PLASMA CATALYST

CROSS-REFERENCE OF RELATED APPLICATIONS

[001] Priority is claimed to U.S. Provisional Patent Application No. 60/378,693, filed May 8, 2002, 60/430,677, filed December 4, 2002, and No. 60/435,278, filed December 23, 2002, all of which are fully incorporated herein by reference.

FIELD OF THE INVENTION

[002] This invention relates to methods and apparatus for igniting, modulating, and sustaining plasmas from gases using plasma catalysts.

BACKGROUND OF THE INVENTION

[003] It is known that a plasma can be ignited by subjecting a gas to a sufficient amount of microwave radiation. Plasma ignition, however, is usually easier at gas pressures substantially less than atmospheric pressure. However, vacuum equipment, which is required to lower the gas pressure, can be expensive, as well as slow and energy-consuming. Moreover, the use of such equipment can limit manufacturing flexibility.

BRIEF SUMMARY OF A FEW ASPECTS OF THE INVENTION

[004] Plasma catalysts for initiating, modulating, and sustaining a plasma may be provided. The plasma catalyst can be passive or active. A passive plasma catalyst can include any object capable of inducing a plasma by deforming a local electric field (e.g., an electromagnetic field) consistent with this invention, without necessarily adding additional energy. An active plasma catalyst, on the other hand, is any particle or high energy wave packet capable of transferring a sufficient amount of energy to a gaseous atom or molecule to remove at least one electron from the gaseous atom or molecule in the presence of electromagnetic radiation. In both cases, a plasma catalyst can improve, or relax, the environmental conditions required to ignite a plasma.

[005] Method and apparatus for forming a plasma are also provided. In one embodiment consistent with this invention, the method includes flowing a gas into a multi-mode processing cavity and igniting the plasma by subjecting the gas in the cavity to electromagnetic radiation having a frequency less than about 333 GHz in the presence of at least one passive plasma catalyst comprising a material that is at least electrically semi-conductive.

[006] In another embodiment consistent with this invention, methods and apparatus are provided for igniting a plasma by subjecting a gas to electromagnetic radiation having a frequency less than about 333 GHz in the presence of a plasma catalyst comprising a powder.

[007] In yet another embodiment consistent with this invention, additional methods and apparatus are provided for forming a plasma using a dual-cavity system. The system can include a first ignition cavity and a second cavity in fluid communication with each other. The method can include: (i) subjecting a gas in the first ignition cavity to electromagnetic radiation having a frequency less than about 333 GHz, such that the plasma in the first cavity causes a second plasma to form in the second cavity, and (ii) sustaining the second plasma in the second cavity by subjecting it to additional electromagnetic radiation.

[008] Additional plasma catalysts, and methods and apparatus for igniting, modulating, and sustaining a plasma consistent with this invention are provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[009] Further aspects of the invention will be apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which like reference characters refer to like parts throughout, and in which:

[010] FIG. 1 shows a schematic diagram of an illustrative plasma system consistent with this invention;

[011] FIG. 1A shows an illustrative embodiment of a portion of a plasma system for adding a powder plasma catalyst to a plasma cavity for igniting, modulating, or sustaining a plasma in a cavity consistent with this invention;

FIG. 2 shows an illustrative plasma catalyst fiber with at least one component having a concentration gradient along its length consistent with this invention;

[012] FIG. 3 shows an illustrative plasma catalyst fiber with multiple components at a ratio that varies along its length consistent with this invention;

[013] FIG. 4 shows another illustrative plasma catalyst fiber that includes a core underlayer and a coating consistent with this invention;

[014] FIG. 5 shows a cross-sectional view of the plasma catalyst fiber of FIG. 4, taken from line 5--5 of FIG. 4, consistent with this invention;

[015] FIG. 6 shows an illustrative embodiment of another portion of a plasma system including an elongated plasma catalyst that extends through ignition port consistent with this invention;

[016] FIG. 7 shows an illustrative embodiment of an elongated plasma catalyst that can be used in the system of FIG. 6 consistent with this invention;

[017] FIG. 8 shows another illustrative embodiment of an elongated plasma catalyst that can be used in the system of FIG. 6 consistent with this invention; and

[018] FIG. 9 shows an illustrative embodiment of a portion of a plasma system for directing radiation into a radiation chamber consistent with this invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[019] This invention may relate to methods and apparatus for initiating, modulating, and sustaining a plasma for a variety of applications, including heat-treating, synthesizing and depositing carbides, nitrides, borides, oxides, and other materials, doping, carburizing, nitriding, and carbonitriding, sintering, multi-part processing, joining, decrystallizing, making and operating furnaces, gas exhaust-treating, waste-treating, incinerating, scrubbing, ashing, growing carbon structures, generating hydrogen and other gases, forming electrodeless plasma jets, plasma processing in manufacturing lines, sterilizing, cleaning, etc.

[020] This invention can be used for controllably generating heat and for plasma-assisted processing to lower energy costs and increase heat-treatment efficiency and plasma-assisted manufacturing flexibility.

[021] Therefore, a plasma catalyst for initiating, modulating, and sustaining a plasma is provided. The catalyst can be passive or active. A passive plasma catalyst can include any object capable of inducing a plasma by deforming a local electric field (e.g., an electromagnetic field) consistent with this invention without necessarily adding additional energy through the catalyst, such as by applying a voltage to create a spark. An active plasma catalyst, on the other hand, may be any particle or high energy wave packet capable of transferring a sufficient amount of energy to a gaseous atom or ion to remove at least one electron from the gaseous atom or molecule, in the presence of electromagnetic radiation.

