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Mitzel

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[54] **GASEOUS PLASMA REACTION APPARATUS**

[75] Inventor: **James W. Mitzel,** Richmond, Calif.

[73] Assignee: **Tegal Corporation,** Richmond, Calif.

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[52] **U.S. Cl.**..... **250/531,** 204/164, 250/542

[51] **Int. Cl.**..... **H01t 19/00,** B01k 3/00

[58] **Field of Search**..... 204/164, 165, 193, 195 R, 204/195 B; 250/531, 542

[56] **References Cited**

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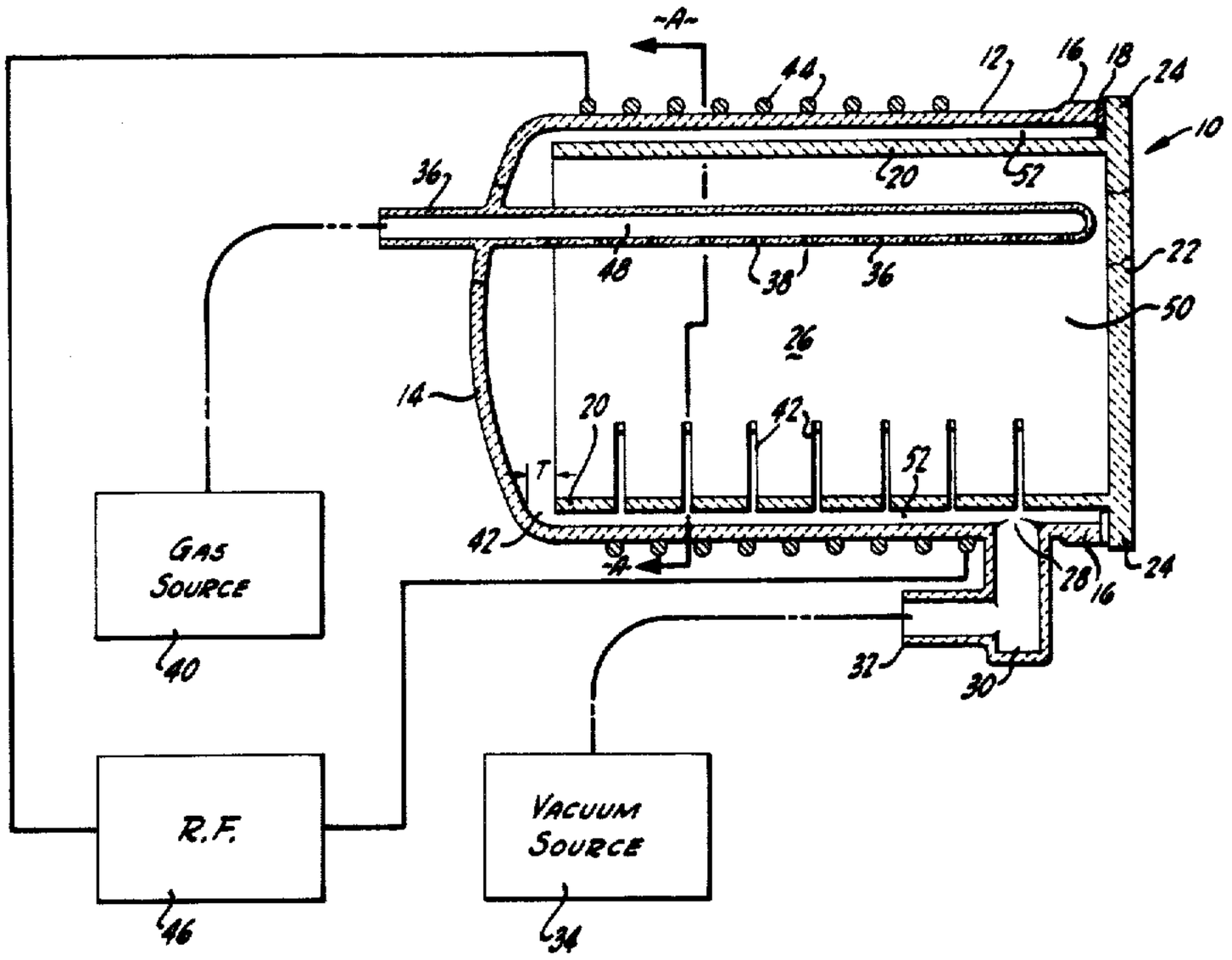
Primary Examiner—F. Edmundson

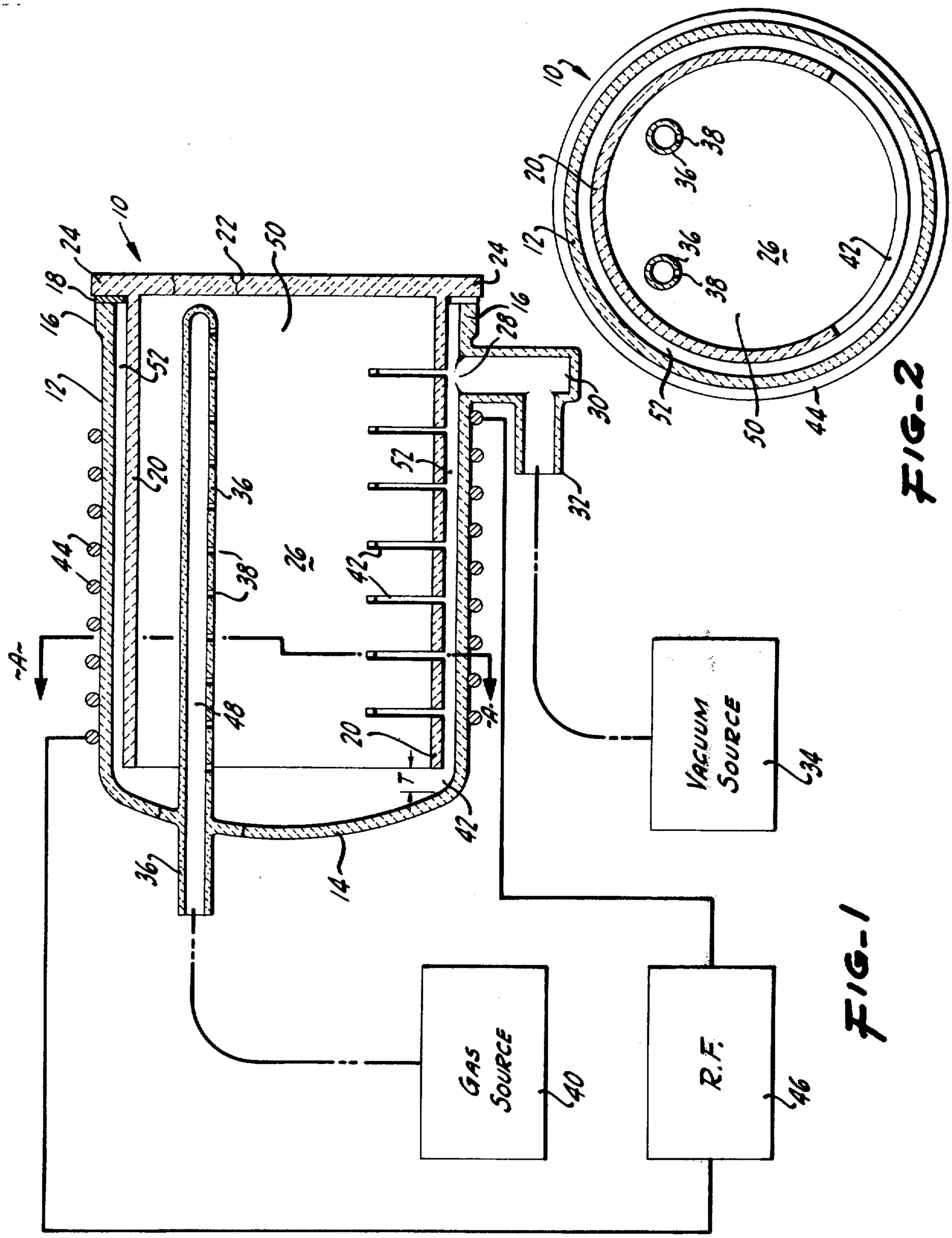
Attorney, Agent, or Firm—David E. Newhouse

[57] **ABSTRACT**

A low-temperature, gaseous, plasma reaction apparatus is described in which the reaction vessel is formed by two coaxially nested cylindrical chambers. A gas is introduced into the vessel and ionized by an R.F. electromagnetic field inductively coupled to the gas within the vessel by an exciter coil around the outer chamber. The inner chamber defines a central reaction region and is designed to optimize both the flow and distribution of gaseous ions around a non-gaseous specimen disposed in that region for efficient and uniform reaction therewith. The inner vessel is adapted to be removed from the outer vessel to thereby allow modular processing of non-gaseous specimens. The coaxial configuration of the dual chamber reaction vessel reduces contamination in the reaction region, provides means for conveniently and precisely positioning non-gaseous samples in the reaction region, and circumvents devitrification problems.

