6-28-1994

Radio-frequency powered glow discharge device and method with high voltage interface

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[45] Date of Patent: Jun. 28, 1994

[54] RADIO-FREQUENCY POWERED GLOW DISCHARGE DEVICE AND METHOD WITH HIGH VOLTAGE INTERFACE

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[73] Assignee: **Clemson University**, Clemson, S.C.

[21] Appl. No.: **944,216**

[22] Filed: **Sep. 11, 1992**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 886,030, Apr. 9, 1992, abandoned.

[51] **Int. Cl.**[5] **H01J 7/24**

[52] **U.S. Cl.** **315/111.51**; 315/176; 250/288; 250/281

[58] **Field of Search** ..... 250/288, 281; 315/221 R, 244, 163, 176, 111.21, 111.41, 111.81, 111.51

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Primary Examiner—Robert J. Pascal
Assistant Examiner—Arnold Kinkead
Attorney, Agent, or Firm—Dority & Manning

[57] **ABSTRACT**

A high voltage accelerating potential, which is supplied by a high voltage direct current power supply, is applied to the electrically conducting interior wall of an RF powered glow discharge cell. The RF power supply desirably is electrically grounded, and the conductor carrying the RF power to the sample held by the probe is desirably shielded completely excepting only the conductor's terminal point of contact with the sample. The high voltage DC accelerating potential is not supplied to the sample. A high voltage capacitance is electrically connected in series between the sample on the one hand and the RF power supply and an impedance matching network on the other hand. The high voltage capacitance isolates the high DC voltage from the RF electronics, while the RF potential is passed across the high voltage capacitance to the plasma. An inductor protects at least the RF power supply, and desirably the impedance matching network as well, from a short that might occur across the high voltage capacitance. The discharge cell and the probe which holds the sample are configured and disposed to prevent the probe's components, which are maintained at ground potential, from bridging between the relatively low vacuum region in communication with the glow discharge maintained within the cell on the one hand, and the relatively high vacuum region surrounding the probe and cell on the other hand. The probe and cell also are configured and disposed to prevent the probe's components from electrically shorting the cell's components.

19 Claims, 8 Drawing Sheets

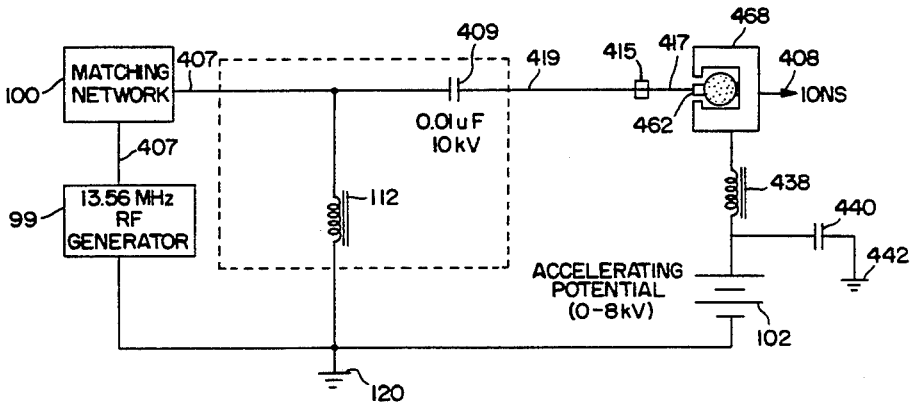

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FIG. 1

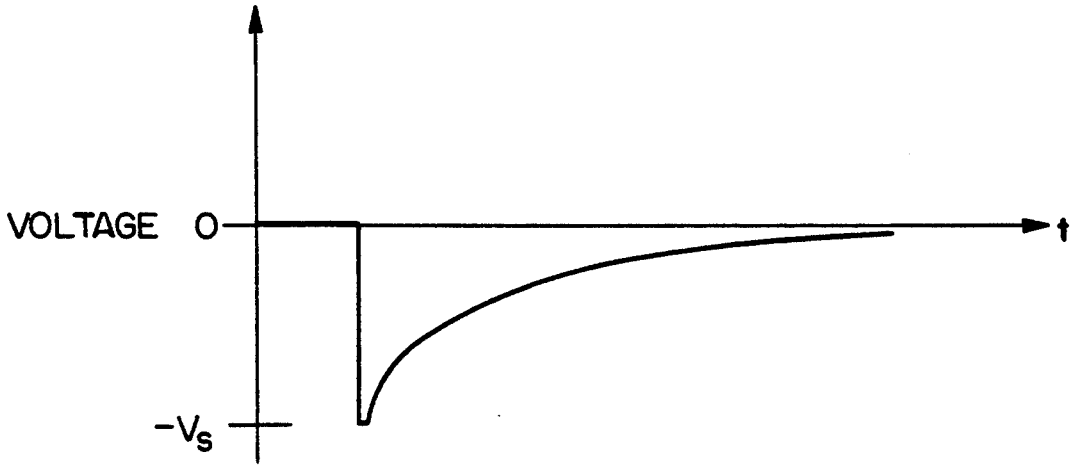
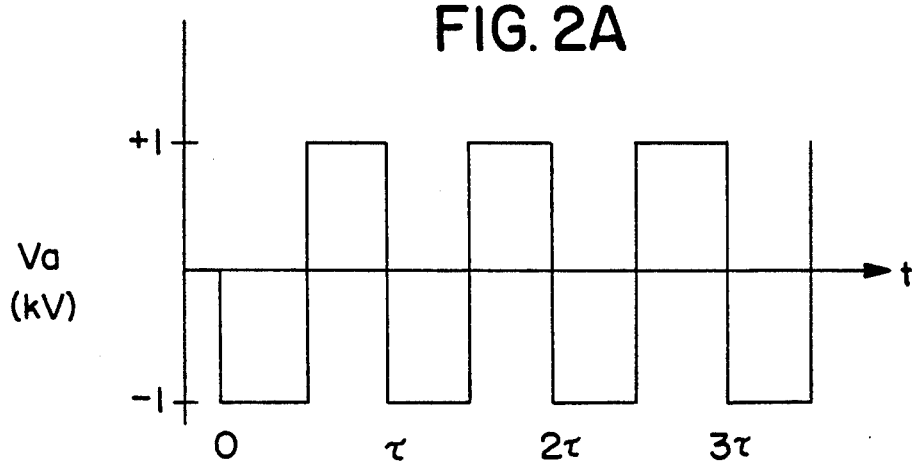


