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Boom

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[54] **METHOD FOR PLASMA TREATMENT OF SUBSTRATES**

[75] Inventor: **Abraham A. Boom,** Martinsville, N.J.

[73] Assignee: **Celanese Corporation,** New York, N.Y.

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[21] Appl. No.: **292,348**

Related U.S. Application Data

[62] Division of Ser. No. 171,282, Aug. 12, 1971, Pat. No. 3,723,289.

[52] **U.S. Cl.**..... **250/325,** 204/164, 250/492, 250/539

[51] **Int. Cl.**..... **G01n 23/00,** H01j 37/00

[58] **Field of Search**..... 204/164, 165, 168; 250/324, 325, 326, 492, 531, 532, 539; 317/4, 262 A

[56] **References Cited**

UNITED STATES PATENTS

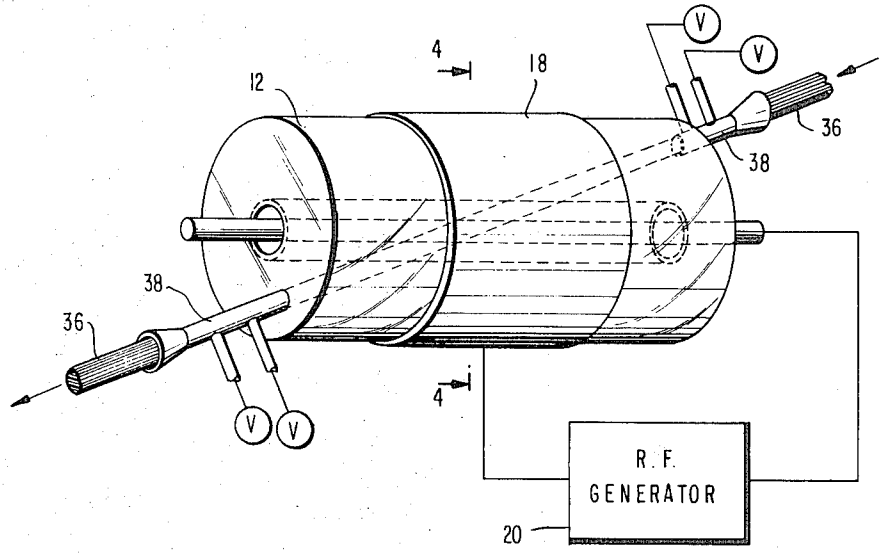
2,939,956	6/1960	Parks	250/324
2,977,475	3/1961	Kassenbeck	250/324
2,985,573	5/1961	Cherrier et al.	204/164
3,655,438	4/1972	Sterling et al.	250/531

Primary Examiner—William F. Lindquist

[57] **ABSTRACT**

A method and apparatus for efficiently generating a gaseous plasma particularly for the treatment of substrates. A radio frequency electrical signal is applied to two electrodes disposed exteriorly of an electrically insulative, gas impervious envelope. A central passage extends into the envelope and one electrode is disposed in the central passage. The electrodes are separated at least in part by the envelope and the radio frequency signal applied to the electrodes excites the gas within the envelope to thereby generate a gaseous plasma therein. The gas conditions within the envelope differ from the gas conditions exteriorly thereof and the amplitude of the radio frequency signal is insufficient to generate a plasma outside the chamber defined by the envelope. Since the plasma does not contact the electrodes, efficiency is maximized and the plasma is not contaminated by the electrodes. In addition, the surface areas of the electrodes differ substantially thereby creating a plasma within the envelope which varies in concentration in a predetermined manner, with the concentration being greatest near the center of the envelope. A substrate may therefore be contacted by varying plasma concentration as it passes through the envelope and the outer wall of the envelope is not contaminated by the plasma. A vacuum lock for preventing gas leakage into the envelope is also disclosed.