31 Claims, 8 Drawing Figures

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38
26
42
44
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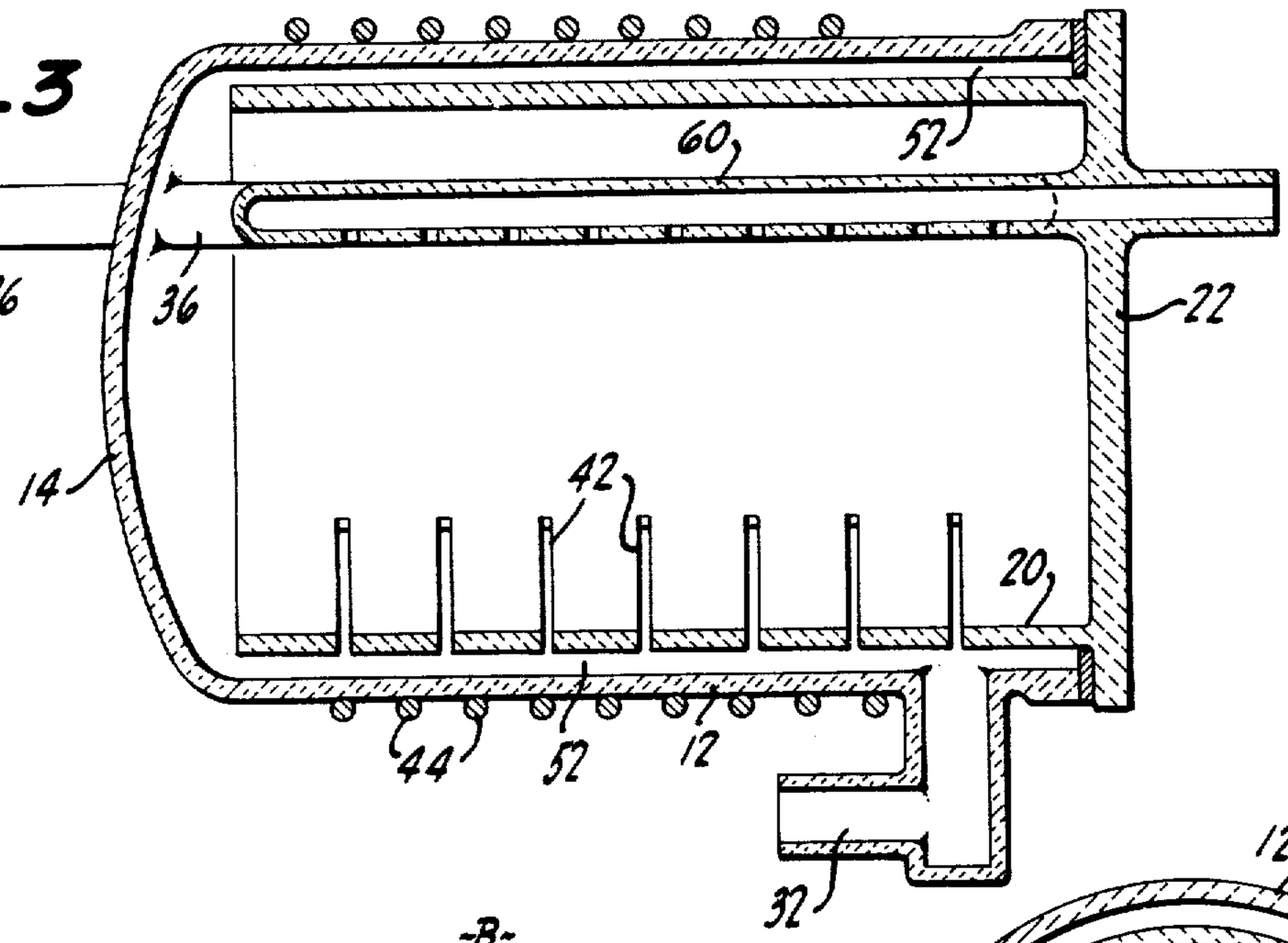
32
48
T
14
A
A
Gas Source
40
Vacuum Source
34
R.F.
46