FIG. 2A



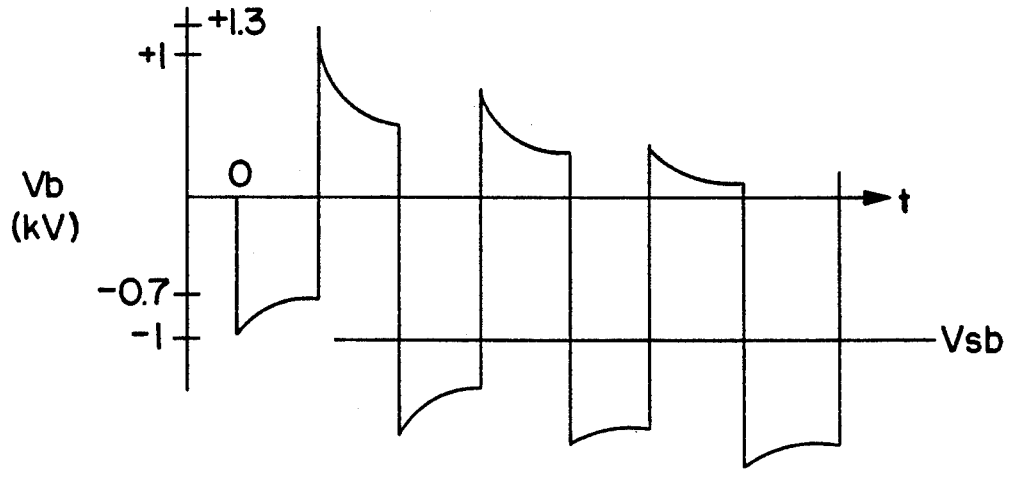


FIG. 2B

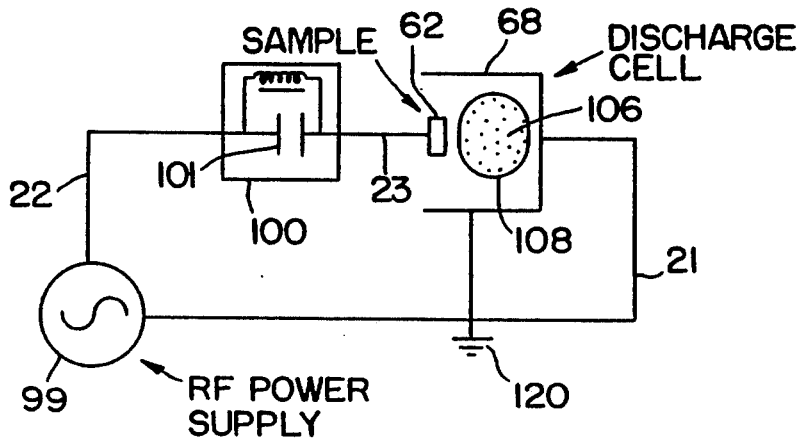


FIG. 3
PRIOR ART

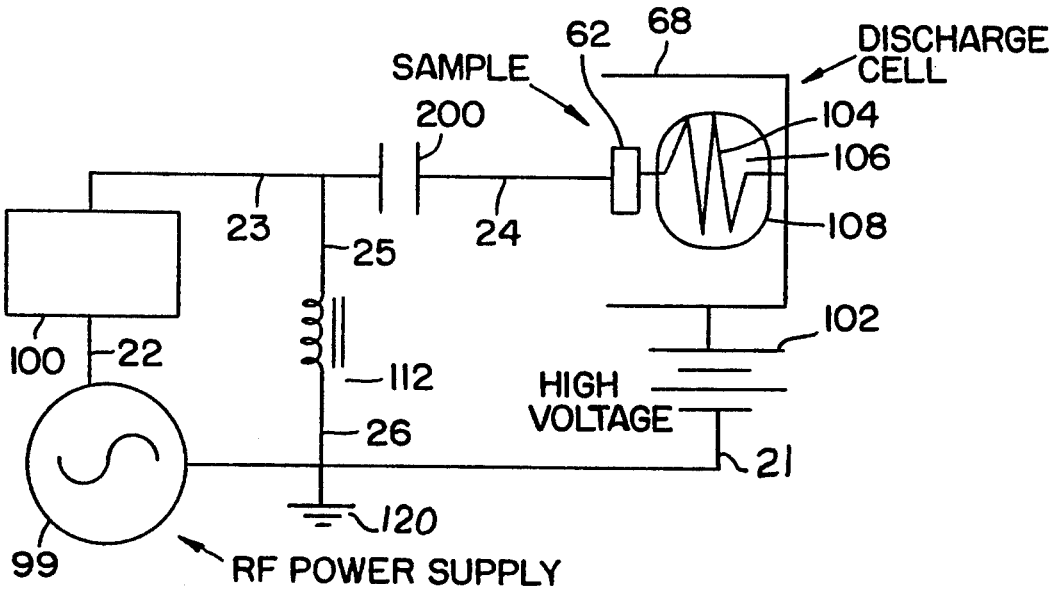
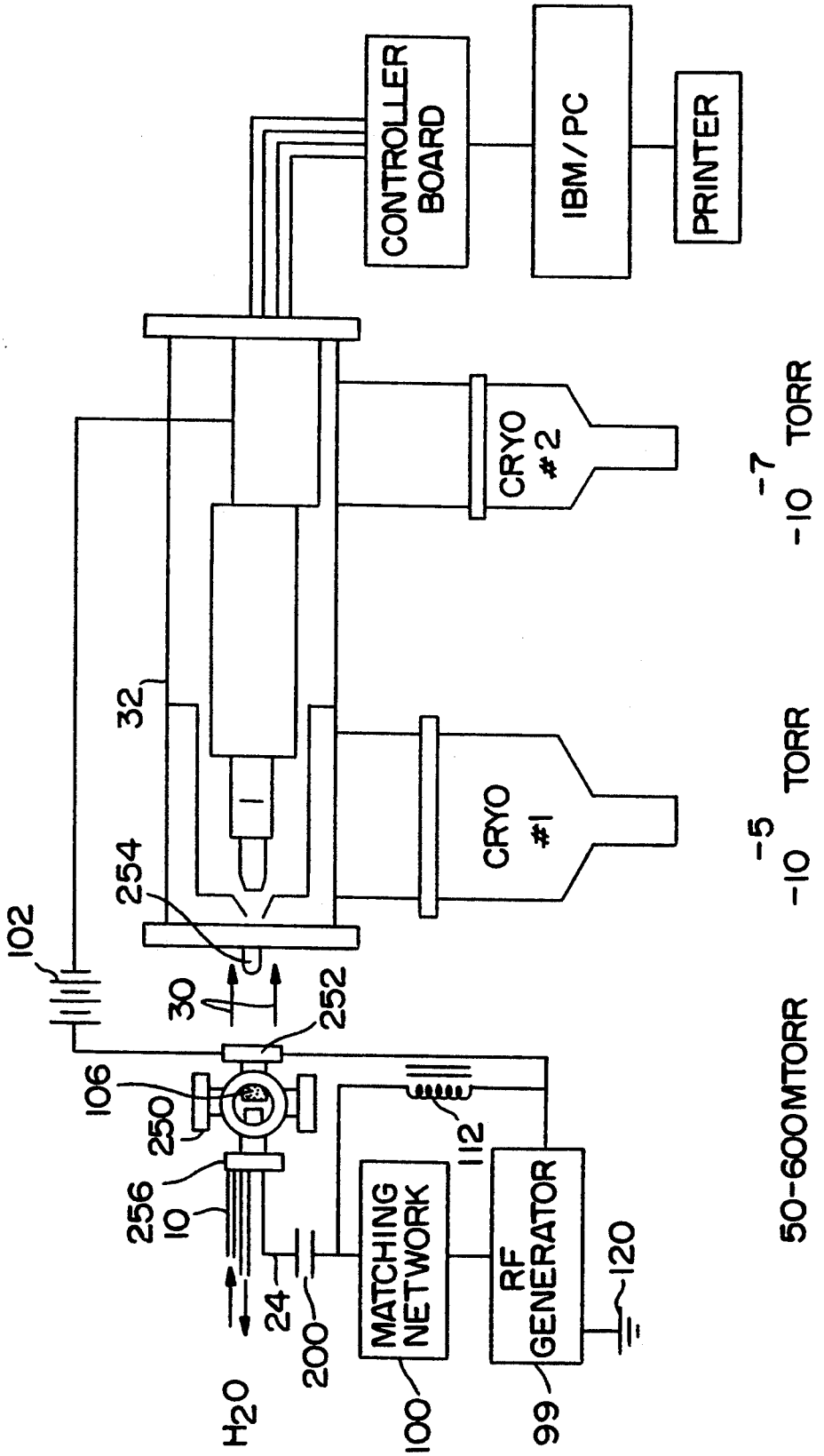


FIG. 4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CRYO #2
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MATCHING NETWORK
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RF GENERATOR
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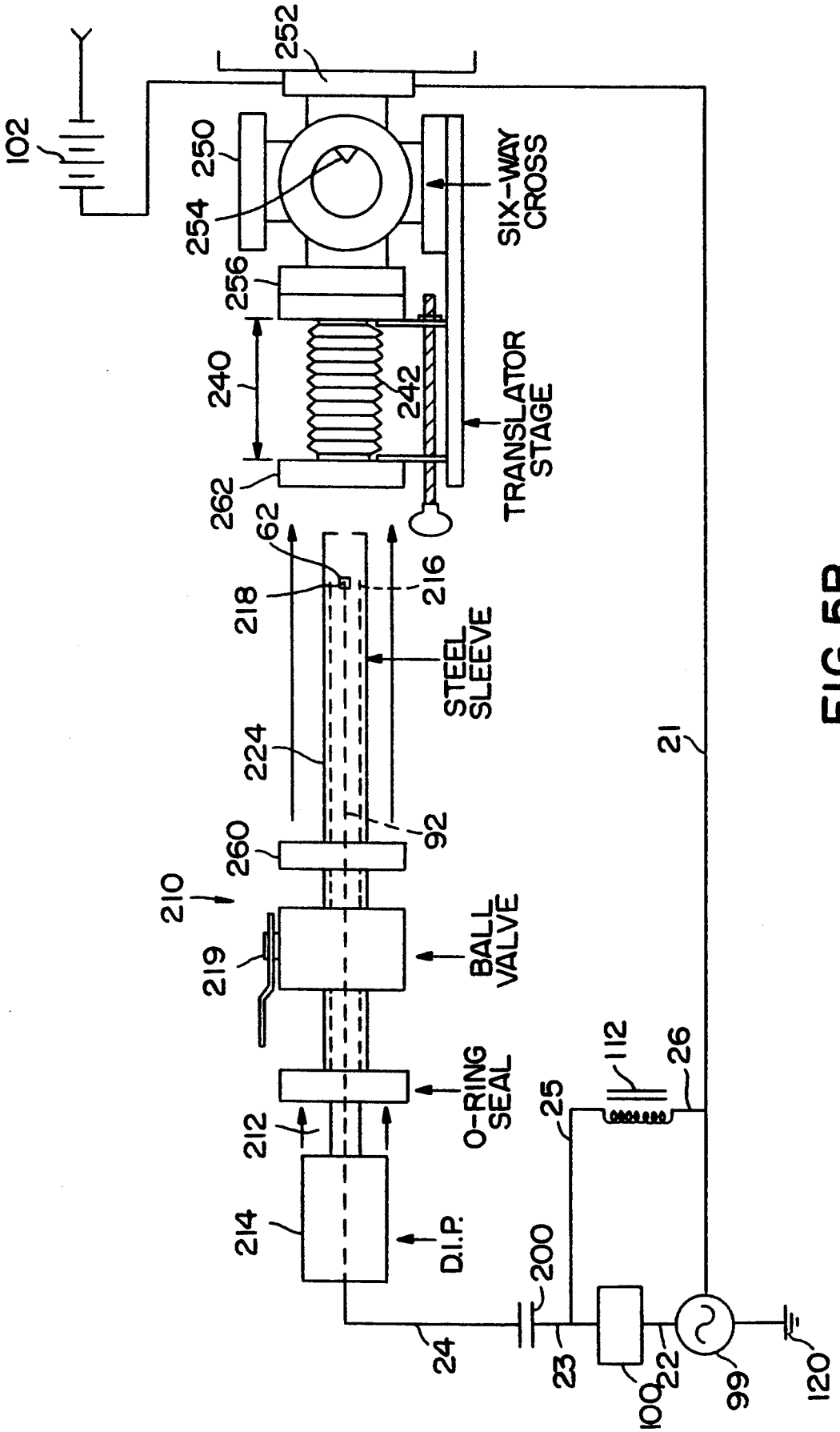
FIG. 5A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STEEL SLEEVE
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BALL VALVE
O-RING SEAL
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FIG. 5B