3 Claims, 8 Drawing Figures



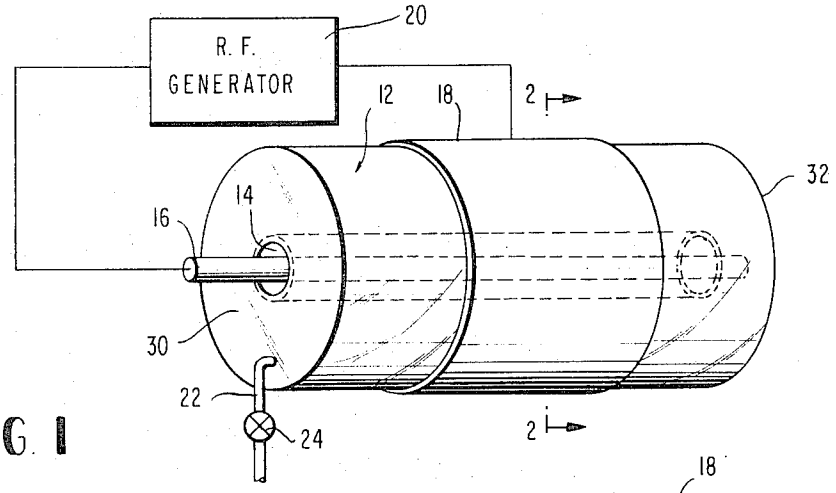


FIG. 1

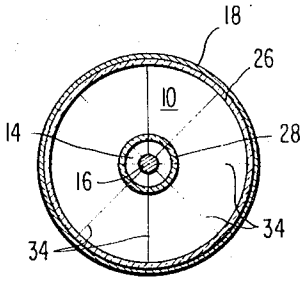


FIG. 2

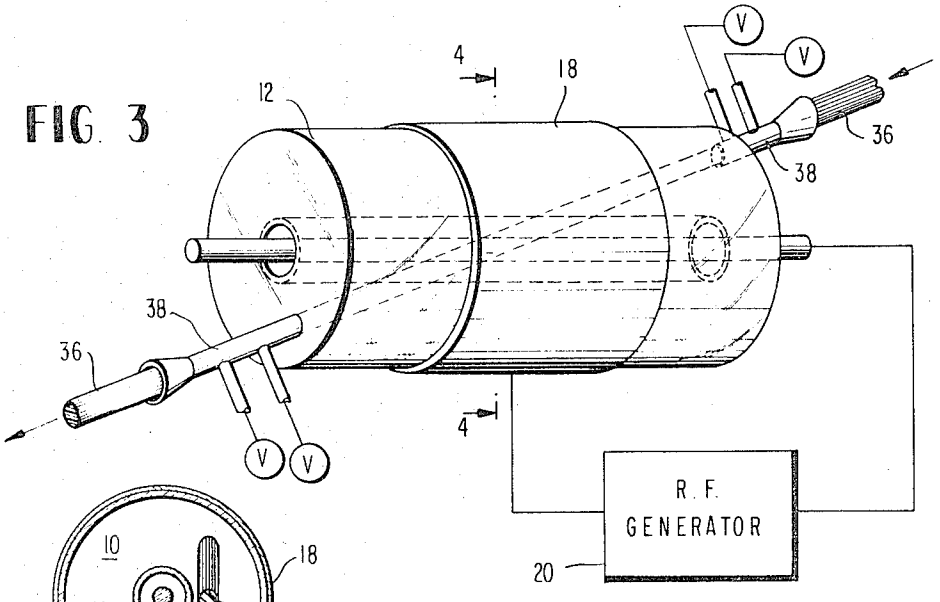


FIG. 3

FIG. 4

FIG. 5

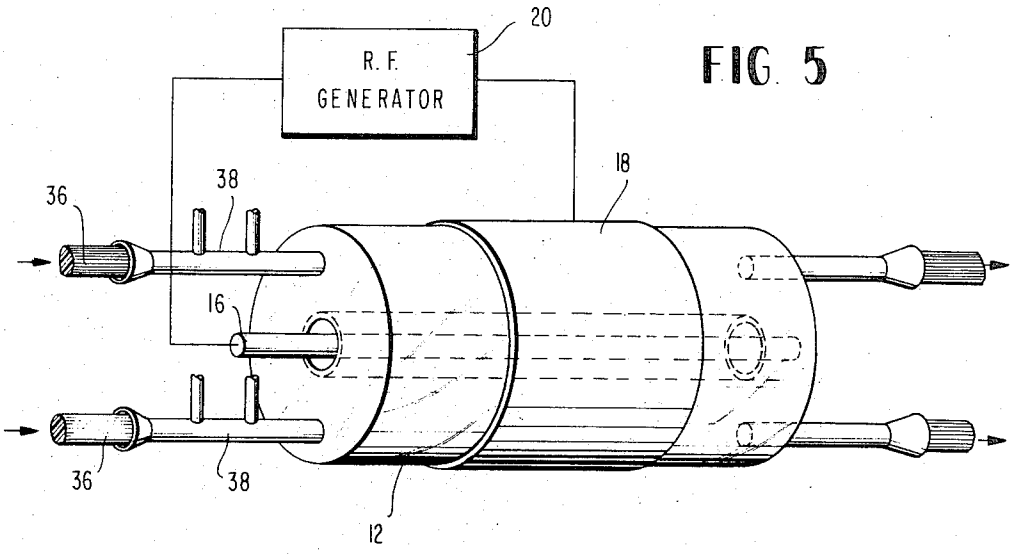
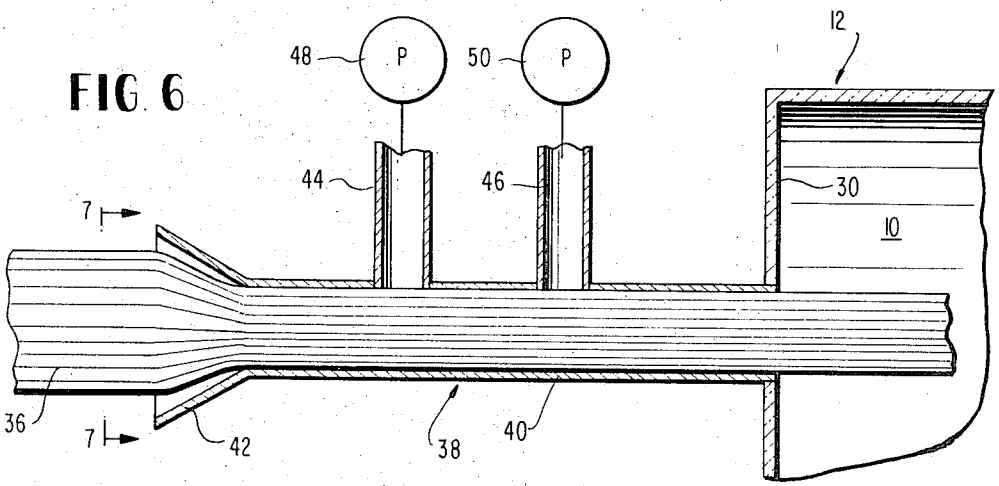


FIG. 6



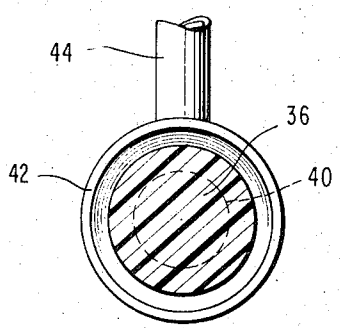


FIG. 7(A)

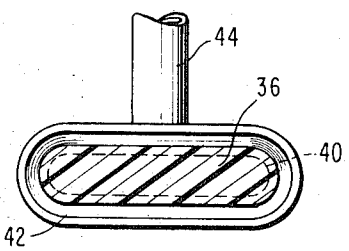


FIG. 7(B)

METHOD FOR PLASMA TREATMENT OF SUBSTRATES

This is a division of application Ser. No. 171,282 filed Aug. 12, 1971, now issued as U.S. Pat. No. 3,723,289 and assigned to the assignee hereof.

BACKGROUND OF THE INVENTION

The present invention relates to a method for treating substrates and specifically to a method for more efficiently generating a plasma for the treatment of substrates and for subjecting a substrate to varying plasma concentrations during the treatment thereof.

Various substrates have been treated in gaseous plasmas to obtain desired substrate characteristics. An example of one such process is disclosed and claimed in U.S. Pat. application Ser. No. 93,350 filed Nov. 27, 1970, by Forschirm et al for "Surface Modification of Organic Polymeric Materials" and assigned to the assignee of the present invention. In the Forschirm et al application, an organic polymeric fiber is introduced into a gaseous plasma for modification of the surface thereof. For example, a polymeric continuous filament yarn may be exposed to a gaseous plasma formed by exciting argon or other suitable gases at a pressure of about 2 mm Hg. with a 4 megahertz, 1,000 watt radio frequency signal, to modify the yarn to obtain desirable surface characterisitcs.