FIG-1

10
20
12
36
38
26
42
52
50
44

FIG-2

FIG-3



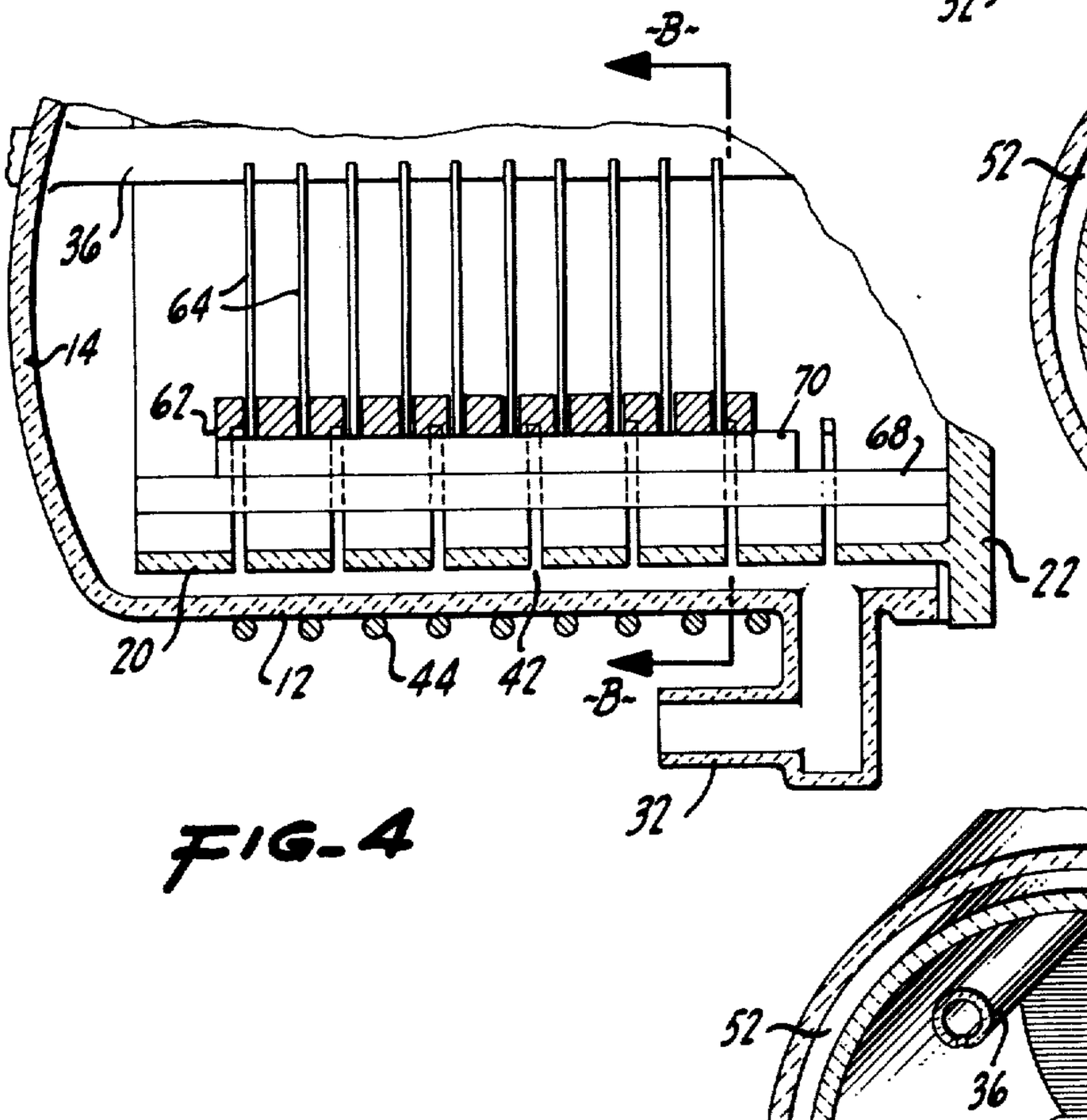


FIG-4

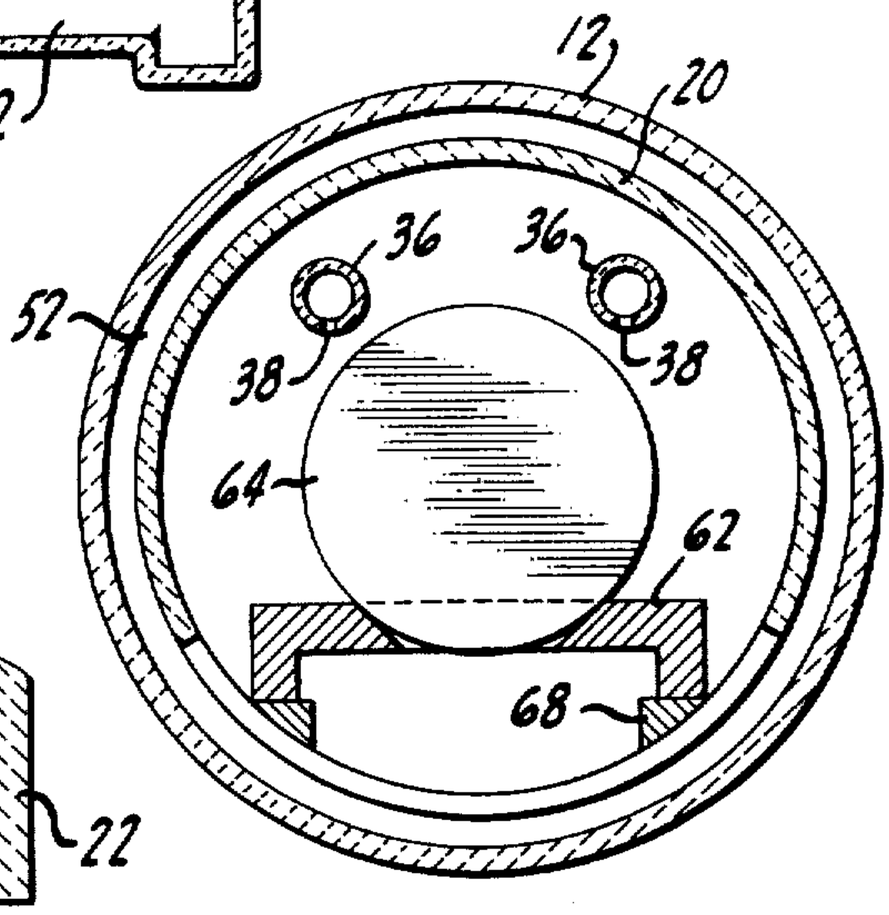


FIG-5

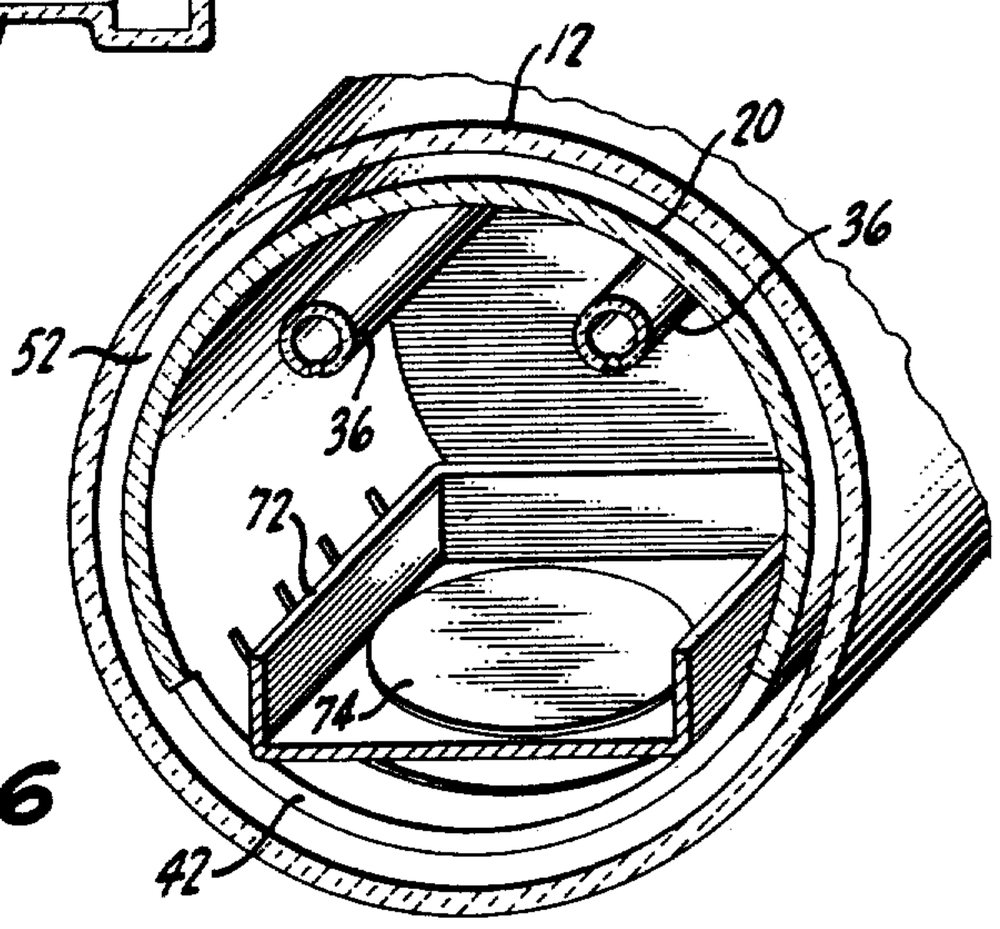
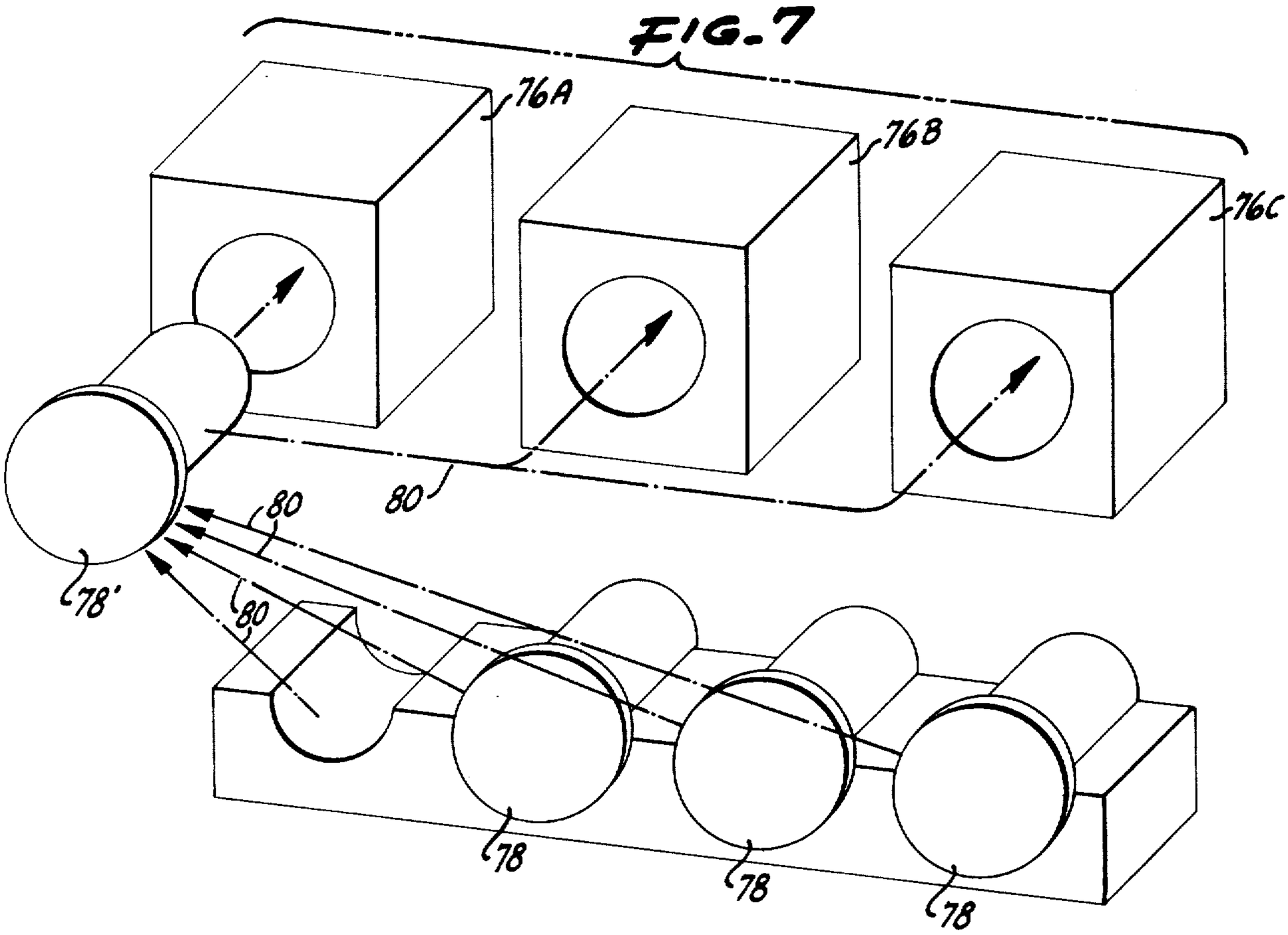