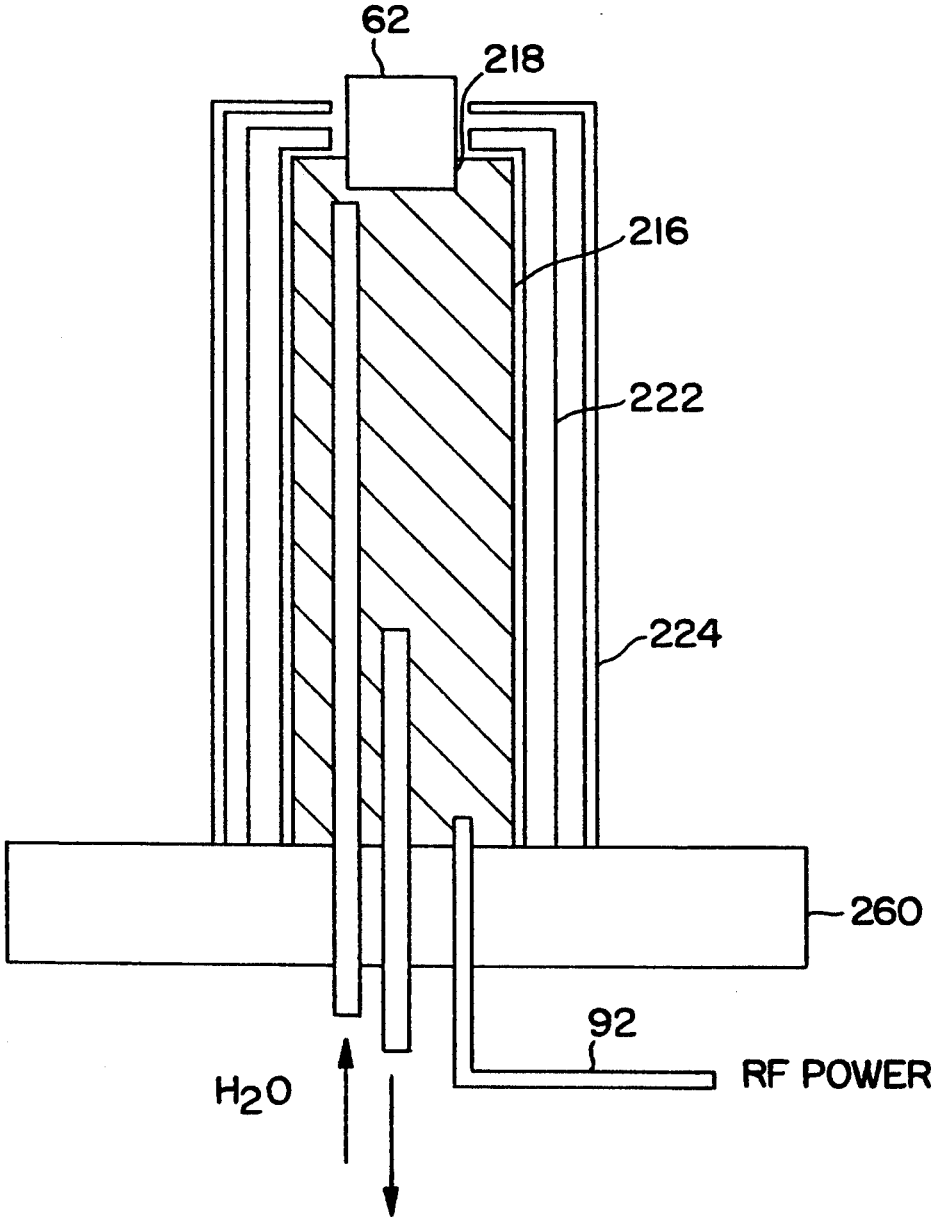

FIG.5C

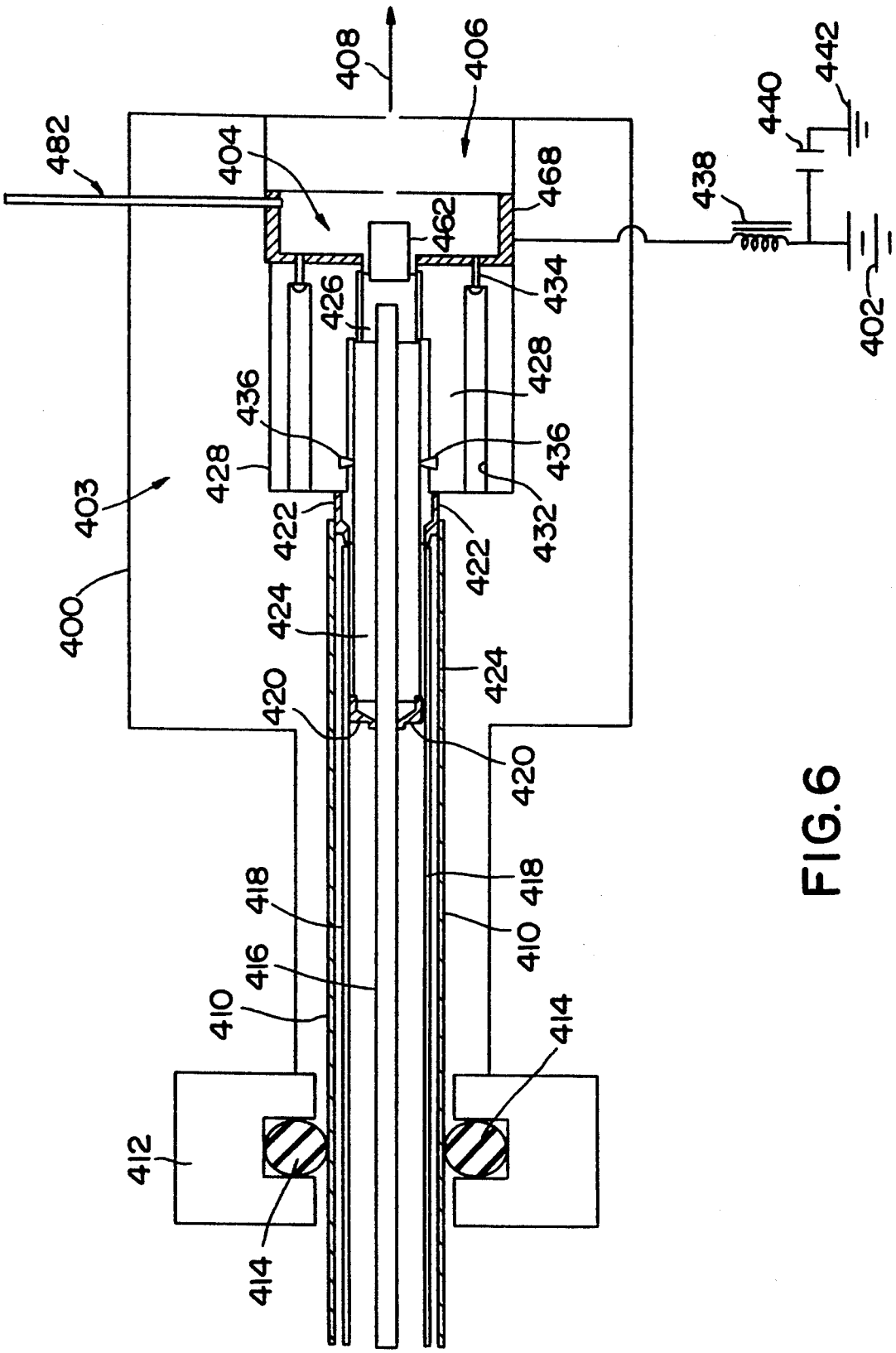
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FIG. 6