Another process for treating fibers in a gaseous plasma is disclosed and claimed in U.S. Pat. application Ser. No. 88,358 filed Nov. 10, 1970, for "Vapor Phase Boron Deposition by Pulse Discharge" by Kenneth C. Hou and assigned to the assignee of the present invention. In the Hou process, a boron coating is deposited on a suitable substrate by generating a boron-hydrogen excited gas species or plasma and contacting the substrate with the plasma. The plasma is generated by applying pulsed high frequency electrical power to a gaseous mixture of boron and hydrogen at a pressure of about 1 to 3 atmospheres. For example, a 3,000 volt peak-to-peak a.c. signal having a frequency of 13.6 megahertz in pulses of 100 microseconds duration at a pulse repetition rate of 1 kilohertz may be utilized to excite the gaseous mixture within a coating zone into which the substrate is introduced to provide a smooth, firmly adhering layer of boron 1 to 2 mils in thickness.

Carbonaceous fibrous materials have been treated in plasmas as is described in U.S. Pat. application Ser. No. 99,169 filed Dec. 17, 1970, for "Surface Modification of Carbon Fibers," by Kenneth C. Hou and assigned to the assignee of the present invention. In this Hou process, a carbonaceous fibrous material is contacted for a brief time with an excited gas species generated by applying high frequency electrical energy in pulsed form to a gaseous mixture of a monotonic inert gas and a surface modification gas. For example, a carbonaceous yarn may be passed through a gaseous mixture of helium and oxygen wherein the oxygen is present in the mixture in a concentration of about 0.5 percent by weight. A 3 kilovolt peadk-to-peak a.c. signal having a frequency of 13.56 megahertz may be utilized to excite the gaseous mixture thereby contacting the yarn with the excited gas species to modify the surface thereof.

In the above-described processes, the excited gas species or plasma is generated by electrically exciting

the gas or gaseous mixture. For example, energy may be imparted to gas capacitively and a plasma thereby generated. The plasma is highly electrically conductive and a high conduction current flows between the capacitor plates or electrodes because of the resultant decrease in the electrical resistance of the gas between the electrodes. In the treatment of fibers for commercial uses, the cost of the power required to generate the plasma becomes an important factor.

It is desirable to keep current flow to a minium since the efficiency of the processes decreases and the cost of treating fibers increases with an increase in current. In addition, the amount of wasted power in transmission lines will be reduced as current requirements decrease. Moreover, by providing control of the location of the major concentration of the generated plasma, the plasma may be utilized in a more efficient manner.

The cost of treating substrates may also be dependent upon the length of time during which a reaction chamber may be operated without shutdown for maintenance. It may be necessary to frequently change the gas within the chamber if the gas is contaminated by the electrodes. Also, the useful life of the reaction chamber may be adversely affected by material buildup on the walls thereof during the treatment operation.

It is therefore an object of the present invention to provide a novel method and apparatus for more efficiently generating a plasma.

It is a further object of the present invention to provide a novel method for generating a plasma within a reaction chamber for the treatment of fibers.

It is another object of the present invention to provide a novel method for reducing the current flow between electrodes in a capacitive plasma generator, and particularly in chambers adapted for the treatment of fibers.

It is still another object of the present invention to provide a novel method wherein contamination of the plasma by the electrodes is prevented.

It is yet a further object of the present invention to provide a novel method wherein contamination of the interior walls defining the chamber is minimized.

In some applications utilizing the present invention, it is desirable to selectively expose a substrate to a plasma to achieve selectable surface modification or coating of the substrate. For example, the amount of time during which the substrate is exposed to the plasma may be selectively varied to provide the desired end product. This may be accomplished through control of the speed at which the substrate passes through the plasma, assuming that other conditions remain constant.

Moreover, other conditions to which the substrate is subjected within a plasma reaction chamber may have an effect on the resultant treated substrate. The substrate may, for example, be adversely affected by excess heat or the sudden exposure to high temperatures. It may therefore be desirable to expose the substrate to the plasma in a controllable manner.