[022] The following commonly owned, concurrently filed U.S. patent applications are hereby incorporated by reference in their entireties: U.S. Patent Application No. 10/___,___ (Atty. Docket No. 1837.0008), No. 10/___,___ (Atty. Docket No. 1837.0009), No. 10/___,___ (Atty. Docket No. 1837.0010), No. 10/___,___ (Atty. Docket No. 1837.0011), No. 10/___,___ (Atty. Docket No. 1837.0012), No. 10/___,___ (Atty. Docket No. 1837.0013), No. 10/___,___ (Atty. Docket No. 1837.0015), No. 10/___,___ (Atty. Docket No. 1837.0016), No. 10/___,___ (Atty. Docket No. 1837.0017), No. 10/___,___ (Atty. Docket No. 1837.0018), No. 10/___,___ (Atty. Docket No. 1837.0020), No. 10/___,___ (Atty. Docket No. 1837.0021), No. 10/___,___ (Atty. Docket No. 1837.0023), No. 10/___,___ (Atty. Docket No. 1837.0024), No. 10/___,___ (Atty. Docket No. 1837.0025), No. 10/___,___ (Atty. Docket No. 1837.0026), No. 10/___,___ (Atty. Docket No. 1837.0027), No. 10/___,___ (Atty. Docket No. 1837.0028), No. 10/___,___ (Atty. Docket No. 1837.0030), No. 10/___,___ (Atty. Docket No. 1837.0032), and No. 10/___,___ (Atty. Docket No. 1837.0033).

[023] Illustrative Plasma System

[024] FIG. 1 shows illustrative plasma system 10 consistent with one aspect of this invention. In this embodiment, cavity 12 is formed in a vessel that is positioned inside radiation chamber (i.e., applicator) 14. In another embodiment (not shown), the vessel 12 and radiation chamber 14 are the same, thereby eliminating the need for two separate components. The vessel in which cavity 12 is formed can include one or more radiation-transmissive insulating layers to

improve its thermal insulation properties without significantly shielding cavity 12 from the radiation.

[025] In one embodiment, cavity 12 is formed in a vessel made of ceramic. Due to the extremely high temperatures that can be achieved with plasmas consistent with this invention, a ceramic capable of operating at about 3,000 degrees Fahrenheit can be used. The ceramic material can include, by weight, 29.8% silica, 68.2% alumina, 0.4% ferric oxide, 1% titania, 0.1% lime, 0.1% magnesia, 0.4% alkalies, which is sold under Model No. LW-30 by New Castle Refractories Company, of New Castle, Pennsylvania. It will be appreciated by those of ordinary skill in the art, however, that other materials, such as quartz, and those different from the one described above, can also be used consistent with the invention.

[026] In one successful experiment, a plasma was formed in a partially open cavity inside a first brick and topped with a second brick. The cavity had dimensions of about 2 inches by about 2 inches by about 1.5 inches. At least two holes were also provided in the brick in communication with the cavity: one for viewing the plasma and at least one hole for providing the gas. The size of the cavity can depend on the desired plasma process being performed. Also, the cavity should at least be configured to prevent the plasma from rising/floating away from the primary processing region.

[027] Cavity 12 can be connected to one or more gas sources 24 (e.g., a source of argon, nitrogen, hydrogen, xenon, krypton) by line 20 and control valve 22, which may be powered by power supply 28. Line 20 may be tubing (e.g., between about 1/16 inch and about ¼ inch, such as about 1/8"). Also, if desired, a vacuum pump can be connected to the chamber to remove fumes that may be generated during plasma processing. In one embodiment, gas can flow in and/or out of cavity 12 through one or more gaps in a multi-part vessel. Thus, gas ports consistent with this invention need not be distinct holes and can take on other forms as well, such as many small distributed holes.

[028] A radiation leak detector (not shown) was installed near source 26 and waveguide 30 and connected to a safety interlock system to automatically turn off the radiation (e.g., microwave) power supply if a leak above a predefined safety

limit, such as one specified by the FCC and/or OSHA (e.g., 5 mW/cm^2), was detected.

[029] Radiation source 26, which may be powered by electrical power supply 28, directs radiation energy into chamber 14 through one or more waveguides 30. It will be appreciated by those of ordinary skill in the art that source 26 can be connected directly to cavity 12, thereby eliminating waveguide 30. The radiation energy entering cavity 12 is used to ignite a plasma within the cavity. This plasma can be substantially sustained and confined to the cavity by coupling additional radiation with the catalyst. Also, the frequency of the radiation (e.g., microwave radiation) is believed to be non-critical in many applications.

[030] Radiation energy can be supplied through circulator 32 and tuner 34 (e.g., 3-stub tuner). Tuner 34 can be used to minimize the reflected power as a function of changing ignition or processing conditions, especially after the plasma has formed because microwave power, for example, will be strongly absorbed by the plasma.

[031] As explained more fully below, the location of radiation-transmissive cavity 12 in chamber 14 may not be critical if chamber 14 supports multiple modes, and especially when the modes are continually or periodically mixed. As also explained more fully below, motor 36 can be connected to mode-mixer 38 for making the time-averaged radiation energy distribution substantially uniform throughout chamber 14. Furthermore, window 40 (e.g., a quartz window) can be disposed in one wall of chamber 14 adjacent to cavity 12, permitting temperature sensor 42 (e.g., an optical pyrometer) to be used to view a process inside cavity 12. In one embodiment, the optical pyrometer output can increase from zero volts as the temperature rises to within the tracking range.

[032] Sensor 42 can develop output signals as a function of the temperature or any other monitorable condition associated with a work piece (not shown) within cavity 12 and provide the signals to controller 44. Dual temperature sensing and heating, as well as automated cooling rate and gas flow controls can also be used. Controller 44 in turn can be used to control operation of power

supply 28, which can have one output connected to source 26 as described above and another output connected to valve 22 to control gas flow into cavity 12.

[033] The invention has been practiced with equal success employing microwave sources at both 915 MHz and 2.45 GHz provided by Communications and Power Industries (CPI), although radiation having any frequency less than about 333 GHz can be used. The 2.45 GHz system provided continuously variable microwave power from about 0.5 kilowatts to about 5.0 kilowatts. A 3-stub tuner allowed impedance matching for maximum power transfer and a dual directional coupler was used to measure forward and reflected powers. Also, optical pyrometers were used for remote sensing of the sample temperature.