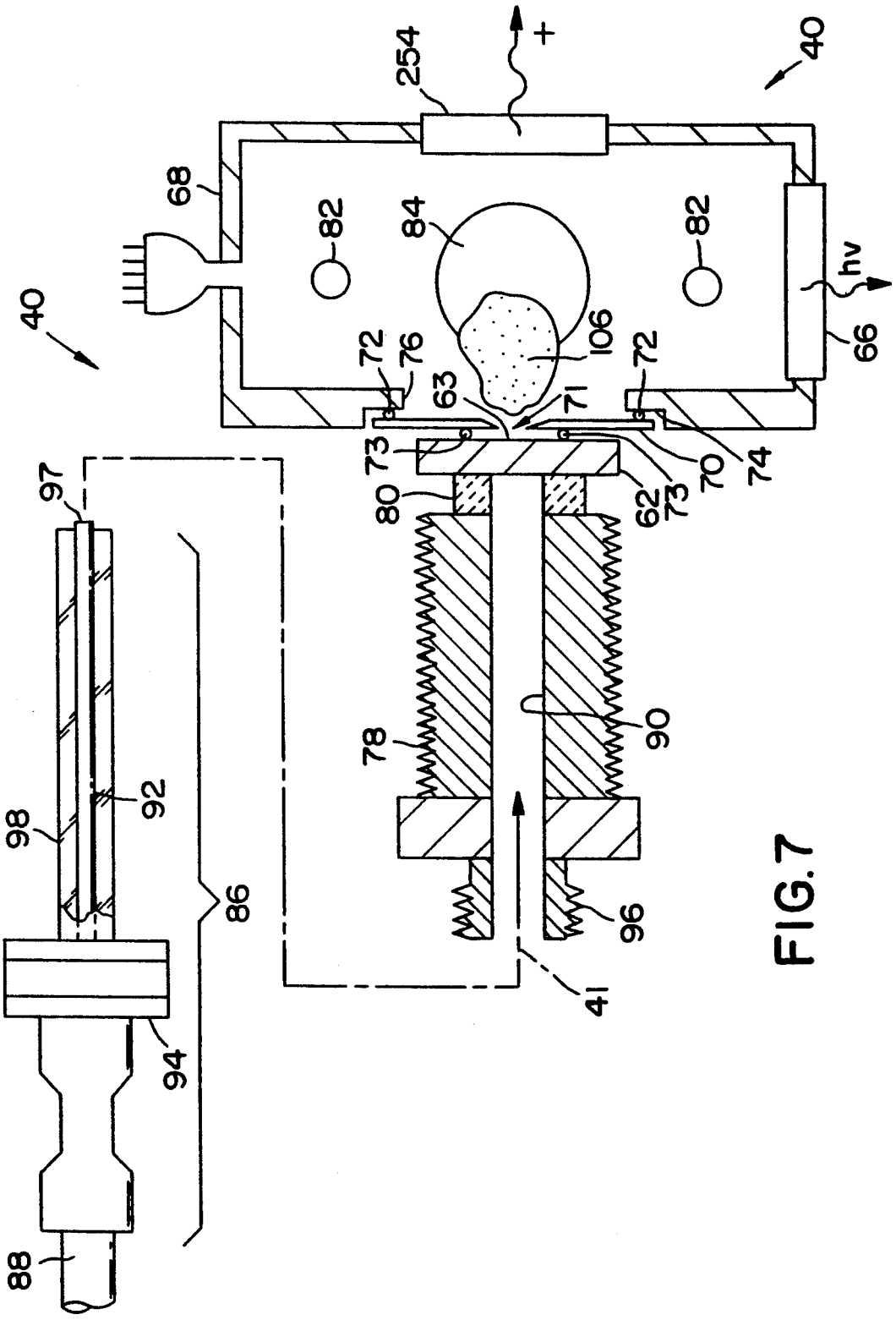
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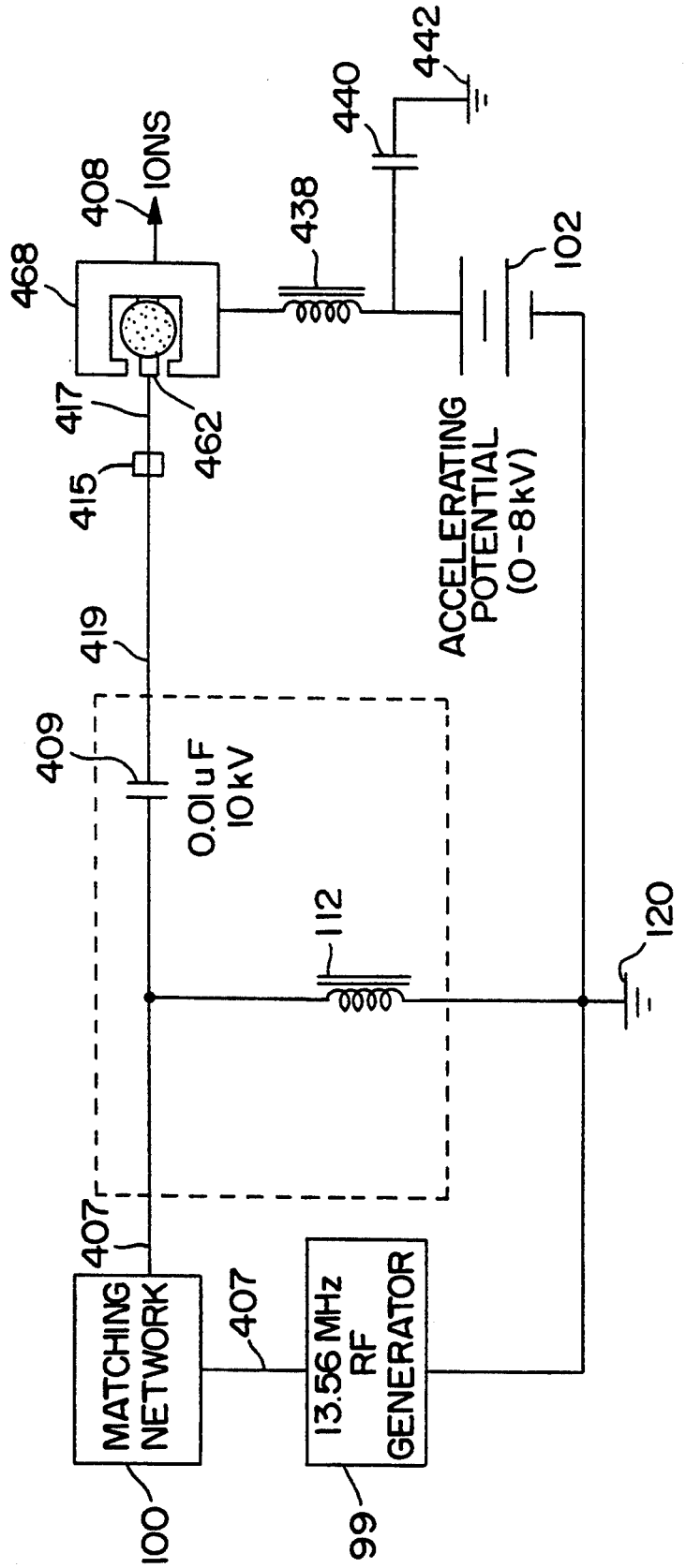
FIG. 7


442
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IONS
408
438
102
468
417
462
415
ACCELERATING POTENTIAL (0-8kV)
419
409
0.01uF 10kV
112
120
407
MATCHING NETWORK
407
13.56 MHz RF GENERATOR
100
99

FIG. 8

RADIO-FREQUENCY POWERED GLOW DISCHARGE DEVICE AND METHOD WITH HIGH VOLTAGE INTERFACE

This invention was made with United States Government support to Martin Marietta by the Department of Energy under Contract No. DE-AC05-840R21400, pursuant to which DOE Contract Martin Marietta awarded Contract Nos. AJ871GA1 and AH580GA1 to Clemson University, and thus the Government may have certain rights in the invention.

This is a continuation-in-part application to application Ser. No. 07/866,030 filed on Apr. 19, 1992, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a radio frequency (RF) powered glow discharge sputtering source for mass spectrometric analysis of non-conducting solids as well as metals, alloys, semiconductors and the like.

The application of conventional direct current (DC) powered glow discharge devices for the direct analysis of conductive solids such as metals, alloys and semiconductors is well known in the art and is discussed as background to the discussion of the RF powered glow discharge devices and methods. Generally, these DC powered glow discharge devices employ low pressure, inert atmosphere plasmas to initiate cathodic sputtering of solid samples that atomizes the sample material and produces a so-called "negative glow," also called a "glow discharge." In the negative glow, sputtered material collides with electrons and metastable discharge gas atoms to produce excited state atoms and ionic species. The electromagnetic radiation produced during the decays from excited energy states to lower energy states is responsible for the "glow" phenomenon.

In a so-called "diode" design of a DC powered glow discharge device, the conducting sample being analyzed takes the form of a cathode, which is housed in a vacuum chamber along with an anode sleeve. The walls of the vacuum chamber are electrically conducting and usually also act as an anode. The vacuum chamber is filled with an inert gas such as argon. When a sufficiently high electrical potential exists between the sample forming the cathode and the chamber walls and/or sleeve forming the anode, this causes the gas to dissociate into electrons and positively charged ions, which form part of what is sometimes called the "glow discharge" or the "negative glow." Much of this atomic dissociation occurs in a particular spatial region inside the vacuum chamber, and this region is sometimes called the "discharge excitation region" or the "negative glow region."

Since the sample is the negatively charged cathode of a DC powered glow discharge device, the negative field potential attracts the positively charged ions to the sample's surface. The so-called "sputtering" phenomenon occurs when the positively charged ions are accelerated toward the surface of the sample and eventually hit the cathode surface and dislodge atoms, ions and molecules of the cathode material. By virtue of the electrical biasing created by the electrical field inside the vacuum chamber, all of the negatively charged species (e.g., electrons, negative ions, and negatively charged molecules) will be accelerated away from the negatively biased cathode surface and all of the positively charged species in the vicinity will be accelerated to the cathode surface. The vast majority of sputtered particles are not charged and can either diffuse back to the cathode surface or into the discharge excitation region. The percentage of atoms entering the discharge excitation region is a function of the discharge pressure and cathode geometry.

In theory, the sputtering process acts as a cascade of inelastic collisions with the incoming ion imparting some portion of its kinetic energy, which approaches that of the electrical potential applied to the cathode, into the cathode material's lattice structure. According to this theory, if the sputtering ion has sufficient energy and directionality, the cascade will propagate back to the surface and result in the ejection of cathode material. The atoms ejected from the cathode material diffuse into the glow discharge region and become part of the so-called glow discharge. Sputter yields, the ratio of the average number of sputtered atoms to incident ions, are a function of the relative masses of the collision partners, the incident angle and energy of the sputtering ion, and the cathode material's binding energy.

DC powered glow discharge devices are currently employed to enable the sample to be subjected to elemental analysis by atomic absorption, atomic emission, atomic mass spectrometry, and a number of laser-based spectroscopic methods. These DC powered glow discharge devices, known commonly as "sources," have been limited by the fact that the sample must be conductive in nature so that it may act as a cathode in a conventional DC diode type design of the device. In an effort to analyze nonconducting solids without dissolution, nonconducting powder samples have been mixed with a conducting powder matrix. The resulting powder mixture is pressed into a disc sample, which, because of the conductive portion, allows for the required flow of current, but which also permits the sputtering of atoms of the nonconductive material upon impingement by a discharge ion. However, the mixing of the original sample with the conducting material introduces certain problems. For example, the dilutive effect of the conducting material results in both a loss of sensitivity and an increase in the likelihood of contamination. Moreover, many nonconducting solids are not easily transformed into powders, and the transformation of the solid into a powder precludes any depth resolved analyses.