It is therefore yet another object of the present invention to provide a novel method for selectively exposing a substrate to a plasma.

It is still a further object of the present invention to provide a novel method for selectively exposing the substrate to varying concentrations of a plasma within a reaction chamber.

These and other objects of the present invention will become apparent to one skilled in the art to which the invention pertains from a perusal of the following description when read in conjunction with the appended drawings.

THE DRAWINGS

FIG. 1 is a schematic representation of a reaction chamber embodying the present invention;

FIG. 2 is a view in cross section of the reaction chamber of FIG. 1, taken along the line 2—2;

FIG. 3 is a schematic representation of the reaction chamber of FIG. 1 with a substrate being treated therein;

FIG. 4 is a view in cross section of the reaction chamber of FIG. 3, taken along the line 4—4;

FIG. 5 is a schematic representation of a reaction chamber similar to the chamber shown in FIG. 3 with a plurality of substrates being treated therein;

FIG. 6 is a view in partial cross section of the reaction chamber of FIG. 5 illustrating the vacuum lock of the present invention; and,

FIGS. 7A and 7B are end views of the vacuum lock of FIG. 6, taken along the line 7—7 thereof, and illustrate two of the alternative shapes which the vacuum lock may have.

DETAILED DESCRIPTION

Referring to FIGS. 1 and 2 wherein a preferred embodiment of a reaction chamber constructed in accordance with the present invention is illustrated, a reaction chamber 10 is formed by a substantially gas impervious, generally electrically non-conductive or insulative envelope 12 into which a central passage 14 extends. An electrode 16 extends into the central passage 14 and is isolated from the chamber 10 by the radially inward wall of the envelope 12. An electrode 18 is disposed radially outward of the envelope 12, and is separated at least in part from the centrally disposed electrode by at least a portion of the envelope 12, thereby defining an area within the envelope 12, i.e., at least a portion of the chamber 10, which is disposed between the electrodes 16 and 18.

A high frequency electrical potential is applied between the electrodes 16 and 18 from a suitable source such as a variable frequency and amplitude radio frequency (FR) generator 20 to thereby subject the chamber as defined by the envelope 12 between the electrodes 16 and 18 to a selectable time varying electrical field. A suitable fill tube 22 may be provided communicating with the chamber 10 through the envelope 12 and having a valve or other suitable closure means 24 therein to selectively control the nature and pressure of the gas within the envelope 12.

With continued reference to FIGS. 1 and 2, the envelope 12 defining the chamber 10 preferably comprises an outer elongated hollow glass cylindrical member 26, an inner elongated hollow glass cylindrical member 28, and apertured end plates 30 and 32 sealed therebetween in a suitable conventional manner. The cylindrical member 28 illustrated is substantially coextensive with the member 26 and is disposed in telescoping relationship thereto coaxially within the member 26 to define a chamber annular in cross section as is shown in FIG. 2.

The central electrode 16 is preferably an elongaged metallic cylindrical member, e.g., a wire, telescoped within the central passage 14, but may be hollow. The outer electrode 18 is preferably a hollow cylindrical electrically conductive member circumferentially disposed round at least a portion of the insulative member 26 and may, for example, be a metallic foil conformed to the radially outer surface of the envelope. The central electrode 16 preferably extends axially into the central passage 14 sufficiently so that an elongated annular portion of the chamber 10 is located between the electrodes 16 and 18.

The application of a potential between the electrodes 16 and 18 creates an electric field between these electrodes, as is indicated by the lines 34 in FIG. 2. The electrode configuration, i.e., the relative positions of the electrode and the relative dimensions thereof, cause the electric field to be more concentrated or dense in the vicinity of the central electrode 16 near the axis of the annular chamber 10.

If the intensity of the electric field is sufficient, the gas in the chamber 10 will be excited sufficiently to create a gaseous plasma in the chamber. The plasma generally comprises highly reactive species such as ions, electrons and neutral fragmented particles in highly excited states. Since the exciting of the gas by the electric field creates the plasma, the plasma concentration of density generally conforms to the electric field concentration or density. Thus, the concentration or density of the plasma generated within the gas impervious envelope 12 varies between the outer cylindrical member 26 and the inner cylindrical member 28 in a manner related to the electric field concentration of density.