[034] As mentioned above, radiation having any frequency less than about 333 GHz can be used consistent with this invention. For example, frequencies, such as power line frequencies (about 50 Hz to about 60 Hz), can be used, although the pressure of the gas from which the plasma is formed may be lowered to assist with plasma ignition. Also, any radio frequency or microwave frequency can be used consistent with this invention, including frequencies greater than about 100 kHz. In most cases, the gas pressure for such relatively high frequencies need not be lowered to ignite, modulate, or sustain a plasma, thereby enabling many plasma-processes to occur at atmospheric pressures and above.
The equipment was computer controlled using LabView 6i software, which provided real-time temperature monitoring and microwave power control. Noise was reduced by using sliding averages of suitable number of data points. Also, to improve speed and computational efficiency, the number of stored data points in the buffer array were limited by using shift-registers and buffer-sizing.

[035] The pyrometer measured the temperature of a sensitive area of about 1 cm^2, which was used to calculate an average temperature. The pyrometer sensed radiant intensities at two wavelengths and fit those intensities using Planck's law to determine the temperature. It will be appreciated, however, that other devices and methods for monitoring and controlling temperature are also available and can be used consistent with this invention. Control software that can be used consistent with this invention is described, for example, in commonly

owned, concurrently filed U.S. Patent Application No. 10/___,___ (Attorney Docket No. 1837.0033), which is hereby incorporated by reference in its entirety.

[036] Chamber 14 had several glass-covered viewing ports with radiation shields and one quartz window for pyrometer access. Several ports for connection to a vacuum pump and a gas source were also provided, although not necessarily used.

[037] System 10 also included a closed-loop deionized water cooling system (not shown) with an external heat exchanger cooled by tap water. During operation, the deionized water first cooled the magnetron, then the load-dump in the circulator (used to protect the magnetron), and finally the radiation chamber through water channels welded on the outer surface of the chamber.

[038] Plasma Catalysts

[039] A plasma catalyst consistent with this invention can include one or more different materials and may be either passive or active. A plasma catalyst can be used, among other things, to ignite, modulate, and/or sustain a plasma at a gas pressure that is less than, equal to, or greater than atmospheric pressure.

[040] One method of forming a plasma consistent with this invention can include subjecting a gas in a cavity to electromagnetic radiation having a frequency less than about 333 GHz in the presence of a passive plasma catalyst. A passive plasma catalyst consistent with this invention can include any object capable of inducing a plasma by deforming a local electric field (e.g., an electromagnetic field) consistent with this invention, without necessarily adding additional energy through the catalyst, such as by applying an electric voltage to create a spark.

[041] A passive plasma catalyst consistent with this invention can also be a nano-particle or a nano-tube. As used herein, the term "nano-particle" can include any particle having a maximum physical dimension less than about 100 nm that is at least electrically semi-conductive. Also, both single-walled and multi-walled carbon nanotubes, doped and undoped, can be particularly effective for igniting plasmas consistent with this invention because of their exceptional electrical conductivity and elongated shape. The nanotubes can have any convenient length and can be a powder fixed to a substrate. If fixed, the nanotubes can be oriented

randomly on the surface of the substrate or fixed to the substrate (e.g., at some predetermined orientation) while the plasma is ignited or sustained.

[042] A passive plasma catalyst can also be a powder consistent with this invention, and need not comprise nano-particles or nano-tubes. It can be formed, for example, from fibers, dust particles, flakes, sheets, etc. When in powder form, the catalyst can be suspended, at least temporarily, in a gas. By suspending the powder in the gas, the powder can be quickly dispersed throughout the cavity and more easily consumed, if desired.

[043] In one embodiment, the powder catalyst can be carried into the cavity and at least temporarily suspended with a carrier gas. The carrier gas can be the same or different from the gas that forms the plasma. Also, the powder can be added to the gas prior to being introduced to the cavity. For example, as shown in FIG. 1A, radiation source 52 can supply radiation to radiation cavity 55, in which plasma cavity 60 is placed. Powder source 65 provides catalytic powder 70 into gas stream 75. In an alternative embodiment, powder 70 can be first added to cavity 60 in bulk (e.g., in a pile) and then distributed in the cavity in any number of ways, including flowing a gas through or over the bulk powder. In addition, the powder can be added to the gas for igniting, modulating, or sustaining a plasma by moving, conveying, drizzling, sprinkling, blowing, or otherwise, feeding the powder into or within the cavity.

[044] In one experiment, a plasma was ignited in a cavity by placing a pile of carbon fiber powder in a copper pipe that extended into the cavity. Although sufficient radiation was directed into the cavity, the copper pipe shielded the powder from the radiation and no plasma ignition took place. However, once a carrier gas began flowing through the pipe, forcing the powder out of the pipe and into the cavity, and thereby subjecting the powder to the radiation, a plasma was nearly instantaneously ignited in the cavity.

[045] A powder plasma catalyst consistent with this invention can be substantially non-combustible, thus it need not contain oxygen or burn in the presence of oxygen. Thus, as mentioned above, the catalyst can include a metal, carbon, a carbon-based alloy, a carbon-based composite, an electrically

conductive polymer, a conductive silicone elastomer, a polymer nanocomposite, an organic-inorganic composite, and any combination thereof.

[046] Also, powder catalysts can be substantially uniformly distributed in the plasma cavity (e.g., when suspended in a gas), and plasma ignition can be precisely controlled within the cavity. Uniform ignition can be important in certain applications, including those applications requiring brief plasma exposures, such as in the form of one or more bursts. Still, a certain amount of time can be required for a powder catalyst to distribute itself throughout a cavity, especially in complicated, multi-chamber cavities. Therefore, consistent with another aspect of this invention, a powder catalyst can be introduced into the cavity through a plurality of ignition ports to more rapidly obtain a more uniform catalyst distribution therein (see below).