FIG-6

FIG. 7


76A
76B
76C
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78'
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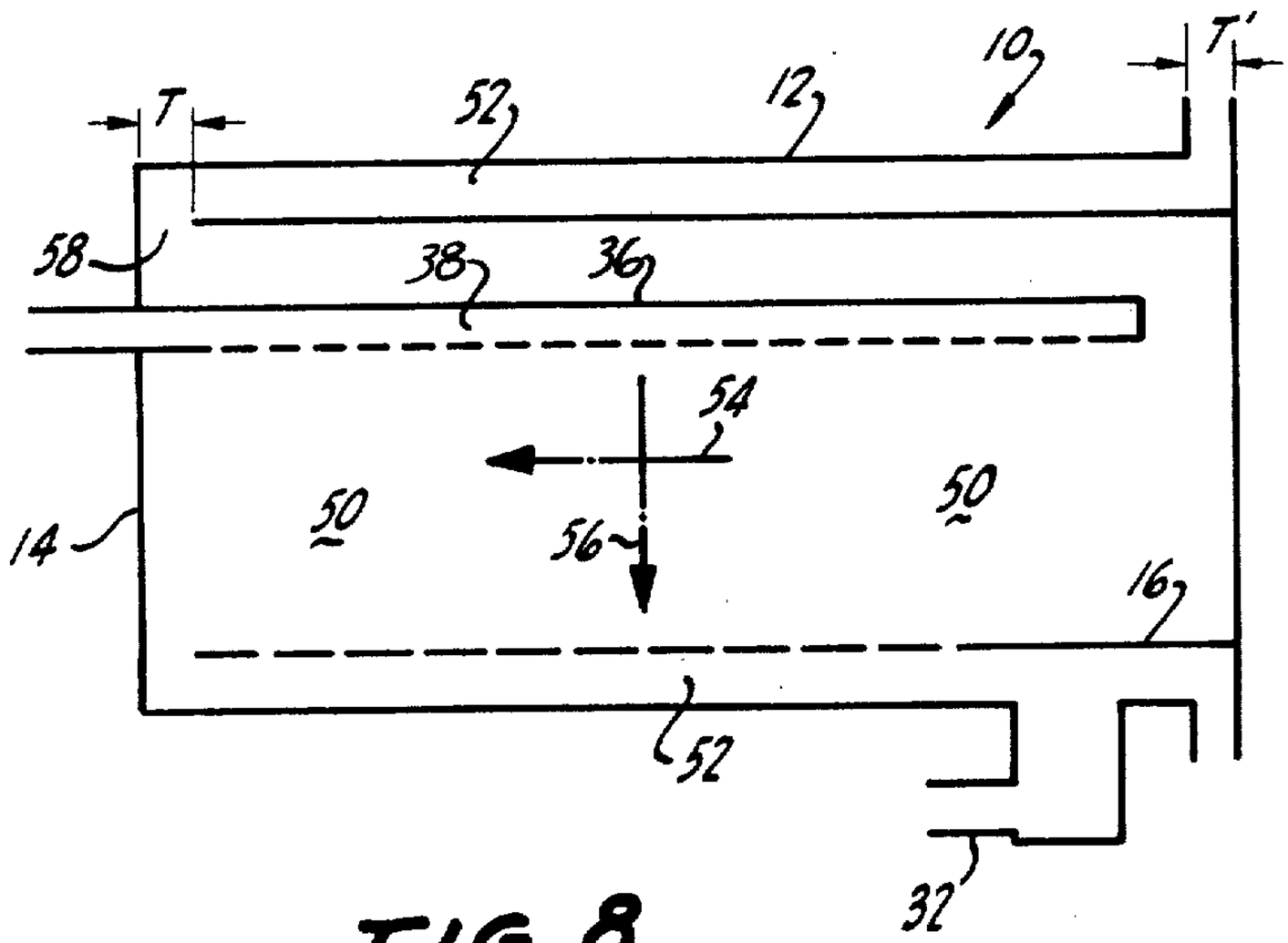
T
T'
10
12
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58
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50
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14
16
52
32

FIG. 8

GASEOUS PLASMA REACTION APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a low temperature gaseous plasma reactor apparatus. More particularly, the invention relates to a highly efficient gaseous plasma reaction vessel, which provides for uniform flow and distribution of gaseous ions around a non-gaseous material for reaction therewith.

2. Prior Art

The number of applications for low temperature gaseous plasma is increasing. For example, in fields of analytical chemistry, such low temperature gaseous plasmas are used for the following purposes: ashing organic materials at low temperatures; structural and chemical phase analysis of solid substances; low temperature pyrolyses; specimen pre-concentration; trace material analysis and gas-phase or gas/solid studies. In the biomedical field, gaseous plasmas are used for preparing solid samples for electron and optical microscopic examination; investigation of cell biology and structure and micro-incineration of specimens at low temperatures. Such gaseous plasmas are also extremely useful in fabrication and processing of electronic components; e.g., stripping photo-resist from etching and cleaning surfaces of semiconductor elements. Such gaseous plasmas are also used for preparing bonding surfaces and for cleaning optical surfaces.

Gaseous plasma chemistry techniques involve basically the following steps and apparatus: A material or specimen is placed in a sample "boat" which is loaded into a reaction chamber. The chamber is evacuated to a mild vacuum (approximately 1 Torr) by a mechanical vacuum pump. A carrier gas such as oxygen is drawn through the chamber and over the sample. Radiofrequency power is applied (usually 13.56 MHz) to excite the carrier gas molecules and change some of them to other species, such as atoms, radicals, ions, and free electrons.

This gaseous plasma is highly reactive and it causes a gentle, low-temperature combustion of the organic materials or impurities in the sample. The combustion products are carried away in the gas stream, leaving the base material for further processing or analysis. By using different gases, highly selective reactions with the sample can be obtained. The gas can be an oxidizing or reducing gas. It can also be chosen for different ratios of RF excited species. Typical gases used are oxygen, nitrogen, hydrogen, ammonia, helium, argon, and methane.

There are basically three different types of apparatus described in the prior art for carrying out gaseous plasma-solid chemical reaction. Each type of the prior art apparatus is briefly described below, and its particular defects and disadvantages are pointed out.

The first type of prior art apparatus is described in U.S. Pat. No. 3410776, issued to R. BERSIN. Briefly, the BERSIN apparatus includes a vessel having two chambers connected in an L configuration. A gas, e.g., oxygen, is introduced into one of the chambers, i.e., the ionization chamber, and is ionized into a plasma or activated gaseous medium by a R.F. electromagnetic field, inductively coupled into the gas by an exciter coil around the ionization chamber. The gaseous plasma flows from the ionization chamber into the reaction or material-handling chamber containing the solid substance. The neutral and active species of the gaseous plasma, as well as the gaseous reaction products from the plasma solid reaction, exhaust from the reaction chamber of the BERSIN apparatus via an exhaust port at the end of the material-handling chamber.

The primary defects of the BERSIN apparatus relate to the distribution of the gas or the plasma in the material-handling chamber. Specifically, because of the L-shaped configuration of the vessel, the plasma is not uniformly distributed in the material-handling chamber; consequently, the plasma-solid reaction cannot occur at a uniform rate, thus making precision processing with the plasma impossible. An extension of the BERSIN apparatus, described in U.S. Pat. No. 3428548, issued to J. R. HOLLAHAN, improves the distribution of the plasma in the material-handling chamber by providing multiple ionization chambers. However, the HOLLAHAN apparatus has relatively high power requirements in that a plurality of inductive exciter coils must be driven by a single R.F. generator. For that reason the generator must also be relatively sophisticated. Finally, if the HOLLAHAN apparatus is to be used around other sensitive electronic devices, the exciter coils must be extensively shielded.

A description of the second type of plasma-solid reaction apparatus can be found in U.S. Pat. No. 3547802, issued to C. E. GLEIT, et al. Briefly, the GLEIT apparatus, comprises a single tubular vessel with smoothly curved end sections. An inductive R. F. exciter coil is wound around a linear portion of the tubular vessel for generating a gaseous plasma. A solid materials receiving section is located in the linear portion of the tube just downstream from the exciter coil. A gas is introduced into the vessel at one of the curved ends and exits out the opposite curved end.