The use of a radio frequency (RF) powered, as opposed to DC powered, glow discharge in argon to sputter and ionize a solid hollow cathode sample for analysis has been described (*Analytical Chemistry,* 47 (9), 1528, (1975). However, the hollow cathode geometry requires that the sample itself be machined into a cylinder. Machining the sample into a cylinder requires considerable labor and prevents depth profiling analysis.

The use of any glow discharge sampling geometry in which the sample must be inserted into the vacuum chamber, automatically restricts the size and shape of the sample to be analyzed. In such instances, metals and alloys must be machined to the proper geometry. Machining and grinding eliminate the possibility of performing depth-resolved analyses. Electrically nonconductive materials such as glasses and ceramics are often nonmachineable. Nonmachineable bulk solids must first be ground into a powder and then pressed to form a solid powder sample of compatible size and shape. Additionally, the combination of powdered nonconductive samples with a conducting material results in both a loss

of sensitivity and an increase in the likelihood of contamination.

A Grimm-Type high frequency powered glow discharge device (such as disclosed in Dec. 16, 1988 French Publication No. 2 616 545), which mounts the sample outside the vacuum chamber, disposes the cathode between the sample and the anode, and thus runs the risk of contamination from sputtering of the cathode material.

In order to analyze the sample in a mass spectrometer, the ionized sputtered material from the glow discharge must be transported from within the vacuum chamber of the glow discharge cell to the mass spectrometer. In a DC powered glow discharge source, a high DC voltage is applied to the walls of the vacuum chamber of the glow discharge cell in order to accelerate the charged sputtered material into the mass spectrometer. However, when this conventional method of applying a high DC voltage to both the sample and the discharge cell walls is tried in a RF powered glow discharge device, it destroys the ability of the device to maintain an analytically useful glow discharge.

Moreover, the RF glow discharge apparatus disclosed in U.S. Pat. Nos. 5,006,706 and 5,086,226 to Marcus (commonly assigned to the owner of the present application) pertain to cells maintained at ground potential. Any attempt to raise all of the RF electronics (RF generator and impedance matching network) to the same high DC electrical potential as the vacuum chamber walls have required using an isolation transformer (such as proposed at column 8, lines 8–11 in U.S. Pat. No. 4,501,965 to Douglas). This fails to provide a satisfactory solution because it causes additional problems of high voltage hazard, inconvenience, and electronic noise. For example, maintaining the RF electronics at the typical high voltage applied to the discharge cell means that the laboratory workers are subjected to the potential hazards of a five to ten thousand volt shock. Precautions needed to avoid encountering such electrical shock result in practical inconveniences in the performance of the measurements on the sample. In addition, it becomes impossible to shield the mass spectrometer system electronics adequately from RF electronic noise. Such electronic noise poses detriments to the desired limits of detection, experimental precision, and instrument calibration. Such noise also adversely affects the operation of other electronic instrumentation in the vicinity of the RF electronics because of the propagation of radio waves through this space.

OBJECTS AND SUMMARY OF THE INVENTION

It is a principal object of the present invention to provide a novel RF powered apparatus and method that operates on a solid material of any shape or electrical conductivity and presents same for direct analysis by mass spectrometry.

It is a further principal object of the present invention to provide a novel apparatus and method employing RF powered glow discharges to atomize solid samples for direct analysis by mass spectrometry without the hazards of maintaining the RF electronics at high voltages.

It is another principal object of the present invention to provide a novel apparatus and method employing RF powered glow discharges to atomize solid samples for direct analysis by mass spectrometry without subjecting the RF electronics or other electronic equipment in the vicinity of the RF electronics, to detrimental levels of electronic noise.

It is still another object of the present invention to provide such an apparatus which provides for the fast, successive analysis of a plurality of samples.

Yet another object of the present invention is to provide an apparatus and method for atomizing solid samples for analysis regardless of the electrical conductivity of the sample and without the need for such modifications of the sample as machining, dissolving, pulverizing, pressing or molding.

A further object of the present invention is to provide an apparatus and method for atomizing solid samples for analysis without having to insert the sample into the chamber where the glow discharge plasma is formed.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

To achieve the objects and in accordance with the purpose of the invention, as embodied and broadly described herein, an RF power supply can be used to generate the glow discharge for a conventional mass spectrometer with a conventional arrangement for applying an accelerating potential to the ions produced in the glow discharge generated from the sample to be analyzed. This includes magnetic sector mass spectrometers, time-of-flight mass spectrometers, and other mass spectrometers which employ the exit slit as a high voltage repeller electrode. A high voltage accelerating potential, which is supplied by a high voltage direct current power supply, is applied to the electrically conducting interior wall of the discharge cell in order to be able to repel the positive ions formed in the discharge. However, the high voltage DC accelerating potential is not supplied to the sample. A capacitive matching network is used to match the impedance of the plasma inside the discharge cell to the impedance of the RF power supply circuit, which includes an RF power supply. In addition, the invention includes a high voltage capacitance electrically connected in series between the sample on the one hand and the RF power supply and impedance matching network on the other hand. The high voltage capacitance isolates the high DC voltage from the RF electronics, while the RF potential is passed across the high voltage capacitance to the plasma. The RF power supply desirably is electrically grounded, and the conductor carrying the RF power to the sample is desirably shielded completely excepting only the conductor's terminal point of contact with the sample.

In further accordance with the present invention, an inductor is added in the circuit in a manner that protects at least the RF power supply, and desirably the impedance matching network as well, from a short that might occur across the high voltage capacitance.

In yet further accordance with the present invention, an inductor is electrically connected in series between the discharge cell walls and the source of the direct current accelerating potential used to remove ions from the cell for use by the mass spectrometer. In addition, one end of a capacitor is electrically connected between this inductor and this DC high voltage source, while the other end of the capacitor is electrically connected to

ground. This inductor and capacitor aid in isolating the accelerating potential from the RF power source.

In still further accordance with the present invention, the probe and cell are configured and disposed to prevent the components of the probe maintained at ground potential from shorting the cell components maintained at relatively high voltages on the order of 1 to 10 kilovolts.

In yet further accordance with an embodiment of the present invention, the probe and cell are configured and disposed to prevent the components of the probe maintained at ground potential from bridging between the relatively low vacuum region in communication with the glow discharge maintained within the cell and the relatively high vacuum region surrounding the probe and cell.

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate one embodiment of the invention and, together with the description, serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graphical representation of the effect of the application of a high voltage pulse to an insulating surface;

FIG. **2A** is a graphical representation of a 2 kV peak-to-peak square wave electrical potential provided by a power supply;

FIG. **2B** is a graphical representation of the effect of the application of the 2 kV peak-to-peak square wave electrical potential of FIG. **2A** to a pair of electrodes of a glow discharge device;

FIG. **3** is a schematic diagram of a conventional RF powered glow discharge source;

FIG. **4** is a schematic representation of an embodiment of the present invention;

FIG. **5A** is a schematic representation of a preferred embodiment of the present invention;

FIG. **5B** is a schematic diagram of embodiments of components for use in the present invention;

FIG. **5C** is a schematic diagram of embodiments of components for use in the present invention;

FIG. **6** is a schematic diagram of embodiments of components for use in the preferred embodiment of the present invention shown in FIG. **8**;

FIG. **7** is a schematic representation of components of an embodiment of the present invention; and

FIG. **8** schematically represents a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference now will be made in detail to the presently preferred embodiments of the invention, one or more examples of which are illustrated in the accompanying drawings. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. In the FIGS., the same components are numbered consistently throughout the drawings.

(Because the electrode defined by the electrically conducting wall **68** of the discharge cell is maintained at the opposite electrical polarity to the electrical polarity of a sample **62** to be analyzed, the electrode formed by wall **68** of the discharge cell is sometimes referred to as the counterelectrode.) Although no distinctly defined ground exists in the RF discharge apparatus of the present invention, sample **62** is often referred to as the cathode by analogy to the DC discharge apparatus. This convention is used in the present description.

As noted above, one of the factors which has tended to limit the application of glow discharges has been the requirement that the sample be conductive in nature. Conventional DC powered glow discharge devices cannot be used for the sputtering of purely nonconductive material, because in a DC system, if one of the electrodes in the system is an electrically insulating material, the required flow of current cannot occur.

However, the application of a high voltage electrical pulse to the surface of an article formed of material that is electrically insulating, can be considered analogous to the charging of a capacitor. In FIG. **1**, the vertical axis represents the voltage (V) at the surface of an article formed of material that is electrically insulating, and the horizontal axis represents the time (t) at which this surface voltage is measured. As shown in FIG. **1**, as a high negative (represented by the minus sign [−]) voltage of magnitude V_s is applied to the surface of an article formed of material that is electrically insulating, the electrical potential of this surface initially drops instantaneously to $-V_s$ and then gradually charges to more positive electrical potentials as a function of time. This gradual positive charging behavior is not due to the accumulation of positive charges at the surface of the electrically insulating material but rather is due to the loss of electrons through ion neutralization reactions at the material's surface. As explained below, the time scale of this process is such that the application of voltage pulses at frequencies on the order of one megahertz (MHz) and above results in a pseudo-continuous residual negative electrical potential at the surface of the article formed of electrically insulating material.