[047] In addition to powder, a passive plasma catalyst consistent with this invention can include, for example, one or more microscopic or macroscopic fibers, sheets, needles, threads, strands, filaments, yarns, twines, shavings, slivers, chips, woven fabrics, tape, whiskers, or any combination thereof. In these cases, the plasma catalyst can have at least one portion with one physical dimension substantially larger than another physical dimension. For example, the ratio between at least two orthogonal dimensions should be at least about 1:2, but could be greater than about 1:5, or even greater than about 1:10.

[048] Thus, a passive plasma catalyst can include at least one portion of material that is relatively thin compared to its length. A bundle of catalysts (e.g., fibers) may also be used and can include, for example, a section of graphite tape. In one experiment, a section of tape having approximately thirty thousand strands of graphite fiber, each about 2-3 microns in diameter, was successfully used. The number of fibers in and the length of a bundle are not critical to igniting, modulating, or sustaining the plasma. For example, satisfactory results have been obtained using a section of graphite tape about one-quarter inch long. One type of carbon fiber that has been successfully used consistent with this invention is sold under the trademark Magnamite®, Model No. AS4C-GP3K, by the Hexcel Corporation, of Anderson, South Carolina. Also, silicon-carbide fibers have been successfully used.

[049] A passive plasma catalyst consistent with another aspect of this invention can include one or more portions that are, for example, substantially spherical, annular, pyramidal, cubic, planar, cylindrical, rectangular or elongated.

[050] The passive plasma catalysts discussed above include at least one material that is at least electrically semi-conductive. In one embodiment, the material can be highly conductive. For example, a passive plasma catalyst consistent with this invention can include a metal, an inorganic material, carbon, a carbon-based alloy, a carbon-based composite, an electrically conductive polymer, a conductive silicone elastomer, a polymer nanocomposite, an organic-inorganic composite, or any combination thereof. Some of the possible inorganic materials that can be included in the plasma catalyst include carbon, silicon carbide, molybdenum, platinum, tantalum, tungsten, carbon nitride, and aluminum, although other electrically conductive inorganic materials are believed to work just as well.

[051] In addition to one or more electrically conductive materials, a passive plasma catalyst consistent with this invention can include one or more additives (which need not be electrically conductive). As used herein, the additive can include any material that a user wishes to add to the plasma. For example, in doping semiconductors and other materials, one or more dopants can be added to the plasma through the catalyst. See, e.g., commonly owned, concurrently filed U.S. Patent Application No. 10/___,___ (Attorney Docket No. 1837.0026), which is hereby incorporated by reference in its entirety. The catalyst can include the dopant itself, or it can include a precursor material that, upon decomposition, can form the dopant. Thus, the plasma catalyst can include one or more additives and one or more electrically conductive materials in any desirable ratio, depending on the ultimate desired composition of the plasma and the process using the plasma.

[052] The ratio of the electrically conductive components to the additives in a passive plasma catalyst can vary over time while being consumed. For example, during ignition, the plasma catalyst could desirably include a relatively large percentage of electrically conductive components to improve the ignition conditions. On the other hand, if used while sustaining the plasma, the catalyst could include a relatively large percentage of additives. It will be appreciated by

those of ordinary skill in the art that the component ratio of the plasma catalyst used to ignite and sustain the plasma could be the same.

[053] A predetermined ratio profile can be used to simplify many plasma processes. In many conventional plasma processes, the components within the plasma are added as necessary, but such addition normally requires programmable equipment to add the components according to a predetermined schedule. However, consistent with this invention, the ratio of components in the catalyst can be varied, and thus the ratio of components in the plasma itself can be automatically varied. That is, the ratio of components in the plasma at any particular time can depend on which of the catalyst portions is currently being consumed by the plasma. Thus, the catalyst component ratio can be different at different locations within the catalyst. And, the current ratio of components in a plasma can depend on the portions of the catalyst currently and/or previously consumed, especially when the flow rate of a gas passing through the plasma chamber is relatively slow.

[054] A passive plasma catalyst consistent with this invention can be homogeneous, inhomogeneous, or graded. Also, the plasma catalyst component ratio can vary continuously or discontinuously throughout the catalyst. For example, in FIG. 2, the ratio can vary smoothly forming a gradient along a length of catalyst 100. Catalyst 100 can include a strand of material that includes a relatively low concentration of a component at section 105 and a continuously increasing concentration toward section 110.

[055] Alternatively, as shown in FIG. 3, the ratio can vary discontinuously in each portion of catalyst 120, which includes, for example, alternating sections 125 and 130 having different concentrations. It will be appreciated that catalyst 120 can have more than two section types. Thus, the catalytic component ratio being consumed by the plasma can vary in any predetermined fashion. In one embodiment, when the plasma is monitored and a particular additive is detected, further processing can be automatically commenced or terminated.

[056] Another way to vary the ratio of components in a sustained plasma is by introducing multiple catalysts having different component ratios at different times or different rates. For example, multiple catalysts can be introduced at

approximately the same location or at different locations within the cavity. When introduced at different locations, the plasma formed in the cavity can have a component concentration gradient determined by the locations of the various catalysts. Thus, an automated system can include a device by which a consumable plasma catalyst is mechanically inserted before and/or during plasma igniting, modulating, and/or sustaining.

[057] A passive plasma catalyst consistent with this invention can also be coated. In one embodiment, a catalyst can include a substantially non-electrically conductive coating deposited on the surface of a substantially electrically conductive material. Alternatively, the catalyst can include a substantially electrically conductive coating deposited on the surface of a substantially electrically non-conductive material. FIGS. 4 and 5, for example, show fiber 140, which includes underlayer 145 and coating 150. In one embodiment, a plasma catalyst including a carbon core is coated with nickel to prevent oxidation of the carbon.

[058] A single plasma catalyst can also include multiple coatings. If the coatings are consumed during contact with the plasma, the coatings could be introduced into the plasma sequentially, from the outer coating to the innermost coating, thereby creating a time-release mechanism. Thus, a coated plasma catalyst can include any number of materials, as long as a portion of the catalyst is at least electrically semi-conductive.