The plasma is thereby concentrated around the inner cylindrical member 28 rather than being dispersed evenly throughout the chamber 10. This central concentration permits more efficient utilization of the plasma for treating substrates and permits selective exposure of the substrate to the plasma as will hereinafter be described. In addition, this central concentration of the plasma prevents excessive buildup of material on the inner wall of the outer cylindrical member 26.

The relationship between the gas conditions within the envelope 12 and the gas conditions exteriorly thereof is desirably such that the plasma may be confined to the chamber 10. The electric potential applied to the electrodes 16 and 18 may thus be lower and the current density will be correspondingly less. This desirable relationship may be obtained by utilizing selected gases at predetermined pressures within the chamber 10, while exposing the electrodes outside the envelope 12 to the atmosphere.

By way of example, a monatomic inert gas, such as argon or helium at atmospheric or slightly less than atmospheric pressure may be utilized in the chamber 10. When the RF signal is applied to the electrodes 16 and 18, a plasma will be more readily generated within the chamber 10 than exteriorly thereof. With the potential of the RF signal applied to the electrodes set at a value corresponding to the potential required to generate a plasma within the chamber 10, but below the potential required to generate a plasma in the vicinity of the electrodes 16 and 18 externally of the chamber 10, the current which flows between the electrodes 16 and 18 will not be appreciably affected by the ion flow within the highly electrically conductive plasma since these electrodes are electrically isolated from the plasma. The plasma within the chamber 10 is not contacted by the

electrodes **16** and **18** and therefore not contaminated by the electrodes.

Referring now to FIG. **3,** a substrate **36** to be treated within the generated plasma may be introduced into the chamber **10** through a vacuum lock **38** subsequently described in greater detail in connection with FIGS. **6** and **7.** The substrate **36** may be passed through the chamber **10** in contact with the plasma therein at a rate determined by the particular treatment process to which the substrate is being subjected. For example, the substrate **36** may be an organic polymeric fiber, such as a thermoplastic or thermosetting polyester, polyamide, cellulosic or polyolefin material, the surface of which is to be treated in the plasma to obtain a paticular surface modification as is described in greater detail in the previously discussed U.S. Pat. application Ser. No. 93,350, by Florschirm et al. The substrate **36** may alternatively be a carbonaceous fibrous material to be treated in the plasma within the chamber **10** as is described in greater detail in the previously discussed U.S. Pat. application Ser. No. 99,169, by Kenneth C. Hou. In a further application of the present invention to the treatment of substrates, a coating may be deposited on a suitable substrate by generating a suitable gaseous plasma and contacting the substrate with this plasma. A more detailed description of the substrate and gases utilized in one such coating technique may be had by reference to the previously discussed U.S. Pat. application Ser. No. 88,358, by Kenneth C. Hou. The above referenced Forschirm and Hou patent applications are hereby incorporated herein by reference.

The substrate **36** may be introduced into the chamber **10** at an a angle with respect to the central electrode **16** as is illustrated in FIG. **3.** The substrate **36** might thereby follow a path generally indicated at **40** which subjects the substrate **36** to varying concentrations of the plasma as it passes through the chamber **10.** Alternatively, as is shown in FIG. **5,** one or more substrates **36** may be passed through the chamber **10** substantially parallel to the electrodes **16** at a selected radial distance thereform, thereby permitting the exposure of the substrates **36** to a selected plasma concentration.

Referring now to FIGS. **6** and **7** wherein the vacuum lock **33** of FIGS. **3** and **5** is illustrated in greater detail, a hollow tube **40** sealed to the end plate **30** of the envelope **12** communicates interiorly with the chamber **10** and provides a passage through which the substrate **36** may be introduced into the chamber **10.** The substrate **36** may be, for example, a loosely packed fiber bundle through which air leakage ordinarily occurs during the passage thereof between chambers at different pressures.