As explained in column 7 of U.S. Pat. No. 5,086,226 to Marcus, which patent is hereby incorporated herein by reference, a key aspect of the application of a RF powered glow discharge to the sputtering of a surface of the sample to be analyzed, is the "self-biasing" electrical potential which exists between the electrodes which generate the plasma. For example, FIG. **2** schematically illustrates the application of a 2 kilovolt (kV) peak-to-peak square wave potential (Va) by an RF power supply to a pair of electrodes. FIG. **2A** schematically represents an output of a 2 kilovolt (kV) peak-to-peak square wave potential (Va) generated by an RF power supply to a pair of electrodes. FIG. **2B** schematically represents the voltage of an insulating sample to which this voltage from FIG. **2A** has been applied. As shown in FIG. **2B**, at the very beginning (at time t=0) of the initial half-cycle, the voltage (Vb) of the primary cathode goes to −1 kV and then begins positive charging over time (t) to approximately −0.7 kV. As the applied voltage Va is switched to +1 kV, a surface potential of +1.3 kV is produced. During this half-cycle, electrons are accelerated to the electrode's surface. The greater mobility of the plasma electrons (compared to the much heavier positive ions) results in a

faster surface neutralization during this-half-cycle such that the electrode's surface potential approaches zero much faster than the previous half-cycle and thus reaching a value of +0.2 kV. When the voltage polarity is switched to the start of the second full cycle, the potential on this electrode will reach −1.8 kV (+0.2–2 kV). As successive cycles proceed, the wave form of Vb will reach a constant offset value which is significantly displaced in the negative direction. This constant negative voltage component is known as the "self-biasing" potential Vsb and is for all intents and purposes continuous. The magnitude of the self-biasing potential Vsb generally has an approximate value of one-half of the applied peak-to-peak potential (the applied peak-to-peak potential is 2×Va in the example shown in FIGS. 2A and 2B). The electrode is bombarded alternately by high energy ions and low energy electrons and is, therefore, employed as the sputtering target (cathode). While the potentials supplied to the electrodes are alternating, a time averaged cathode and anode are established. As discussed in U.S. Pat. No. 5,086,226 to Marcus, self-biasing is also a function of the respective electrode sizes. Thus, it is preferable to apply the RF potential to the sputtering target and to make its exposed area much smaller than the vacuum chamber anode, which is usually held at ground potential.

The present invention provides means for modifying a conventional mass spectrometer such as shown for example in U.S. Pat. No. 4,853,539 to Hall et al (the disclosure of which patent is hereby incorporated herein by this reference), U.S. Pat. No. 4,912,324 to Clark et al (the disclosure of which patent is hereby incorporated herein by this reference), or the VG 9000 TM (commercially available from Fisons Instruments, VG Elemental, Winsford, Chesire, ENGLAND), by replacing the direct current (DC) powered glow discharge with a radio frequency (RF) powered glow discharge having a high voltage interface.

FIG. 3 schematically illustrates an RF powered glow discharge apparatus such as discussed in U.S. Pat. No. 5,006,706 to Marcus (the disclosure of which patent is hereby incorporated herein by this reference). This is a so-called ground potential arrangement, because as is schematically represented by the numeral **120**, the discharge cell is maintained at ground electrical potential along with the RF electronics. A first electrical lead **21** connects an RF power supply to electrically conducting walls **68** of the discharge cell in which a glow discharge plasma **106** is to be generated from a sample **62** to be analyzed. In order to achieve efficient energy transfer to the plasma **106**, an impedance matching network **100** is incorporated electrically in series with the RF generator **99** via a second lead **22**. A third lead **23** electrically connects impedance matching network **100** in series with sample **62**. As schematically shown in FIG. **3**, matching network **100** desirably is an LC circuit which is tuned such that the total impedance of matching network **100** and plasma **106** equals the output impedance of the RF generator **99**.

As schematically shown in FIG. **3**, matching network **100** should employ a capacitive coupling, such as a high voltage blocking capacitor **101** connected in series with the RF generator **99**, to prevent any net current from flowing through the electrode circuit formed by sample **62**, cell walls **68** and plasma **106** (the latter being schematically represented in FIG. **4** as an internal resistance **104**). It should be noted that if the glow discharge is directly coupled (i.e., no blocking capacitor is interposed between the sample and one of the presently available RF generators), bias potentials are not allowed to develop for an electrically conducting sample, since the bias potentials would be continuously compensated by electron flow through the electrode circuit. Thus, a capacitive matching network connected in series between the cathode and the RF power supply is essential when using one of the presently available RF power sources to generate the glow discharge for an electrically conducting sample. A suitable RF generator **99** and matching network **100** are a model RF5S and a model AM-5, respectively, available from RF Plasma Products, Inc., of Marlton, N.J. A driving potential provided by RF generator **99** desirably is unmodulated at frequencies above one megahertz, and 13.56 megahertz has been used with success. The RF generator desirably should be able to maintain the nonconducting sample at a potential of at least 300 volts at one megahertz. The waveform can be of any shape, including sinusoidal, square, triangular, etc. The RF generator **99** desirably should be able to supply power over a range of from zero to 1,000 watts. The optimum power for any given sample, depends in large measure on the type of material forming the sample.

In the case of a mass spectrometer that incorporates a magnetic sector analyzer such as illustrated in FIG. **1** of U.S. Pat. No. 4,853,539 to Hall et al, the extraction of the ions from the ion source is achieved by an electrostatic field maintained between the body of the glow discharge source and an apertured (or slitted) electrode that is disposed between the source and the entrance to a flight tube as in a conventional mass spectrometer. This electrostatic field is the accelerating potential that moves the ions from the source into the flight tube leading to the conventional mass spectrometer. The accelerating potential is created by maintaining the apertured electrode in the wall of the discharge cell at the accelerating potential of the spectrometer. Consequently, the power supply for the glow discharge source as well as the associated electronics for the power supply, must be capable of safe operation at that accelerating potential, which typically is about 10,000 volts above ground potential.

However, the Hall et al arrangement for the mass spectrometer requires use of a direct current power supply glow discharge cell as the source. If one were to substitute an RF power supply for the DC power supply in the Hall et al arrangement in the absence of the present invention, the high voltage direct current accelerating potential would result in an equalization of the DC bias potential (Vsb schematically shown in FIG. 2B) which develops between the sample and the discharge cell. Such equalization results in an electrical short which distributes the RF-induced bias potential equally between the two electrodes, namely, the sample **62** and the discharge cell walls **68**. Such removal of the self-biasing electrical potential between the electrodes prevents the sputtering phenomenon needed for formation of an adequate glow discharge for analyzing the sample.

In accordance with the present invention, an RF power supply can be used to generate the glow discharge source for a conventional mass spectrometer with a conventional arrangement for applying an accelerating potential to the ions produced in the glow discharge generated from the sample to be analyzed. As shown in FIG. **4** for example, a high voltage accelerating potential, which is supplied by a high voltage direct

current power supply schematically represented by the symbol designated **102**, must be supplied to the electrically conducting discharge cell wall **68** in order to be able to repel the positive ions formed in the glow discharge. A direct current transformer can supply the high voltage direct current power and thus provide the means for applying a preselected high direct current voltage to the counterelectrode formed by cell walls **68**, which form the enclosure that defines the vacuum chamber in which the low vacuum containing argon or another inert gas is introduced.

In accordance with the present invention, the high voltage DC accelerating potential provided by direct current high voltage source **102** is supplied solely to the discharge cell wall **68**. As shown in FIGS. **4**, **5A** and **5B** according to the invention, the high voltage DC accelerating potential is not supplied to the sample **62**. The inventors have found that the sample **62** is subsequently charged up by the direct current power source **102** applying high direct current voltage on the discharge cell. As schematically illustrated in FIG. **4** for example, the charging occurs through the internal resistance (schematically represented by the jagged line designated **104**) of the plasma **106** (the boundary of the plasma **106** being schematically represented by the closed oval line designated **108**) inside the discharge cell. As illustrated schematically in FIG. **4**, this plasma **106** is an electrically conducting medium with a finite resistance **104**.

Moreover, in further accordance with the present invention, a means is provided for matching the impedance of the glow discharge plasma **106** to the impedance of the RF power supply circuit. As shown in FIGS. **4** and **5** for example, a matching network **100** is used to match the impedance of the plasma **106** to the impedance of the RF power supply circuit.

In still further accordance with the present invention, a means is provided for blocking direct current from flowing back-and-forth between the impedance matching means and introducing an isolating high voltage capacitance electrically in series between the impedance matching means and the sample to be analyzed. As embodied herein and schematically shown in FIG. **4** .for example, the isolating capacitance means includes a blocking capacitor **200** electrically disposed in the RF circuit in order to sustain a DC bias on the surface of the sample **62** to be analyzed by a mass spectrometer (not shown in FIG. **4** but shown in FIG. **5A** as generally **32**) that uses a high voltage accelerating potential. As schematically shown in FIG. **4** for example, high voltage capacitor **200** is electrically connected in series via a fourth lead **24** to the sample **62**. Leads **22**, **23**, and **24** desirably are formed as RF coaxial cable so that the conductor carrying the RF voltage is electrically shielded. High voltage capacitor **200** is electrically connected in series between the sample **62** on the one hand and the RF power circuit **99** and impedance matching network **100** on the other hand. The RF power circuit **99** desirably is electrically grounded, as indicated schematically by the symbol designated **120**. The high voltage capacitor **200** isolates the high DC voltage from the RF electronics, while the RF potential is passed across the capacitor **200** to the plasma **106**.

In further accordance with the present invention and as shown schematically in FIGS. **4**, **5A**, **5B**, and **8** for example, an inductance **112** is added in the circuit in a manner that protects at least the RF power supply **99**, and desirably the impedance matching network **100** as well, from a short that might occur across the high voltage capacitor **200**. As shown schematically in FIG. **4** for example, a fifth lead **25** connects inductance, such as a choke coil **112**, to third lead **23**, and a sixth lead **26** connects choke coil **112** to first lead **21**.

Electronic components simulating the electrical characteristics of any of the RF power supply, capacitances, inductances, and impedances can be used without departing from the invention.