[059] Consistent with another embodiment of this invention, a plasma catalyst can be located entirely within a radiation cavity to substantially reduce or prevent radiation energy leakage. In this way, the plasma catalyst does not electrically or magnetically couple with the vessel containing the cavity or to any electrically conductive object outside the cavity. This prevents sparking at the ignition port and prevents radiation from leaking outside the cavity during the ignition and possibly later if the plasma is sustained. In one embodiment, the catalyst can be located at a tip of a substantially electrically non-conductive extender that extends through an ignition port.

[060] FIG. 6, for example, shows radiation chamber 160 in which plasma cavity 165 is placed. Plasma catalyst 170 is elongated and extends through

ignition port 175. As shown in FIG. 7, and consistent with this invention, catalyst 170 can include electrically conductive distal portion 180 (which is placed in chamber 160) and electrically non-conductive portion 185 (which is placed substantially outside chamber 160). This configuration prevents an electrical connection (e.g., sparking) between distal portion 180 and chamber 160.

[061] In another embodiment, shown in FIG. 8, the catalyst can be formed from a plurality of electrically conductive segments 190 separated by and mechanically connected to a plurality of electrically non-conductive segments 195. In this embodiment, the catalyst can extend through the ignition port between a point inside the cavity and another point outside the cavity, but the electrically discontinuous profile significantly prevents sparking and energy leakage.

[062] Another method of forming a plasma consistent with this invention includes subjecting a gas in a cavity to electromagnetic radiation having a frequency less than about 333 GHz in the presence of an active plasma catalyst, which generates or includes at least one ionizing particle.

[063] An active plasma catalyst consistent with this invention can be any particle or high energy wave packet capable of transferring a sufficient amount of energy to a gaseous atom or molecule to remove at least one electron from the gaseous atom or molecule in the presence of electromagnetic radiation. Depending on the source, the ionizing particles can be directed into the cavity in the form of a focused or collimated beam, or they may be sprayed, spewed, sputtered, or otherwise introduced.

[064] For example, FIG. 9 shows radiation source 200 directing radiation into radiation chamber 205. Plasma cavity 210 is positioned inside of chamber 205 and may permit a gas to flow therethrough via ports 215 and 216. Source 220 directs ionizing particles 225 into cavity 210. Source 220 can be protected, for example, by a metallic screen which allows the ionizing particles to pass through but shields source 220 from radiation. If necessary, source 220 can be water-cooled.

[065] Examples of ionizing particles consistent with this invention can include x-ray particles, gamma ray particles, alpha particles, beta particles, neutrons, protons, and any combination thereof. Thus, an ionizing particle catalyst

can be charged (e.g., an ion from an ion source) or uncharged and can be the product of a radioactive fission process. In one embodiment, the vessel in which the plasma cavity is formed could be entirely or partially transmissive to the ionizing particle catalyst. Thus, when a radioactive fission source is located outside the cavity, the source can direct the fission products through the vessel to ignite the plasma. The radioactive fission source can be located inside the radiation chamber to substantially prevent the fission products (i.e., the ionizing particle catalyst) from creating a safety hazard.

[066] In another embodiment, the ionizing particle can be a free electron, but it need not be emitted in a radioactive decay process. For example, the electron can be introduced into the cavity by energizing the electron source (such as a metal), such that the electrons have sufficient energy to escape from the source. The electron source can be located inside the cavity, adjacent the cavity, or even in the cavity wall. It will be appreciated by those of ordinary skill in the art that the any combination of electron sources is possible. A common way to produce electrons is to heat a metal, and these electrons can be further accelerated by applying an electric field.

[067] In addition to electrons, free energetic protons can also be used to catalyze a plasma. In one embodiment, a free proton can be generated by ionizing hydrogen and, optionally, accelerated with an electric field.

[068] One advantage of the active and passive catalysts consistent with this invention is that they can catalyze a plasma in a substantially continual manner. A sparking device, for example, can only catalyze a plasma when a spark is present. A spark, however, is usually generated by applying a voltage across two electrodes. In general, sparks are generated periodically and separated by periods in which no spark is generated. During these non-sparking periods, a plasma is not catalyzed. Also, sparking devices, for example, normally require electrical energy to operate, although the active and passive plasma catalysts consistent with this invention do not require electrical energy to operate.

[069] Multi-mode Radiation Cavities

[070] A radiation waveguide, cavity, or chamber can be designed to support or facilitate propagation of at least one electromagnetic radiation mode. As used

herein, the term "mode" refers to a particular pattern of any standing or propagating electromagnetic wave that satisfies Maxwell's equations and the applicable boundary conditions (e.g., of the cavity). In a waveguide or cavity, the mode can be any one of the various possible patterns of propagating or standing electromagnetic fields. Each mode is characterized by its frequency and polarization of the electric field and/or the magnetic field vectors. The electromagnetic field pattern of a mode depends on the frequency, refractive indices or dielectric constants, and waveguide or cavity geometry.

[071] A transverse electric (TE) mode is one whose electric field vector is normal to the direction of propagation. Similarly, a transverse magnetic (TM) mode is one whose magnetic field vector is normal to the direction of propagation. A transverse electric and magnetic (TEM) mode is one whose electric and magnetic field vectors are both normal to the direction of propagation. A hollow metallic waveguide does not typically support a normal TEM mode of radiation propagation. Even though radiation appears to travel along the length of a waveguide, it may do so only by reflecting off the inner walls of the waveguide at some angle. Hence, depending upon the propagation mode, the radiation (e.g., microwave) may have either some electric field component or some magnetic field component along the axis of the waveguide (often referred to as the z-axis).

