hydrocarbon oligomers or Alpha Terpenene or fluorinated counterparts.

**[0047]** The sensor **400** detects the light emitted by the plasma and converts it into a voltage signal. The light emitted by the plasma indicates the types and concentrations of gases in the plasma 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 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 response to be linear. The sensor 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 is a Perkin-Elmer model TPS434 NDIR gas analysis IR sensor in conjunction with correct bandpass infrared filter such as Barr Associates bandpass filter for 3-8.5 micrometer wavelength.

**[0048]** The controller **134** is used to operate both the process chamber **110** and the effluent treatment reactor **300** of the substrate processing apparatus **101**, as shown in FIG. **3**. The controller **134** comprises electronic hardware including integrated circuits that are suitable for operating both the process chamber **110** and the effluent treatment reactor **300**. The controller **134** is adapted to accept data input, run algorithms, produce date output signals, detect data signals from sensors and other chamber components, and monitor process conditions within the substrate processing apparatus **101** (FIG. **4**). The controller **134** comprises effluent treatment control **192** instruction sets which has program code to receive a signal from the infrared sensor **400** and activate the gas energizer **322** of the effluent treatment reactor **300** when the signal indicates that hydrocarbon is present in the effluent. The effluent treatment control **292** also has safety code to turn off the effluent treatment reactor should unsafe conditions occur or be measured. The program code to activate the gas energizer **322** controls the power supply which applies power to for example, the electrode or coil of the gas energizer.

**[0049]** A scrubber **509** containing a scrubbing fluid such as $H_2O$, can be provided in the apparatus **101**. The scrubbing fluid provided in the scrubber can convert reaction products in the abated effluent exiting from the process pump **504** and traveling through exhaust line **506** to exhaustible product.

**[0050]** The effluent treatment reactor **300** and gas treating process are successful in reducing the hazardous gas content of an effluent by at least about 90% in a well controlled and consistent manner. The effluent treatment reactor **300** may be a self-contained and integrated unit that is compatible with various process chambers **110**. The effluent treatment reactor **300** can be used to reduce a large variety of hazardous gases, including substantially all types of hydrocarbons. The effluent treatment reactor **300** has no impact on process chamber **110** operation and may be used with any process chamber that exhausts hazardous gases. The plasma abatement apparatus is convenient to handle and occupies less than 3 cubic feet for treating effluent from a single process chamber **110** and less than 40 cubic feet for treating effluent from multiple process chambers.

**[0051]** Although the present invention has been described in considerable detail with regard to certain preferred versions thereof, other versions are possible. For example, the additive gas source **335** and the gas energizers **322** may be interchangeable with each other. Also, the reactor **300** of the present invention can be used in other chambers and for other processes, such as physical vapor deposition and etching chambers. Therefore, the appended claims should not be limited to the description of the preferred versions contained herein.

**1**. A method of depositing carbon-doped silicon and treating an effluent comprising unreacted precursor gas and byproducts from the carbon-doped silicon deposition process, the method comprising:

(a) depositing carbon-doped silicon by exposing a substrate in a process zone to a plasma of a precursor gas comprising a hydrocarbon gas and a silicon-containing gas;

(b) exhausting from the process zone, an effluent comprising unreacted precursor gas and byproducts from the carbon-doped silicon deposition process;

(c) passing the effluent to an effluent treatment zone;

(d) introducing an additive gas comprising an oxygen-containing gas into the effluent treatment zone; and

(e) forming a plasma of the effluent and additive gas in the effluent treatment zone to treat the effluent to reduce the content of unreacted precursor gas and byproduct of the carbon-doped silicon deposition process in the effluent.

**2**. A method according to claim **1** wherein in (b), the hydrocarbon gas comprises cumene.

**3**. A method according to claim **1** wherein in (b), the precursor gas comprises cyclohexadiene.

**4**. A method according to claim **1** wherein the effluent comprises alpha-terpenene, and the additive gas comprises an oxygen-containing gas so that the ratio of oxygen atoms in the additive gas to carbon atoms in the effluent gas is at least about 1.33:1.

**5**. A method according to claim **1** wherein the additive gas comprises a halogen containing gas.

**6**. A method according to claim **1** wherein the additive gas comprises $O_2$.

**7**. A method according to claim **1** wherein the additive gas further comprises an inert or non-reactive gas.

**8**. A method according to claim **7** wherein the additive gas further comprises an inert gas so that the volumetric flow ratio of inert gas to oxygen-containing gas is 2.

**9**. A method according to claim **1** wherein in (e), the plasma power level is at least about 1200 watts.

**10**. A method according to claim **1** wherein in (e), the plasma power level is from about 100 to about 3000 watts.

**11**. A method according to claim **1** comprising performing steps (d) and (e) only when a presence of the hydrocarbon precursor in the effluent is detected.

**12**. A method according to claim **11** comprising detecting the presence of the hydrocarbon precursor by an infrared signature of the hydrocarbon precursor.

**13**. A substrate processing apparatus capable of depositing carbon-doped silicon and treating an effluent comprising unreacted precursor gas and byproducts from the carbon-doped silicon deposition process, the apparatus comprising:

(a) a process chamber comprising a housing enclosing a substrate support, a gas distributor to introduce a precursor gas into the housing, a plasma generator to form a plasma of the precursor gas, and a gas exhaust port to remove effluent comprising unreacted precursor gas and byproducts from the housing;

(b) an effluent treatment reactor comprising:

(i) an enclosure having an inlet to receive the effluent from the gas exhaust port of the process chamber,

(ii) an additive gas port through which an additive gas can be provided to the enclosure; and

(iii) a gas energizer to energize the effluent and additive gas in the enclosure;

(c) an infrared sensor capable of generating a signal upon detection of an infrared signature of a hydrocarbon gas in the effluent, the infrared sensor located outside of a window in a gas line between the gas exhaust port of the process chamber and the gas inlet of the effluent treatment reactor;

(d) a controller to operate the process chamber and effluent treatment reactor, the controller comprising effluent treatment control program code to receive the signal from the infrared sensor and activate the gas energizer of the effluent treatment reactor when the signal indicates that hydrocarbon is present in the effluent.

**14**. An apparatus according to claim **13** wherein the infrared sensor is capable of detecting an infrared signature corresponding to hydrocarbon oligomers or Alpha Terpenene or fluorinated counterparts.

**15**. An apparatus according to claim **13** wherein the gas energizer inductively or capacitively couples RF energy to the effluent.

**16**. An apparatus according to claim **13** wherein the enclosure comprises a ceramic.

**17**. An apparatus according to claim **16** wherein the ceramic is an $Al_2O_3$ cylinder.

**18**. A method according to claim **1** wherein the additive gas further comprises at least one of:

(i) an oxygen-containing gas comprising $O_2$;

(ii) a halogen containing gas;

(iii) an inert gas; and

(iv) a non-reactive gas.

* * * * *