FIG. **5A** is a diagrammatic representation of an embodiment of the apparatus of the present invention as assembled for analysis with a conventional mass spectrometer. The apparatus which holds and presents the sample inside the vacuum chamber of six-way cross **250** for generating the glow discharge ion source for the mass spectrometer (indicated generally at **32**) is generally indicated by the numeral **10** and is mounted coaxially with the axis of the mass spectrometer. Apparatus **10** also provides a means for electrically connecting the RF potential generated by RF generator **99** to the sample to be analyzed. The walls of six-way cross **250** define the electrically conducting counterelectrode of the glow discharge source. Port **256** of the six-way cross cooperates with apparatus **10** to provide a means for disposing the sample relative to the counterelectrode such that application of the appropriate RF potential between the sample and the counterelectrode in the presence of an inert gas, forms a sustainable glow discharge.

The ports of the six-way cross **250** other than the port **256** used to mount or receive the sample and the port **252** connecting the source to the ion extraction interface of the mass spectrometer, are utilized for the mounting of fused silica optical windows, vacuum and gas inlet attachments, and pressure monitoring thermocouples. The arrows **30** in FIG. **5A** schematically indicate that connecting port **252** of cross **250** is to be connected to the mass spectrometer instrument as shown in FIG. **5B** wherein ion sampling cone **254** is shown inserted into the vacuum .chamber of six-way cross **250**.

As shown in FIG. **5A**, a high direct current voltage source **102** applies an accelerating potential to the ions generated in the glow discharge region **106** that have diffused outwardly from the relatively higher pressure region inside the discharge cell. High direct current voltage source **102** thereby accelerates the positive ions exiting the vacuum chamber inside cross **250** and passes them through an intermediate vacuum region and into the analyzer region **32** for analysis. The DC high voltage power source **102** applies the accelerating potential which renders the cell walls at a positive electric potential of about 1,000 to 10,000 volts. The DC high voltage accelerating potential placed on the discharge cell requires the high voltage capacitor **200** to be placed in series with the sample **62** in order to isolate the resulting extremely positive electrical potential of the sample **62** from the RF power supply **99** and from the matching network **100**. The high voltage capacitor **200** isolates the matching network **100** and the RF power supply **99** from the high direct current voltage applied to the discharge cell by the source **102** of direct current potential. Capacitor **200** blocks the direct current voltage from reaching the impedance matching network and RF power supply. The inductance **112** prevents rapid voltage fluctuations in the RF circuit and acts as a choke coil.

A preferred embodiment of means for electrically connecting a radio frequency electromagnetic potential

between the counterelectrode, which is exposed to the interior of the vacuum chamber, and the sample, can employ a direct insertion probe. The probe provides means for electrically connecting to the sample, the radio frequency electromagnetic potential generated by an RF generator. As embodied herein and shown schematically in FIG. **5B** for example, further details of preferred components forming the arrangement generally indicated at **10** in FIG. **5A** are schematically illustrated in FIG. **5B** wherein ion sampling cone **254** is shown inserted into the vacuum chamber of six-way cross **250** via connecting port **252**.

In particular, FIG. **5B** schematically illustrates a preferred embodiment of a sample holder and sleeve assembly in the form of a direct insertion probe (DIP) for use with the present invention. The direct insertion probe is generally designated by the number **210** and mates with six-way cross **250** through a translator stage **240**. Adaptor flange **260** allows ball valve **219** to be connected to translator stage **240** via mating flange **262**. An electrically conducting and grounded probe body **212** is provided for shielding conductor rod **92**, which carries the RF potential, and has one end mounted onto the coaxial connector base **214** of probe **210**. A small sample **62** to be analyzed is mounted within a recess **218** of an electrically conducting sample holder body **216**, which acts as the cathode by being electrically connected to the conductor rod **92** that is electrically shielded within probe body **212**. The electrical shielding continues in the form of an electrically grounded steel sleeve that forms a grounded anode cap **224** which is drawn over the sample holder body **216**. The anode cap **224** is within one dark space from the cathode **216** to preclude discharge therein. Translator stage **240** includes a bellows **242** in conjunction with a ball valve **219** and serves as a vacuum interlock that allows for insertion and withdrawal of probe **210** without adjustment of the argon pressure within the six-way cross vacuum chambers thereby permitting faster analysis of a series of samples. Thus, a series of probes **210** may be provided such that numerous samples **62** can be prepared for a fast, easy analysis of a batch of materials. As shown in FIG. **5B** of the present application, the RF generator, impedance matching network **100**, high direct current power supply **102** for the accelerating potential, high voltage capacitance **200**, and choke coil **112** are configured and arranged as above-described for FIG. **4** and **5A**.

Moreover, as schematically shown in detail in FIG. **5C** for example, components carrying the RF power to the sample **62** desirably are completely shielded, electrically, upstream of the sample. Conductor **92** and cathode **216** carry the RF power to the sample **62**. Thus, electrically conducting steel sleeve **224** coaxially shields cathode **216** excepting only the terminal point of contact with the sample **62** at recess **218** of cathode **216**. Sleeve **224** is electrically connected to the electrically conducting and grounded shielding of the coaxial cable carrying the RF power to probe **210**. Thus, in accordance with the present invention, the conductors carrying the RF power to the sample are completely electrically shielded upstream of the sample and thereby avoid the problems associated with an arrangement such as shown in FIG. **2** of U.S. Pat. No. 4,853,539 to Hall et al with its unshielded contact spring **27**.

In yet further accordance with the present invention, the RF powered glow discharge high voltage interface of the present invention can be used in converting a conventional VG 9000 TM mass spectrometer into an instrument that has a capability of analyzing both conducting and nonconducting species. Moreover, the high voltage capacitor **409** (FIG. **8**) electrically connected in series between the sample **462** and the RF electronics (the RF electronics includes the impedance matching network) provides the VG 9000 TM mass spectrometer with dramatically improved performance. In addition, as shown in FIGS. **5B**, and **6–8** for example, the present invention alleviates much of the RF noise by shielding the electrically conducting components which carry the RF power to the sample to be analyzed. This improves detection limits and prevents such noise from influencing the calibration of the mass spectrometer. For example, when compared to attempts to float the RF generator in a conventional VG 9000 TM mass spectrometer system at the high voltage accelerating potential, the present invention has improved signal-to-noise ratios by a factor of approximately 1,000.

In accordance with the present invention, FIG. **6** schematically represents another preferred embodiment of an apparatus including an RF probe which is shown inserted into an RF glow discharge cell, wherein the probe and cell have been configured to be used in a conventional VG 9000 TM double-focusing mass spectrometer, also known as a sector mass spectrometer (available from Fisons Instruments, VG Elemental, Winsford, Chesire, ENGLAND). The electrically conducting walls of the RF glow discharge cell are schematically indicated by the cross-hatched enclosure identified by the numeral **468** and define the so-called counterelectrode of the discharge cell. As shown, the probe and cell are housed within a vacuum chamber capable of maintaining a high vacuum on the order of 10^{-7} torr within walls schematically represented by the continuous line identified by the numeral **400**. The arrow designated by the numeral **403** indicates the high vacuum region maintained within the vacuum chamber **400** surrounding the glow discharge cell **468**. The arrow designated by the numeral **404** indicates the region inside the glow discharge cell **468**, which region is maintained at a much higher pressure ($\sim$1 torr), and therefore a relatively lower vacuum, by the introduction of an inert discharge gas (such as argon) through a gas inlet that is schematically indicated by the tube passing through walls **468** and identified by the numeral **482**. The region outside the vacuum chamber walls **400** is at atmospheric pressure. The standard lens stack of the mass spectrometer is schematically represented by the rectangular area identified by the numeral **406**. The arrow designated by the numeral **408** schematically indicates the ions from the glow discharge that are provided to the mass spectrometer for analysis.

In accordance with the present invention, FIG. **8** schematically presents the overall arrangement for the probe and cell combination shown in FIG. **6**. As schematically shown in FIG. **8**, an RF power supply **99** provides means for generating a radio frequency electromagnetic potential. RF power supply **99** is electrically connected in series to a matching network **100** via coaxial cable **407** and thence to a 0.01×10^{-6} Farad blocking capacitor **409**, which desirably is rated at 10,000 volts. An appropriately rated choke coil **112** is electrically connected in parallel between the blocking capacitor **409** and the matching network **100** and across the RF power supply **99** to a ground connection **120**. A type HN connector **415** (though other RF connectors could be used) electrically couples the output of the

blocking capacitor **409** in series to the probe **417** via a coaxial cable **419**.

The probe provides means for electrically connecting to the sample, the radio frequency electromagnetic potential generated by RF generator **99**. By introducing an isolating high voltage capacitance electrically in series between the electrically connecting means of the probe and the impedance matching means of the impedance matching network **100**, blocking capacitor **409** provides means for blocking the direct current high voltage between the sample and probe on the one hand and the impedance matching means and RF generating means on the other hand.

As schematically shown in FIG. **6**, most of the length of the probe body is defined by a rigid cylindrical wall constructed from electrically conducting material such as stainless steel tubing **410** (o.d.=0.5", i.d.=0.430"). Steel tubing **410** is electrically connected to the coaxial shielding of the coaxial cable **419** (FIG. **8**) via connector **415** (FIG. **8**) and is electrically grounded to serve as the probe's coaxial shielding of the RF power carried by the probe. Such shielding is required to minimize electrical interference from the RF power.