The primary defects of the GLEIT apparatus relate to its configuration. Specifically, the long tubular vessel must be decoupled from its end sections before a solid specimen can be placed in the vessel. Then, the vessel must be re-connected to its end section, evacuate and the plasma excited. Secondly, the gaseous plasma, once generated, will have an axial density gradient induced by gas flow through the vessel. Hence, the upstream end of the solid sample will react at a different rate than the downstream end. Furthermore, a solid specimen, must be held by an independent boat-structure near the central axis of the tube. Accordingly, the sample essentially acts as a stopper or a baffle which greatly disrupts the flow and the uniformity of the gaseous plasma down the tube. To minimize the baffle or the stopper effect, the relative diameter of the solid specimen must be small as compared to the diameter of the vessel. Accordingly, the tubular GLEIT apparatus is simply not suited for handling bulky solids, such as biological specimens and the like. It is equally obvious, that the GLEIT apparatus does not lend itself to modular processing of solid samples. Finally, because of the variability and non-uniformity of the plasma distribution in the tube induced by the sample, the GLEIT apparatus is not suitable for precision processing samples with gaseous plasmas.

A description of the third type of prior art apparatus can be found in U.S. Pat. No. 3619403 issued to G. J. GORIN. The GORIN apparatus includes a cylindrical reaction vessel with two or more small-diameter gas-inlet tubes, positioned symetrically around the periphery inside the vessel. Each of the gas-inlet tubes is

closed at one end with a series of holes along its respective length. The other end of each tube is connected to a gas-inlet port through the reaction-vessel wall. One end of the reaction vessel is adapted to be removed to provide a material-handling port for inserting and removing solid substances. An exhaust port is centrally located through the opposite end of the chamber. An inductive R.F. exciter coil, connected to a conventional R.F. generator, is wound around the vessel for ionizing the gas.

The primary defects of the GORIN apparatus relate to the location of the exhaust port. Specifically, as the gas enters the chamber via the inlet tubes, it flows preferentially towards that port. Accordingly, the distribution of the plasma ions in the chamber is not uniform either in an axial direction or in a radial direction. In addition, because of the numerous gas-inlet tubes and the centrally located exhaust port, there is a relatively large mass flow of gas through the chamber of the GORIN apparatus. Accordingly, the GORIN apparatus requires a substantial amount of R.F. energy to maintain the proper ion-density level in the chamber.

Still another defect of the GORIN apparatus relates to the vacuum seal, disposed between the chamber and the closure lid. Specifically, the seal is exposed to the plasma and, therefore, is a source of contamination in the chamber.

From the above descriptions of the prior art plasma/-solid reaction devices, it is apparent that they can not provide a uniform distribution of ions in the reaction chamber. Moreover, the reaction vessels of prior art devices do not include any internal structure for positioning or holding solid specimens in the reaction region of the chamber. Accordingly, separate structures, such as boats or racks holding the solid specimens must be slid into and out of the chamber manually. Such structures materially affect the distribution of the plasma and the reaction region of the vessels. Moreover, because such structures must be manually positioned in the chamber, it is practically impossible to expose two identical specimens to an identical plasm region within the vessel. Finally, the walls of the reaction vessel are often scratched by the boats. Such scratches serve as initiation sites for devitrification of the glass walls of the chamber. In particular the reaction chamber of each of the prior art apparatus is a single-wall vessel, usually composed of glass or other transparent mediums to allow the radiation energy to escape from the plasma. Devitrification results from the combined effect of atmospheric pressure; the R.F. field and a defect such as a scratch of the vessel wall, which causes the glass in the region of the defect to transform from an amorphous or glassy state to a crystalline state and become opaque. The opaque region then absorbs energy radiating from the plasma, heats up and liquefies, whereupon the pressure differential across the vessel wall causes a hole to form. In such instances, the entire reaction vessel must be replaced. The replacement of the reaction vessels can become expensive, especially where the vessel is a complicated structure, such as that described in the GORIN patent.

Still another drawback of the single vessel configuration as taught by the prior art is that the reaction products from the plasma/solid reaction often deposit on the interior walls of the reaction vessel. Such deposits are not easily removed because the chamber cannot be easily disengaged from the rest of the reaction apparatus for cleaning. This factor greatly limits the utility of the prior art devices because deposits from one plasma/solid reaction are often contaminents to another such reaction.

More importantly, the prior art apparatus have not been extensively utilized for processing sensitive semiconductor elements, e.g., metal-oxide-silicon (MOS) devices, because the elements, after being treated in the apparatus, developed instabilities. Specifically, when, for example, MOS devices are placed in prior art apparatus, a surface charge builds up. This surface charge creates an electric field across the device inducing drift. The subsequent instability in the MOS devices are directly attributable to that drift which occurs while the device was in the apparatus.

Another drawback of the prior art plasma/solid reaction apparatus relates to reacting a gaseous plasma with a powdered solid specimen. Specifically, due to the unimpeded exhaust ports, such powder specimens tend to blow around the chamber as it is evacuated or as the chamber is re-pressurized for removal of the reaction products. Accordingly, the prior devices require bleed valves and the like to slow evacuation and re-pressurization of the chamber, thereby greatly increasing the time for processing such powdered samples, or resultant powdered or delicate solid residues.

SUMMARY OF THE INVENTION

In accordance with the teachings of the present invention, a gaseous plasma/solid reaction apparatus is provided wherein the distribution of gaseous ions and activated gaseous species in a central reaction region is controlled by controlling the flow of gas from that region. Such a flow-control is implemented by appropriately porting an inner chamber defining a reaction region. Such porting can take into account the shape of the non-gaseous substance reacting with the plasma, as well as any structures holding the substance in plasma. Accordingly, highly precise and efficient processing of the non-gaseous materials with a gaseous plasma is made possible.

More particularly, in accordance with the present invention, a reaction vessel for conducting precision, gaseous plasma/solid chemical reactions is formed by two coaxially cylindrical chambers, each having an open and a closed end. A gas is introduced and distributed in the vessel via a plurality of small diameter finger tubes, each with a series of holes along its respective length and projecting through the end wall of the outer chamber, into a central reaction region, defined by the inner chamber. The inner chamber is appropriately ported to optimize the flow and distribution of gaseous ions in the reaction region around a non-gaseous material for efficient and uniform reaction therewith. Neutral and active species of the gaseous plasma, together with the gaseous reaction products, exit from the central reaction region, into an annular exhaust region, defined between the two nested cylindrical chambers. An exhaust port for removing gas from the vessel is located near the open end of the outer chamber and thus is operatively isolated from the central reaction region by the inner chamber wall.

In addition, the inner chamber includes the structural means integral therewith for positioning non-gaseous substances in the central reaction region so that repeatable precision reactions can be conducted. The inner vessel also serves as a shield and as a collector of con-

taminants to thereby reduce contamination in the central reaction region. Accordingly, the invented apparatus, provides means for better quality control over the gaseous plasma/solid reactions.

Still another advantage of the invented apparatus relates to the interchangeability of the inner chambers; in particular, each apparatus can include a plurality of inner chambers, each specifically designed to perform either different or identical functions. Accordingly, because of the interchangeability of the inner chambers, the invented apparatus is substantially more versatile than those devices described and taught in the prior art.

Moreover, the present invention makes a modular processing of solid samples with a series of gaseous plasmas possible. For example, a non-gaseous specimen can be loaded into a single cylindrical inner chamber. The inner chamber can then be inserted into a first outer outer chamber to form a first reaction vessel for treating the specimen at a first station with a gaseous plasma. The inner chamber can then be removed from the first outer chamber carrying the specimen therewith and inserted into a second outer chamber to form a second reaction vessel for treating the specimen with a second gaseous plasma reaction, and so on. Such a process can be carried out without directly handling the specimen.

An important advantage of the invented vessel configurations is that it minimizes the build-up of a surface charge on the specimens being processed. Accordingly, very sensitive semiconductor elements, e.g., MOS, devices can be processed in the chamber without fear of inducing an instability.

Still another advantage of the invented apparatus relates to the elimination devitrification failure of the reaction vessel. Specifically, the reaction vessel is provided by two coaxially nested cylindrical chambers, the inner chamber carrying the sample. Accordingly, the probability of scratching the outer chamber is greatly decreased, and if the inner chamber deteriorates due to devitrification, it can be easily removed and replaced. However, such an event is unlikely since the side walls of the inner vessel are not subject to atmospheric pressure.

The foregoing and other objects and advantages of the instant invention will become apparent to those skilled in the art upon examination of the following detailed description of an illustrative embodiment of the invention, together with the accompanying figures.

DESCRIPTION OF THE FIGURES

FIG. 1 is a cross-sectional view of the invented gas reaction apparatus.