[072] The actual field distribution inside a cavity or waveguide is a superposition of the modes therein. Each of the modes can be identified with one or more subscripts (e.g., TE_{10} ("tee ee one zero"). The subscripts normally specify how many "half waves" at the guide wavelength are contained in the x and y directions. It will be appreciated by those skilled in the art that the guide wavelength can be different from the free space wavelength because radiation propagates inside the waveguide by reflecting at some angle from the inner walls of the waveguide. In some cases, a third subscript can be added to define the number of half waves in the standing wave pattern along the z-axis.

[073] For a given radiation frequency, the size of the waveguide can be selected to be small enough so that it can support a single propagation mode. In such a case, the system is called a single-mode system (i.e., a single-mode

applicator). The TE_{10} mode is usually dominant in a rectangular single-mode waveguide.

[074] As the size of the waveguide (or the cavity to which the waveguide is connected) increases, the waveguide or applicator can sometimes support additional higher order modes forming a multi-mode system. When many modes are capable of being supported simultaneously, the system is often referred to as highly moded.

[075] A simple, single-mode system has a field distribution that includes at least one maximum and/or minimum. The magnitude of a maximum largely depends on the amount of radiation supplied to the system. Thus, the field distribution of a single mode system is strongly varying and substantially non-uniform.

[076] Unlike a single-mode cavity, a multi-mode cavity can support several propagation modes simultaneously, which, when superimposed, results in a complex field distribution pattern. In such a pattern, the fields tend to spatially smear and, thus, the field distribution usually does not show the same types of strong minima and maxima field values within the cavity. In addition, as explained more fully below, a mode-mixer can be used to "stir" or "redistribute" modes (e.g., by mechanical movement of a radiation reflector). This redistribution desirably provides a more uniform time-averaged field distribution within the cavity.

[077] A multi-mode cavity consistent with this invention can support at least two modes, and may support many more than two modes. Each mode has a maximum electric field vector. Although there may be two or more modes, one mode may be dominant and has a maximum electric field vector magnitude that is larger than the other modes. As used herein, a multi-mode cavity may be any cavity in which the ratio between the first and second mode magnitudes is less than about 1:10, or less than about 1:5, or even less than about 1:2. It will be appreciated by those of ordinary skill in the art that the smaller the ratio, the more distributed the electric field energy between the modes, and hence the more distributed the radiation energy is in the cavity.

[078] The distribution of plasma within a processing cavity may strongly depend on the distribution of the applied radiation. For example, in a pure single

mode system, there may only be a single location at which the electric field is a maximum. Therefore, a strong plasma may only form at that single location. In many applications, such a strongly localized plasma could undesirably lead to non-uniform plasma treatment or heating (i.e., localized overheating and underheating).

[079] Whether or not a single or multi-mode cavity is used consistent with this invention, it will be appreciated by those of ordinary skill in the art that the cavity in which the plasma is formed can be completely closed or partially open. For example, in certain applications, such as in plasma-assisted furnaces, the cavity could be entirely closed. See, for example, commonly owned, concurrently filed U.S. Patent Application No. 10/___,___ (Attorney Docket No. 1837.0020), which is fully incorporated by reference herein. In other applications, however, it may be desirable to flow a gas through the cavity, and therefore the cavity must be open to some degree. In this way, the flow, type, and pressure of the flowing gas can be varied over time. This may be desirable because certain gases that facilitate plasma formation, such as argon, are easier to ignite but may not be needed during subsequent plasma processing.

[080] Mode-mixing

[081] For many applications, a cavity containing a uniform plasma is desirable. However, because microwave radiation can have a relatively long wavelength (e.g., several tens of centimeters), obtaining a uniform distribution can be difficult to achieve. As a result, consistent with one aspect of this invention, the radiation modes in a multi-mode cavity can be mixed, or redistributed, over a period of time. Because the field distribution within the cavity must satisfy all of the boundary conditions set by the inner surface of the cavity (if metallic), those field distributions can be changed by changing the position of any portion of that inner surface.

[082] In one embodiment consistent with this invention, a movable reflective surface can be located inside the radiation cavity. The shape and motion of the reflective surface should, when combined, change the inner surface of the cavity during motion. For example, an "L" shaped metallic object (i.e., "mode-mixer") when rotated about any axis will change the location or the orientation of the reflective surfaces in the cavity and therefore change the radiation distribution

therein. Any other asymmetrically shaped object can also be used (when rotated), but symmetrically shaped objects can also work, as long as the relative motion (e.g., rotation, translation, or a combination of both) causes some change in the location or orientation of the reflective surfaces. In one embodiment, a mode-mixer can be a cylinder that is rotable about an axis that is not the cylinder's longitudinal axis.

[083] Each mode of a multi-mode cavity may have at least one maximum electric field vector, but each of these vectors could occur periodically across the inner dimension of the cavity. Normally, these maxima are fixed, assuming that the frequency of the radiation does not change. However, by moving a mode-mixer such that it interacts with the radiation, it is possible to move the positions of the maxima. For example, mode-mixer 38 can be used to optimize the field distribution within cavity 14 such that the plasma ignition conditions and/or the plasma sustaining conditions are optimized. Thus, once a plasma is excited, the position of the mode-mixer can be changed to move the position of the maxima for a uniform time-averaged plasma process (e.g., heating).

[084] Thus, consistent with this invention, mode-mixing can be useful during plasma ignition. For example, when an electrically conductive fiber is used as a plasma catalyst, it is known that the fiber's orientation can strongly affect the minimum plasma-ignition conditions. It has been reported, for example, that when such a fiber is oriented at an angle that is greater than 60° to the electric field, the catalyst does little to improve, or relax, these conditions. By moving a reflective surface either in or near the cavity, however, the electric field distribution can be significantly changed.

[085] Mode-mixing can also be achieved by launching the radiation into the applicator chamber through, for example, a rotating waveguide joint that can be mounted inside the applicator chamber. The rotary joint can be mechanically moved (e.g., rotated) to effectively launch the radiation in different directions in the radiation chamber. As a result, a changing field pattern can be generated inside the applicator chamber.