The tube **40** generally conforms in cross-section to the shape of the substrate, i.e., the bundle of fibers, but is slightly smaller in cross-section than the bundle causing the fibers to be inwardly compressed against each other and against the internal wall of the tube **40.** For example, if the fiber bundle is generally circular in cross-section as in FIG. **7**(A), the tube **40** may also be circular in cross-section with a slightly smaller diameter than that of the bundle. Likewise, if the bundle is elliptical in cross-section as in FIG. **7**(B), the tube **40** preferably conforms to that shape and is scaled down to slightly smaller dimensions.

One end **42** of the tube **40** is flared or funnel-shaped providing a transition zone for gently compressing the fiber bundle without damage thereto. If desired, the tube **40** may also narrow slightly along the length thereof to further compress the fiber bundle during the introduction thereof into the chamber **10.** It should be noted that when the substrate is a tightly packed fiber bundle or a single filament substrate, the diameter of the tube **40** may be the same or slightly larger than the substrate to prevent damage thereto.

At least two fluid passages **44** and **46** are spaced along the length of the tube **40** and communicate with the interior thereof. Each of the passages **44** and **46** is connected to associated pressure sources **48** and **50,** respectively.

The gas pressure applied to the passage **46** preferably approximates the pressure in the chamber **10,** while the pressure applied through the passage **44** is preferably slightly higher than the pressure in the chamber **10,** thereby creating a pressure differential along the interior of the tube **40.** This pressure differential, together with the mechanical compression of the substrate, prevents gas leakage into the chamber **10** when, for example, the pressure in the chamber **10** is less than the pressure outside the chamber **10.**

With the two passages **44** and **46** illustrated in FIG. **6,** gas leakage into the chamber **10** is minimized since a very slight pressure differential, e.g., 1 mm. Hg., can be maintained between the chamber **10** and the passage **46.** An even smaller pressure differential between these two points may be obtained by increasing the number of lateral fluid passages **44** and **46,** thereby providing even greater gas integrity between the spaces.

SUMMARY OF ADVANTAGES AND SCOPE OF THE INVENTION

It is apparent from the description of the invention that numerous advantages result therefrom. For example, the electrodes are isolated from the highly conductive plasma created within the envelope, resulting in greater efficiency as well as greater current control and eliminating contamination of the plasma by the electrodes.

Control of the substrate treatment process is facilitated by the controlled plasma concentration achieved in the present invention. The substrate may be selectively contacted by the proper concentration of plasma by selecting the path which the substrate follows through the generated plasma. Additionally, the plasma is concentrated in one location within the chamber resulting in more efficient substrate treatment and less material buildup on the interior walls of the envelope.

Moreover, continuous substrates may be treated without adverse effects on the conditions within the reaction chamber since isolation is provided between the interior and exterior of the envelope. For example, the substrate may pass from an area at one pressure, into the envelope which may be at another pressure, and then into an area at yet a different pressure without any substantial gas leakage.

The present invention may thus be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The presently disclosed embodiments are therefore to be considered in all aspects as illustrative and not restrictive, the scope of the

invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. A method for creating a plasma for the treatment of a substrate without exposure of the substrate to a high current density comprising the steps of:

providing an electrically insulative, gas-impervious envelope between first and second electrodes of significantly different configuration;

modifying at least one of the pressure and the constituency of the gas within the envelope;

applying a radio frequency electrical signal to the electrodes to thereby create a plasma of varying concentration within the envelope without creating a plasma exteriorly thereof and to thereby reduce the current flow between the electrodes; and

passing a substrate to be treated along a predetermined path through said plasma.

2. A method for treating a substrate comprising the steps of:

providing a pair of electrodes differing significantly in surface area;

applying a radio frequency electrical signal to the electrodes to create a gaseous plasma of varying concentration therebetween; and,

passing a substrate to be treated along a predetermined path through a selected plasma concentration to treat the substrate.

3. A method for creating a plasma for the treatment of a substrate without contamination of the plasma comprising the steps of:

providing an electrically insulative, gas-impervious envelope between first and second electrodes of significantly different configuration, the envelope defining a chamber isolated from the electrodes;

modifying the gas conditions within the envelope;

applying a radio frequency electrical signal to the electrodes of sufficient amplitude to create a plasma of varying concentration within the chamber, the plasma being isolated from the electrodes to prevent contamination of the plasma by the electrodes; and

passing a substrate to be treated along a predetermined path through a selected plasma concentration to treat the substrate.

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