FIG. 2 is a view along line AA of the apparatus shown in FIG. 1.

FIG. 3 is a cross-sectional view of the invented gaseous plasma reaction apparatus wherein the inner chamber has means for introducing a gas.

FIG. 4 is a cross-sectional view of the invented gaseous plasma reaction apparatus with a rack holding silicon wafer samples disposed within the inner chamber of the apparatus.

FIG. 5 is a view along line BB of the apparatus shown in FIG. 4.

FIG. 6 is a perspective view of the invented gaseous plasma reaction apparatus with a sample boat containing a planar sample disposed within the inner chamber of the apparatus.

FIG. 7 is a block diagram showing a method for sequentially treating samples with the invented gaseous plasma reaction apparatus.

FIG. 8 is a line diagram showing the different regions within the invented gaseous plasma reaction apparatus.

DISCLOSURE OF PREFERRED EMBODIMENT

Referring to FIGS. 1, 2, and 8, the invented gaseous plasma reaction apparatus generally designated by the number 10, includes an outer vessel, 12, of a generally cylindrical cup-like configuration having an end wall, 14, while being open at the opposite end. The cylindrical walls of the outer vessel 12 terminate in a raised annular shoulder, 16, having a flat or planar cross-section. An inner vessel, 20, also of a generally cylindrical cup-like configuration, having an end wall 22, while being open at the opposite end, has a lesser diametric dimension than the outer vessel 12. The inner vessel 20 is adapted to fit within the outer vessel 21 in a nested coaxial relationship. The inner vessel 20 has a series of outlet ports, 42, along its axial length.

More particularly, with reference to FIGS. 1 and 2, the outlet ports, 42, comprise slots having a predetermined circumferential length and axial width. As shown in FIG. 1, the ports, 42, are located through the downward side wall of the inner vessel 20 and are regularly spaced axially along its length. It should be noted that the configuration, the location, the circumferential length, the axial width, and the location of the ports, 42, through the walls of the inner vessel 20 may be varied in different inner vessels, to implement desired operational behavior as will be more fully discussed infra.

The end wall 22 of the inner vessel 20 is planar and has a slightly greater diametric dimension than the outer vessel 12. An anular seal 18 is disposed around the outside surface of the inner vessel 20 in an abutting relationship with the raised shoulder 24 integrally provided by the end wall 22 of the inner vessel 20. Accordingly, when the inner vessel 20 is coaxially inserted within the outer vessel 12 the respective shoulders 16 and 24 abutt hermetically against the seal 18 to form an evacuatable chamber 26.

A port, 28, for exhausting the chamber 26 is located through the wall of the outer vessel 12 proximate its open end. The port 28 basically comprises a cylindrical receptacle 30 extending downward from the wall of the outer vessel 12 with a tubular port means 32 connected to a vacuum source 34, extending from the side wall thereof. Accordingly, the exhaust port is multifunctional in that in addition to serving as an exhaust port it also traps unwanted contaminates from the vacuum source as well as acting as a baffle to minimize and disrupt large scale currents in the chamber 26 as it is evacuated or re-pressurized.

Reactant gaseous species are introduced into the chamber 26 via a plurality of finger tubes, 36, projecting through and fused with the end wall 14 of the outer vessel 12. The finger tubes, 36, are closed at the end proximate the opened end of the outer vessel 12 and have a series of holes, 38, generally oriented in a downward direction regularly spaced along their respective lengths. The opened ends, 44, of the finger tubes, 36, are connected to a gas source, 40, by appropriate valving and tubing means as are well known in the art.

A conductive coil is helically wound around the outside cylindrical wall of the outer chamber 12. The coil, 44, is connected to a suitable radio frequency genera-

tor **46** such that the chamber **26** is surrounded with a resonant circuit adapted to couple a radio frequency electromagnetic field to the reactant gasses within the chamber **26.** In particular, the coil **44** inductively couples radio frequency electromagnetic energy (usually 13.56 MHz) to the reactant gaseous molecules to convert some of them to such species as atoms, radicals, ions, and free electrons, or in other words, to convert the reactant gaseous species into a gaseous plasma.

The invented gaseous plasma reaction apparatus design optimizes the volume of the chamber **26,** the design and parameters of the chamber **26** and the gas flow through the chamber **26** such that the load between the R.F. generator **46** and the chamber **26** is balanced. Accordingly, it is possible to minimize the R.F. power requirements and to simplify the electronics which form the radio frequency generator **46** according to principles and teachings well known in the art.

Referring now in particular to FIG. **8,** when the inner vessel **20** is coaxially inserted into the outer vessel **12,** the resultant evacuatable chamber **26** has three regions: an entrant region **48** within the finger tube **36**; a central reaction region **50** defined by the inner cylindrical walls of the inner vessel **20**; and an annular exhaust region **52** between the cylindrical walls of the inner and outer vessels **20** and **12** respectively. The finger tubes **36** project into the upper portion of the central reaction region **50** proximate the inner cylindrical wall of the inner vessel **20.** Gaseous reactant species flow into the entrant region **48** within the finger tube **36** and are slightly ionized by the radio frequency fields inductively coupled into the interior of the chamber **26** by the helical coil **44,** due to the flow rate within the entrant region **48.** The gaseous reactant species then flow out of the entrant region **48** via the holes **38** through the finger tube **36** into the central reaction region wherein they are ionized into a gaseous plasma.

The density and distribution of the gaseous plasma in the central reaction region is highly uniform. In explanation, deleterious local electromagnetic field effects due to the helical induction coil **44** are minimized as will be discussed later. In addition, the gaseous plasma flows both in an axial direction as signified by the arrow **54** and in a radial or diametric direction as signified by the arrow **56.**

More specifically, the central reaction region **50** communicates with the annular exhaust region **52** via the porting **42** through the walls of the inner vessel **20** and through an annular exhaust port **58** defined between the opened end of the inner vessel **20** ad the closed end wall **14** of the outer vessel. The cross-sectional dimension T of the exhaust annulus **58** can be varied by varying the thickness, T', of the annular seal **18.** by increasing the cross-sectional dimension, T, of the annular exhaust port **58** the rate of axial flow in the central region, **50,** can be increased. Similarly, by increasing the cross-sectional dimension T the axial flow rate can be decreased. In addition, the flow of the gaseous plasma in a direction perpendicular to the axis of the central reaction region **50** can be regulated by appropriately porting the vessel wall of the inner chamber **20.** Specifically, to increase the rate of "radial" flow, one merely increases the cross-sectional area of the ports **42.** As shown in FIG. **8,** the ports **42** are located through the downside of the inner vessel wall such that gas will flow perpendicular to the axis of the central reaction region **50** in a more or less straight line fashion from the holes **38** through the finger tubes **36.**

In summary, the distribution of the gaseous plasma in the central reaction region **50** is controlled by controlling the flow of the plasma from that region. The insulative walls of the inner vessel **20** define the central reaction region **50.** The flow of the gaseous plasma is controlled by appropriately porting that inner chamber. Such porting, as should be recognized by those skilled in the art, can take into account the particular shapes of non-gaseous samples and substances placed in the central reaction region **50,** as well as any structures such as boats and racks holding such substances in that region. Accordingly, highly precise and efficient processing of non-gaseous matericals with a gaseous plasma is made possible.

As the gaseous plasma leaves the central reaction region **50** via the exhaust port described above, it enters the annular exhaust region **52.** The plasma flows in an opposite axial direction in the annular exhaust region than it does in the central region. Accordingly, disruptions in the volumetric distribution of the gaseous plasma in the central region due to electromagnetic field effects caused by the flowing gaseous plasma medium are minimized. In addition, the plasma ions species in the exhaust region **52** form a coaxial conductive sheath which effectively isolates the central reaction region **50** from the localized field effects of the helical induction coil **44** wound around the outside wall of the outer vessel **12.**

More specifically, the gaseous plasma in the annular exhaust region **52** phenomenologically functions as a secondary oscillator, which inductively couples the radio frequency electromagnetic field, driving it into the central reaction region. Specifically, the cylindrical walls of the inner vessel is an insulative material, e.g., glass or quartz. Hence, the outer annulus **52** is electronically isolated from the central reaction region **50.** Localized field effects induced by the helical coil wound around the outside wall of the outer vessel **12** are only "seen" by the gaseous plasma in that annular exhaust region. Then, since the plasma in that region is basically a uniform conductive coaxial body, it inductively couples the electromagnetic field driving it uniformly into the cylindrical central reaction region **50** which it surrounds. In effect, the exhaust annulus serves to buffer and eliminate deleterious field effects due to the essentially localized coupling of an R.F. field into the chamber **26** with a conductive helical coil.