[086] Mode-mixing can also be achieved by launching radiation in the radiation chamber through a flexible waveguide. In one embodiment, the

waveguide can be mounted inside the chamber. In another embodiment, the waveguide can extend into the chamber. The position of the end portion of the flexible waveguide can be continually or periodically moved (e.g., bent) in any suitable manner to launch the radiation (e.g., microwave radiation) into the chamber at different directions and/or locations. This movement can also result in mode-mixing and facilitate more uniform plasma processing (e.g., heating) on a time-averaged basis. Alternatively, this movement can be used to optimize the location of a plasma for ignition or other plasma-assisted process.

[087] If the flexible waveguide is rectangular, a simple twisting of the open end of the waveguide will rotate the orientation of the electric and the magnetic field vectors in the radiation inside the applicator chamber. Then, a periodic twisting of the waveguide can result in mode-mixing as well as rotating the electric field, which can be used to assist ignition, modulation, or sustaining of a plasma.

[088] Thus, even if the initial orientation of the catalyst is perpendicular to the electric field, the redirection of the electric field vectors can change the ineffective orientation to a more effective one. Those skilled in the art will appreciate that mode-mixing can be continuous, periodic, or preprogrammed.

[089] In addition to plasma ignition, mode-mixing can be useful during subsequent plasma processing to reduce or create (e.g., tune) "hot spots" in the chamber. When a microwave cavity only supports a small number of modes (e.g., less than 5), one or more localized electric field maxima can lead to "hot spots" (e.g., within cavity 12). In one embodiment, these hot spots could be configured to coincide with one or more separate, but simultaneous, plasma ignitions or processing events. Thus, the plasma catalyst can be located at one or more of those ignition or subsequent processing positions.

[090] Multi-location Ignition

[091] A plasma can be ignited using multiple plasma catalysts at different locations. In one embodiment, multiple fibers can be used to ignite the plasma at different points within the cavity. Such multi-point ignition can be especially beneficial when a uniform plasma ignition is desired. For example, when a plasma is modulated at a high frequency (i.e., tens of Hertz and higher), or ignited in a relatively large volume, or both, substantially uniform instantaneous striking and

restriking of the plasma can be improved. Alternatively, when plasma catalysts are used at multiple points, they can be used to sequentially ignite a plasma at different locations within a plasma chamber by selectively introducing the catalyst at those different locations. In this way, a plasma ignition gradient can be controllably formed within the cavity, if desired.

[092] Also, in a multi-mode cavity, random distribution of the catalyst throughout multiple locations in the cavity increases the likelihood that at least one of the fibers, or any other passive plasma catalyst consistent with this invention, is optimally oriented with the electric field lines. Still, even where the catalyst is not optimally oriented (not substantially aligned with the electric field lines), the ignition conditions are improved.

[093] Furthermore, because a catalytic powder can be suspended in a gas, it is believed that each powder particle may have the effect of being placed at a different physical location within the cavity, thereby improving ignition uniformity within the cavity.

[094] Dual-Cavity Plasma Igniting/Sustaining

[095] A dual-cavity arrangement can be used to ignite and sustain a plasma consistent with this invention. In one embodiment, a system includes at least a first ignition cavity and a second cavity in fluid communication with the first cavity. To ignite a plasma, a gas in the first ignition cavity can be subjected to electromagnetic radiation having a frequency less than about 333 GHz, optionally in the presence of a plasma catalyst. In this way, the proximity of the first and second cavities may permit a plasma formed in the first cavity to ignite a plasma in the second cavity, which may be sustained with additional electromagnetic radiation.

[096] In one embodiment of this invention, the first cavity can be very small and designed primarily, or solely for plasma ignition. In this way, very little microwave energy may be required to ignite the plasma, permitting easier ignition, especially when a plasma catalyst is used consistent with this invention.

[097] In one embodiment, the first cavity may be a substantially single mode cavity and the second cavity is a multi-mode cavity. When the first ignition cavity only supports a single mode, the electric field distribution may strongly vary

within the cavity, forming one or more precisely located electric field maxima. Such maxima are normally the first locations at which plasmas ignite, making them ideal points for placing plasma catalysts. It will be appreciated, however, that when a plasma catalyst is used, it need not be placed in the electric field maximum and, many cases, need not be oriented in any particular direction.

[098] In the foregoing described embodiments, various features are grouped together in a single embodiment for purposes of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the following claims are hereby incorporated into this Detailed Description of Embodiments, with each claim standing on its own as a separate preferred embodiment of the invention.

WE CLAIM:

1. A method of forming a plasma comprising:

flowing a gas into a multi-mode processing cavity; and

igniting the plasma by subjecting the gas in the cavity to electromagnetic radiation having a frequency less than about 333 GHz in the presence of at least one passive plasma catalyst comprising a material that is at least electrically semi-conductive.

2. The method of claim 1, wherein the material comprises at least one of metal, inorganic material, carbon, carbon-based alloy, carbon-based composite, electrically conductive polymer, conductive silicone elastomer, polymer nanocomposite, organic-inorganic composite, and any combination thereof.

3. The method of claim 2, wherein the material is in the form of at least one of a nano-particle, a nano-tube, a powder, a dust, a flake, a fiber, a sheet, a needle, a thread, a strand, a filament, a yarn, a twine, a shaving, a sliver, a chip, a woven fabric, a tape, a whisker, and any combination thereof.

4. The method of claim 3, wherein the material comprises carbon fiber.

5. The method of claim 1, wherein the material comprises carbon and is in the form of at least one of a nano-particle, a nano-tube, a powder, a dust, a flake, a fiber, a sheet, a needle, a thread, a strand, a filament, a yarn, a twine, a shaving, a sliver, a chip, a woven fabric, a tape, a whisker, and any combination thereof.

6. The method of claim 1, wherein the material comprises at least one nano-tube.

7. The method of claim 1, wherein the material is at least partially coated with a second material.

8. The method of claim 1, wherein the at least one passive plasma catalyst comprises a plurality of elongated, electrically conductive items distributed in differing locations in the cavity.