For these and many other reasons which should be obvious to those skilled in the gaseous plasma, physical science, and electronic arts, the central reaction region **50** of the invented apparatus is an ideal region in which higly precise and very sensitive experiments, processes and other such operations with a gaseous plasma can be conducted. It is believed by the inventor and others that the explanation for the absence of a surface charge on semi-conductor elements, e.g., MOS devices, processed in the invented gaseous plasma apparatus is due in large part to the idealized environment within the central reaction region **50.**

Moreover, the highly uniform distribution and density of the gaseous plasma in the central reaction region has been observed. Specifically, the inventor placed a thin aluminum wafer, coated with a photo-resist material on both sides, in the central reaction region and then visually observed the oxidation of the photo-resist

material by a gaseous oxygen plasma. He noted that the photo-resist material disappeared simultaneously from the respective surfaces of the aluminum wafer. Moreover, they noted that the photo-resist material uniformly oxidized, in that no islands and the like of photo-resist material existed while the photo-resist material was being oxidized. The only explanation for such phenomenon was that the gaseous plasma within the central reaction region was extremely uniform in its distribution and density.

Referring now to FIG. **3**, the versatility of the invented plasma reaction apparatus is evident. Specifically, as shown in FIG. **3**, the inner vessel **20** includes a third finger tube **60** projecting through and fused with its end wall **22**. The finger tube **60** is closed at its distal end and has a series of holes through its walls along its length. The tube **60** may lie either in the same plane as the finger tubes **36** projecting through the back wall of the outer vessel **12** or along any circular cord between the finger tubes **36**, in order to preserve axial symmetry. The finger tube **60** is adapted to be connected to a second gas source (not shown in the figure).

Sequential processes can be conducted on the solid specimens with apparatus shown in FIG. **3**. Specifically, a first reaction on such a solid specimen can be conducted with a first reactant gas introduced into the chamber **26** via the finger tubes **36**. After the first reaction has progressed to completion, the chamber is isolated from the first gas source, **40**, by an appropriate valve and the first reactant gas species and reaction products are evacuated from the chamber **26** via the exhaust port **28** connected to the vacuum source **34**. After the first reaction species have been evacuated from the chamber a second reactant gaseous species can be introduced into the chamber via the finger tube **60** to initiate a second gaseous plasma reaction with the solid sample. While the second reaction progresses, a third gas source can be connected to the finger tubes **36** by conventional means well recognized by those skilled in the art. After the second gaseous plasma reaction has progressed to completion, the second gas source can be isolated bia a valving means whereupon the chamber will again be evacuated of all gaseous species. A third gaseous plasma reaction process can be initiated by introducing the gas from the third source. Accordingly, by repeating the above sequential steps many times, a large number of processes can be expeditiously and efficiently carried out on a solid specimen with a single gaseous plasma reaction apparatus.

Referring now to FIGS. **4** and **5**, a rack **62** carrying a plurality of semi-conductor wafers **64**, is disposed within the inner vessel **20** in the central reaction region **50** of the invented apparatus **10**. Such racks **62** are typically composed of quartz or other such non-reactive substances. The legs, **66**, of the rack, **64**, rest on parallel ledges, **68**, longitudinally disposed along the lower wall portion of the inner vessel and fused therewith. The ledges include a stop, **70**, such that the racks can be precisely positioned in the inner vessel, **20**, before the inner vessel is inserted into the outer vessel **12**. Such positioning means for the rack, **52**, makes possible high quality control over the gaseous reaction process occurring within the central reaction region **50**.

Referring now to FIG. **6**, a quartz boat **72** is shown placed within the inner vessel **20** of the invented gaseous plasma reaction apparatus. The boat contains a filter, **74**, which is to be oxidized or reduced by a gaseous plasma. In this instance, the inner walls of the inner vessel **20** do not have precise positioning means in that such are not necessary. Moreover, as shown in FIG. **6**, the ports, **42**, through the vessel wall have not been altered to accomodate or to adjust for the blockage due to the quartz boat **72**. However, as should be obvious to those skilled in the art, it would be an easy matter to appropriately port an inner vessel **20** such that the flow of gaseous plasma out of the central reaction region would be optimal for reacting with samples disposed within a solid reaction boat placed within the inner vessel **20**.

Referring now to the diagram shown in FIG. **7**, the invented gaseous plasma reaction apparatus makes possible sequential treatment of a single specimen with a plurality of chambers **76**. Specifically, a plurality of solid samples (not shown) can be loaded into a plurality of inner vessels, **78**. A first vessel, **78'**, containing its solid specimen is inserted into the first chamber **76A**. The chamber is then evacuated to soft vacuum pressures and the sample processed with a gaseous plasma. The chamber is then re-pressurized, the inner vessel, **78'**, removed therefrom and inserted into the second chamber **76B**, whereupon that chamber is evacuated and a second gaseous plasma reaction conducted on the solid specimen within the chamber **78'**. As shown by the arrows **80** in FIG. **7**, each inner vessel carrying its respective solid sample can be cycled through any number of chamber stations **76** in a sequential fashion.

The process utilizing a single inner vessel **78** and a plurality of chamber stations, **76**, for processing solid specimens with a sequence of gaseous plasma reactions is particularly adapted for high speed processing with different gaseous plasmas wherein:

(1) the reaction gaseous species of a prior process would be a contaminant in a subsequent gaseous plasma process; (2) the reaction gaseous species of a subsequent process are incompatible with prior gaseous reaction species.

Referring now back to FIGS. **1** and **2**, the inner vessel **20** also serves a a baffle to prevent blow-off of powdered specimens when the chamber **26** is evacuated or re-pressurized. Specifically, the cylindrical wall of the inner vessel **20** isolates the exhaust port **28** from the central reaction region. Accordingly, bleed valves and other such devices slow the rate of evacuation and/or re-pressurization of the chamber **26** can be eliminated.

More importantly, referring to FIGS. **1** and **2**, the inner vessel shields the central reaction region from contaminants. Specifically, products of any reactions of the gaseous plasma with the seal **18** which is exposed to the gaseous plasma are confined in the annular exhaust region **52**. Moreover, the cylindrical wall of the inner vessel shields the central reaction region from contaminants originating from the vacuum source or from associated vacuum piping such as the vapors of oils lubricating the vacuum pump and the like. Finally, the cylindrical wall of the inner vessel serves as a collector of reaction products of gaseous plasma-solid reactions which deposit or precipitate on surfaces proximate to the reaction. Accordingly, it is not necessary to clean the outer vessel as frequently as must be done with the prior art apparatus.

Finally, because the outer vessel rarely comes into contact with specimens, boats, racks and other such devices which might scratch its surface, the vessel **12** rarely fails because of devitrification. Moreover, devit-

rification failure of the inner vessel **20** will not significantly disrupt or otherwise affect the gaseous plasma reaction occurring within the central reaction region **50.** In effect, such devitrification failure may only create an additional port through which the gaseous plasma can exhaust into the annular exhaust region **52.**

Finally, the inner and outer vessels, **20** and **12** respectively, as well as the finger tubes, should be composed of transparent insulative medium such as pyrex glass or quartz. The mediums should be transparent to allow the radiations from the excited gaseous plasma to escape from the inner chamber region. The mediums should be insulative to allow the radio frequency field to be inductively coupled into the gaseous reactant species.

Specifications for an exemplary embodiment of the invented gaseous plasma reaction apparatus

Controls and meters: Lighted AC Power switch; vacuum control switch; RF power switch; RF tuning control; RF meter calibrated in watts.

R.F. power: 0-100 Watts, continuously variable at 13.56 MHz, crystal controlled.

R.F. Transfer network: Variable capacitor optimized RF power transfer to plasma load; power amplifier direct coupled to reaction chamber through matched high impedance network.

Chamber: Removable inner chamber, 3¼ inch ID × 5 inch IL; sealed by silicone gasket and vacuum pumpdown; Pyrex standard, quartz optional.

Dimensions: 11 inches wide × 9½ inches high × 15 inches long; weight, 25 pounds.

Facilities required: Mechanical vacuum pump, 50 liters per minute; 115 volts AC, 60 Hz, 15 amps peak line power; gas flow regulator with 0 to 10 PSIG adjustment.

While the invented gaseous plasma reaction apparatus is described with respect to exemplary, representative and schematic embodiments, it should be apparent to those skilled in the art that numerous variations and modifications can be effected within the scope and spirit of the invention as described hereinabove and as defined and set forth in the appended claims.

What is claimed is:

1. A gaseous plasma reaction apparatus comprising in combination:

a reaction chamber having means for introducing and removing non-gaseous materials;

means for introducing and distributing a gas into said reaction chamber;

means for ionizing the gas in the reaction chamber into a plasma;

means for controlling the flow and distribution of said plasma with said reaction chamber;

means for minimizing local electromegnetic field effects on said plasama within said chamber comprises in combination:

an outer vessel of a generally symetrical configuration composed of an insulative material;

an inner vessel of a generally similar symetrical configuration as said outer vessel also composed of an insulative material and disposed in a nested symetrical relationship within said outer vessel, the interior of said inner vessel defining said reaction chamber;

a shell zone surrounding said reaction chamber defined by the interior wall of said outer vessel and the exterior wall of said inner vessel, containing a conductive gaseous plasma; and

means for withdrawing gas from said reaction chamber.

2. The plasma reaction apparatus of claim **1** further defined in that said means for ionizing the gas includes a radio frequency generator means having an output coupled to a resonant circuit surrounding said reaction chamber.

3. The apparatus of claim **2** further defined in that said resonant circuit surrounding said reaction chamber comprises a conductive coil disposed around said outer vessel adapted to inductively coupled a R.F. electromagnetic field resonantly into said reaction chamber.

4. The apparatus of claim **3** further defined in that said inner vessel has a port whereby said gas and said plasma exhausts from said reaction chamber into said shell zone and in that said means for withdrawing gas from said chamber is connected to an exhaust port defined through the wall of said outer vessel.

5. The apparatus of claim **4** further defined in that said inner vessel has a plurality of ports symetrically located around and through said inner vessel wall.

6. The apparatus of claim **5** further defined in that said inner and outer vessels have a generally cylindrical configuration, and said conductive coil has a helical configuration.

7. The apparatus of claim **6** further defined in that said means for controlling the flow and distribution of said plasma within said chamber further comprises in combination means for directing plasma flow within said reaction chamber.

8. The gaseous plasma reaction apparatus of claim **7** further defined in that said outer vessel has a generally cylindrical cup-like configuration having an open and closed end;

and in that said inner vessel has a generally cylindrical cup-like configuration having an open and closed end, said inner vessel being coaxially inserted through said open end and into said outer vessel, and having a raised annular shoulder of greater diametric dimension than said outer vessel such that said shoulder abutts against walls defining said open end of said outer vessel; and

a hermetic seal disposed between said open end of said outer vessel and said shoulder of said inner vessel, composed of relatively inert resilient materials of the class consisting of plastics and silicone rubbers, whereby a hermetic chamber is formed having means for introducing and removing non-gaseous materials therefrom; and

integral structural means within said inner vessel for receiving, positioning and holding said non-gaseous materials in such reaction chamber for reaction with said plasma.

9. The plasma reaction apparatus of claim **8** further defined in that said exhaust port communicating through the wall of said outer vessel is located proximate said open end of said outer vessel and means are connected to said exhaust port for evacuating gas from said hermetic chamber.

10. The plasma reaction apparatus of claim **9** further defined in that said means for introducing and distributing a gas within said closed chamber comprises a plurality of tubes extending from the closed end of said outer vessel through the opened end of said inner vessel

proximate to the interior wall of said inner vessel, each of said tubes having a plurality of holes along their respective lengths each tube being integrally connected to a corresponding gas inlet port defined through said closed end of said outer vessel.

11. The apparatus as defined in claim **10** further defined in that said tubes are symetrically disposed about the interior wall of said inner vessel and have an outer diameter which is small with respect to the inner diameter of said inner vessel.

12. A plasma reaction apparatus comprising in combination;

an outer vessel of a generally cylindrical cup-like configuration having an open and closed end;

an inner vessel of a generally cylindrical cup-like configuration having an open end, a closed end and a raised annular shoulder on its exterior surface proximate the closed end, said inner vessel being coaxially inserted within said outer vessel through said open end thereof whereby said shoulder abuts against the walls defining said open end of said outer vessel to thereby form a closed chamber;

means for making a hermetic seal disposed between said open end of said outer vessel and said shoulder of said inner vessel;

means for introducing and distributing a gas in said closed chamber;

means for ionizing the gas in said chamber into a plasma;

means for controlling the flow and distribution of said plasma within said chamber; and

means for withdrawing gas from said chamber.

13. The plasma reaction apparatus of claim **12** further defined in that said means for ionizing the gas includes a radio frequency generator means having an output coupled to a resonant circuit surrounding said chamber.

14. The apparatus of claim **13** further defined in that said resonant circuit surrounding said chamber comprises a conductive coil disposed around said outer vessel adapted to inductively coupled a R.F. electromagnetic field resonantly into said chamber.

15. The plasma reaction apparatus of claim **14** further defined in that said means for introducing and distributing a gas within said closed chamber comprises a plurality of tubes extending from the closed end of said outer vessel through the open end of said inner vessel proximate to the interior wall of said inner vessel, each of said tubes having a plurality of holes along their respective lengths, each tube being integrally connected to a corresponding gas inlet port defined through said closed end of said outer vessel.

16. The apparatus as defined in claim **15** further defined in that said tubes are symetrically disposed about the interior wall of said inner vessel and have an outer diameter which is small with respect to the inner diameter of said inner vessel.

17. The plasma reaction apparatus of claim **15** further defined in that said means for withdrawing gas from said closed chamber comprises an exhaust port communicating through the wall of said outer vessel proximate said open end of said outer vessel and means connected to said exhaust port for evacuating gas from said chamber.

18. The plasma reaction apparatus of claim **17** wherein said means for introducing and distributing a gas within said closed chamber further comprises a plurality of tubes extending from the closed end of said inner vessel proximate the interior walls of said inner vessel, each of said tubes having a plurality of holes along their respective lengths and each tube being integrally connected to a corresponding gas inlet port defined through said closed end of said inner vessel.

19. The apparatus as defined in claim **18** wherein said tubes extending from the end wall of said inner vessel are symetrically disposed around the interior wall of said inner vessel and have an outer diameter which is small with respect to the inner diameter of said inner vessel.

20. The apparatus of claim **17** further defined in that the walls of said inner vessel define a central reaction region of a generally cylindrical shape; and in that the interior wall of said outer vessel and the exterior wall of said inner vessel define an exhaust region of a generally annular configuration and an orifice of a generally annular configuration between the open end of said inner vessel and the closed end of said outer vessel to thereby induce said plasma to flow axially in said cylindrical reaction region; exhaust from that region via said orifice into said exhaust region, and flow in the opposite axial direction to said exhaust port.

21. The apparatus of claim **20** further defined in that said means for controlling the flow and distribution of said plasma within the chamber includes means for regulating the cross sectional area of said annular orifice whereby axial flow rate of said plasma in the central reaction region is controlled.

22. The apparatus of claim **21** further defined in that said means for making an hermetic seal between said opened end of said outer vessel and said shoulder of said inner vessel comprises an annular gasket.

23. The apparatus of claim **22** further defined in that said means for regulating the cross sectional area of said annular orifice comprises a plurality of annular gaskets, each having a different thickness and each adapted to be disposed between said opened end of said outer vessel and the raised annular shoulder of said inner vessel whereby the thickness of each gasket determines the linear distance between said open end of said inner vessel and said closed end of said outer vessel.

24. The apparatus of claim **23** further defined in that said means for controlling the flow and distribution of said plasma within the chamber further comprises a plurality of ports defined through the cylindrical wall of said inner chamber whereby said plasma exhausts from said central reaction region into said exhaust region via said ports.

25. The apparatus of claim **24** further defined in that said ports are located through the wall of said inner vessel so as to also insure plasma flow in said central reaction region in a generally perpendicular direction with respect to the longitudinal axis of said central reaction region.

26. The apparatus of claim **25** further defined in that said plurality of gas inlet tubes are located generally on one side of said central reaction region and said ports are located on a generally opposite side of said central reaction region from said gas inlet tubes.

27. The apparatus of claim **26** further defined in that said ports comprised slots defined through the walls of said inner vessel generally oriented perpendicularly with respect to the longitudinal axis of said central reaction region, each slot having a particular circumfer-

ential length and width whereby the flow and distribution of said plasma within said central reaction region are controlled.

28. The apparatus of claim **27** further defined in that said slots are located in a cooperative relationship with the holes through said inlet tubes and with said non-gaseous material disposed within the central reaction region to provide a uniform and homogeneous flow of gaseous plasma around the surface of said material whereby said material uniformly reacts with said gaseous plasma.

29. The apparatus of claim **28** further defined in that said inner vessel includes integral structural means within its interior for positioning said non-gaseous material in said contral reaction region with said plasma.

30. The apparatus described in claim **17** further defined in that said inner vessel, outer vessel and gas inlet tubes are composed of transparent and insulative materials of the class consisting of quartz and pyrex glass respectively.

31. The apparatus as described in claim **23** further defined in that said annular gaskets are composed of relatively inert resilient materials of the class consisting of plastics and silicon rubber.

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