9. The method of claim 8, wherein the radiation has electric field lines, wherein each of the elongated items has a longitudinal axis, and wherein the longitudinal axes are not substantially aligned with the electric field lines.

10. The method of claim 1, wherein the plasma catalyst comprises at least one electrically conductive component and at least one additive in a ratio, the method further comprising sustaining the plasma, wherein the sustaining comprises:

directing additional electromagnetic radiation into the cavity; and

allowing the catalyst to be consumed by the plasma such that the plasma contains the at least one additive.

11. The method of claim 10, wherein the ratio differs for differing portions of the catalyst, and wherein the allowing comprises allowing the differing portions of the catalyst to be consumed by the plasma at differing times such that the plasma contains a varying ratio of the electrically conductive component to the at least one additive.

12. The method of claim 1, wherein the multi-mode cavity is configured to support at least a first mode and a second mode of the radiation, each of the modes having a maximum electric field vector in the cavity, each of the vectors having a magnitude, and wherein a ratio between the first mode magnitude and the second mode magnitude is less than about 1:10.

13. The method of claim 12, wherein the ratio is less than about 1:5.

14. The method of claim 13, wherein the ratio is less than about 1:2.

15. The method of claim 14, wherein the multi-mode cavity is configured to support at least a first mode and a second mode of the radiation, each of the modes having at least one maximum electric field vector in the cavity at a position, the method further moving each of the positions by mode-mixing.

16. The method of claim 1, wherein the igniting comprises igniting the plurality of plasma catalysts at differing locations in the cavity

17. The method of claim 1, wherein the cavity is in a radiation chamber and the catalyst is located entirely within the chamber such that the catalyst does not substantially conduct an electrical current to the chamber nor to any electrically conductive object located outside the chamber.

18. The method of claim 1, wherein the catalyst is located at the tip of a substantially electrically non-conductive extender that passes through an ignition port formed in a radiation chamber.

19. The method of claim 1, wherein the catalyst comprises a plurality of discontiguous segments separated by and mechanically connected to a plurality of electrically non-conductive segments, wherein during the igniting the catalyst extends through an ignition port in the cavity between a location inside the cavity and another location outside the cavity.

20. The method of claim 1, wherein the igniting comprises igniting the plasma while the catalyst is suspended in the cavity.

21. A method of forming a plasma comprising igniting a plasma by subjecting a gas to electromagnetic radiation having a frequency less than about 333 GHz in the presence of a plasma catalyst comprising a powder.

22. The method of claim 21, wherein the subjecting occurs in a chamber, the method further comprising flowing a gas into the chamber.

23. The method of claim 21, wherein the subjecting occurs in a cavity, located in the chamber.

24. The method of claim 23, wherein the chamber is a multi-mode chamber.

25. The method of claim 21, further comprising introducing the powder to the radiation using a carrier gas.

26. The method of claim 21, further comprising introducing the powder to the radiation by a technique that at least temporarily suspends the powder in the cavity, the technique being at least one of feeding, gravity feeding, conveying, drizzling, sprinkling, and blowing.

27. The method of claim 21, further comprising introducing the powder into a cavity through a plurality of ignition ports.

28. The method of claim 21, wherein the igniting comprises igniting the plasma while the powder is suspended.

29. The method of claim 21, wherein the plasma catalyst comprises a non-combustible material.

30. The method of claim 29, wherein the plasma catalyst is at least one of metal, carbon, carbon-based alloy, carbon-based composite, electrically conductive polymer, conductive silicone elastomer, polymer nanocomposite, and organic-inorganic composite.

31. A method of forming a plasma comprising subjecting a gas in a cavity to electromagnetic radiation having a frequency less than about 333 GHz in the presence of an active plasma catalyst comprising at least one ionizing particle.

32. The method of claim 31, wherein the at least one ionizing particle comprises a beam of particles.

33. The method of claim 31, wherein the particle is at least one of an x-ray particle, a gamma ray particle, an alpha particle, a beta particle, a neutron, and a proton.

34. The method of claim 31, wherein the at least one ionizing particle is a charged particle.

35. The method of claim 31, wherein the ionizing particle comprises a radioactive fission product.

36. The method of claim 35, wherein a cavity is formed in a vessel that is at least partially transmissive to the product, the method further comprising positioning a radioactive fission source outside the cavity such that the source directs the fission product through the vessel into the cavity.

37. The method of claim 35, wherein the vessel and the radioactive fission source are inside a radiation chamber, and wherein the chamber comprises a material that substantially prevents the product from escaping the chamber.

38. The method of claim 35, further comprising positioning a radioactive fission source in a cavity, wherein the source generates the at least one fission product.

39. The method of claim 31, wherein the ionizing particle is a free electron, the method further comprising generating the electron by energizing an electron source.

40. The method of claim 39, wherein the energizing comprises heating the electron source.

41. The method of claim 31, wherein the particle comprises a free proton, the method further comprising generating the free proton by ionizing hydrogen.

42. The method of claim 31, wherein the cavity is at least partially open, permitting the gas to flow therethrough.

43. A method of forming a plasma in a system, wherein the system has at least a first ignition cavity and a second cavity in fluid communication with the first cavity, the method comprising:

subjecting a gas in the first ignition cavity to electromagnetic radiation having a frequency less than about 333 GHz, such that the plasma in the first cavity causes a plasma to form in the second cavity; and

sustaining the second plasma by subjecting it to additional electromagnetic radiation.

44. The method of claim 43, wherein the subjecting comprises exposing the gas to the radiation in the presence of a plasma catalyst.

45. The method of claim 43, wherein the first cavity is smaller than the second cavity.

46. The method of claim 45, wherein the first cavity is substantially a single mode cavity and the second cavity is a multi-mode cavity.

47. The method of claim 46, wherein the second cavity is highly moded.

48. The method of claim 44, wherein the plasma catalyst comprises carbon fiber.