As shown in FIG. **6**, a compression fitting **412** is disposed at the entrance to the high vacuum chamber defined schematically by walls **400** and carries an O-ring **414** configured and disposed to provide a vacuum seal against the outside diameter of steel tubing **410** when the probe is inserted into the high vacuum chamber. An annular aluminum or teflon handle desirably is slipped around the end (not shown) of the probe body disposed opposite from the end carrying the sample **462** to be analyzed. This handle can be secured to steel tubing **410** by a pair of set screws and facilitates operator manipulation of the probe.

As shown in FIG. **6**, the RF voltage of ~1 kV is carried by an electrical conductor **416** centrally disposed within the probe. Conductor **416** desirably is formed of a copper rod, but may be formed of another electrically conducting material. A circularly cylindrical insulating sleeve **418** forms an insulating sheath that is interposed between steel tubing **410**, which is maintained at ground electrical potential, and center conductor **416** to provide insulation between steel tubing **410** and center conductor **416**. Insulating sleeve **418** desirably is formed of material such as Teflon TM or glass such as Pyrex TM with an i.d. of 0.314" and an o.d. of 0.394".

As shown in FIG. **6**, the probe includes an electrical feedthrough, which facilitates the transition of the center conductor from the atmospheric pressure and electrically shielded environment of the coaxial cable and the probe body, to the terminal point of a sample holder **426** and a sample **462** exposed to the relatively low pressure interior space defined by the cell walls **468**, which are maintained at relatively high voltage. The feedthrough includes a cap **420** formed of electrically conducting material such as 70-30 Cu-Ni, a spacer member **424** formed of electrically insulating material such as Al_2O_3 ceramic material, and an adapter **422** formed of electrically conducting material such as metal.

As shown in FIG. **6**, a metal-to-metal weld forms a vacuum-tight seal between the interior cylindrical surface of cap **420** and a portion of the exterior cylindrical surface of center conductor **416**. Thus, cap **420** will be at the same ~1 kV electrical potential as center conductor **416**. Adapter **422** is welded, such as by soft silver-soldering, to form a vacuum-tight seal with the end of steel tubing **410** that is disposed opposite the end connected to the shielding of the coaxial cable (not shown in FIG. **6**). Thus, adapter **422** will be at the same ground electrical potential as steel tubing **410** of the probe body.

As schematically shown in FIG. **6**, insulator member **424** is configured in an annular shape (o.d. can be 0.280"), and one end of insulator member **424** is connected to cap **420** by a metal-to-ceramic vacuum-tight seal. Annular insulator **424** is configured and disposed to extend into and through adapter **422**. Another metal-to-ceramic vacuum-tight seal is formed between the interior cylindrical surface of adapter **422** and the exterior cylindrical surface of insulator member **424**. Thus, as center conductor **416** passes through adapter **422**, insulator member **424** electrically insulates center conductor **416** (with its RF voltages of ~1 kV) from the ground electrical potential at the steel tubing **410** and adapter **422**.

A sample holder **426** is machined from electrically conducting material like copper and is 0.25" in diameter which typically accommodates samples 0.188" in diameter. Sample holders can be machined to accommodate a range of sample sizes. Sample holder **426** either snug fits over the free end of center conductor **416** or is secured with a set screw (not shown). The sample **462** to be analyzed can be a conducting or nonconducting solid.

In accordance with the present invention, a means is provided for disposing the sample relative to the counterelectrode such that application of a predetermined radio frequency electrical potential between the sample and the counterelectrode in the presence of an inert gas inside the vacuum chamber forms a sustainable glow discharge. As embodied herein and schematically shown in FIG. **6** for example, the disposing means includes a cell assembly that includes an insulator member **428** and a discharge cell defined by electrically conducting walls **468**. The cell walls **468** are constructed from an electrically conducting material such as steel and form a cell having dimensions of 0.748" i.d., 1.07" o.d., and 0.615" height. Insulator member **428** desirably is constructed from boron nitride and has a 1.07" o.d. and 0.35" i.d. at the probe insertion point, but may be configured to accommodate a range of sample sizes. Screw holes **432** allow screws **434** (#2-56) to be inserted through the length of the boron nitride insulator member **428**. The screws **434** connect the boron nitride insulator member **428** to steel walls **468** of the discharge cell. Boron nitride insulator member **428** provides electrical insulation between the steel walls **468** of the cell, which are maintained at a high direct current voltage (~1 to 10 kV), which is schematically indicated by the symbol labelled **102** in FIGS. **6** and **8**, and the probe's stainless steel tubing **410** and adapter **422**, which are maintained at ground electrical potential.

The discharge cell houses the glow discharge which is maintained on the surface of sample **462**. As shown schematically in FIG. **6**, the probe is inserted into insulator member **428** so that sample **462** becomes exposed to the counterelectrode formed by discharge cell walls **468**. The inside diameter of boron nitride insulator **428** may be configured as required to accommodate a particular sample size. In the embodiment under discussion, the inside diameter of boron nitride insulator **428** reduces successively to 0.26" to accommodate the 0.25" o.d. sample holder **426** and thence to 0.20" to accommo-

date the 0.188" o.d. sample **462**, respectively. In so doing, insulator member **428** is configured to position sample holder **426** and sample **462** closer to insulator member **428** than the discharge dark space region, thereby reducing the likelihood of forming a discharge in the regions between insulator **428** and holder **426** or sample **462**. The glow discharge is confined by the steel cell's orifice (diameter=0.216" for 0.188" diameter samples) which is positioned within one dark space of the surface of sample **462**.

Moreover, as shown in FIG. **6**, the disposing means can include an O-ring **436** carried by the 0.35 i.d. portion of insulator member **428**. When the probe is inserted into the cell assembly, ceramic insulator **424** is positioned in vacuum-sealing engagement with O-ring **436** carried by insulator member **428**. In this application, O-ring **436** is a Viton TM O-ring which forms a vacuum-tight seal with the ceramic material forming insulator **424**. This is necessary because the source assembly is housed in a high vacuum ($\sim 1.0\times 10^{-7}$ torr) region **403**, which is within the enclosure schematically indicated by **400**, while the discharge which is maintained inside the cell with steel walls **468** is at a much higher pressure (~ 1 tort) because of the discharge gas being introduced through gas inlet **482**. Thus, the O-ring **436**-to-ceramic **424** seal maintains the differential pressure region. As explained in U.S. Pat. Nos. 5,006,706 and 5,086,226 to Marcus, sampling for mass spectrometric analysis is highly region-specific, and positioning of the negative glow/dark space interface at the sampling cone, is sensitive to adjustments of both pressure and power. In addition, the boron nitride insulator member **428** also provides high thermal conductivity for the standard VG9000 TM cold finger (liquid nitrogen temperature) attachment (not shown).

In addition, insulator member **428** is configured and O-ring **436** is configured and disposed so that no components maintained at ground electrical potential, can become disposed so as to bridge within both the higher pressure region (extending between O-ring **436** and within cell walls **468**) and the lower pressure region (extending between O-ring **436** and within the surrounding vacuum chamber walls **400**). Accordingly, since adapter **422** is the forward-most probe component maintained at ground electrical potential, the probe and cell are configured in accordance with the embodiment of the present invention shown in FIG. **6**, so that adapter **422** does not extend past O-ring **436** and thus does not bridge between the lower pressure region (extending between O-ring **436** and within the surrounding vacuum chamber walls **400**) and the higher pressure region that extends from O-ring **436** and into the discharge cell where the argon gas is introduced. Furthermore, the length of insulator member **428** must be long enough to provide adequate electrical insulation against arcing between adapter **422** at ground potential and cell walls **468** at a high electrical voltage on the order of 8 to 10 kilovolts. Typically, about one half inch of boron nitride between the heads of screws **434** and adapter **422**, suffices for this purpose of providing adequate electrical insulation.

As shown in FIGS. **6** and **8**, a 40×10^{-6} Henry choke coil **438** is electrically connected in series between cell walls **468** and the source **102** of the direct current accelerating potential used to remove ions from the glow discharge and provide these ions to be analyzed by the mass spectrometer. In addition a 200×10^{-12} Farad capacitor **440** has one end electrically connected between choke coil **438** and power source **102** and the other end electrically connected to ground **442**. This additional coil **438** and capacitor **440** aids in isolating the accelerating potential **102** from the RF power source **99**.

In a further embodiment of an apparatus and method according to the present invention, an RF powered glow discharge atomization/excitation source incorporating an external sample mount geometry as described in U.S. Pat. No. 5,086,226 to Marcus, is illustrated schematically in FIG. **7** and designated generally by the numeral **40**. In accordance with the present invention, glow discharge source **40** can be used in conjunction with a conventional mass spectrometer by disposing the source **40** within a high vacuum enclosure such as enclosure **400** shown in FIG. **6** for example. The chamber body **68** of the source **40** desirably can be configured with ports such as shown in FIG. **5B** for example. Such body **68** forms an enclosure that defines a vacuum chamber and is desirably formed of stainless steel. The stainless steel walls forming the interior surface of the vacuum chamber also define a counterelectrode surface area exposed to the interior of the vacuum chamber.

The enclosure further defines a sample port that communicates between the interior and the exterior of the vacuum chamber. As embodied herein and shown schematically in FIG. **7** for example, the sample port is an opening **76** defined in chamber body **68**. An inert gas such as argon can enter the discharge chamber defined by chamber body **68** through one or both of two 0.63 cm diameter circular compression fittings **82** defining gas inlet ports for the introduction of the inert gas. Defined in the top of the chamber is a vacuum port **84** which leads to an adjustable-flow (bellows) vacuum valve (not shown) that controls the degree of vacuum present within the discharge chamber defined by chamber body **68**.

In further accordance with the present invention, a means is provided for disposing the sample relative to the counterelectrode such that application of a predetermined radio frequency electrical potential between the sample and the counterelectrode in the presence of an inert gas inside the vacuum chamber forms a sustainable glow discharge. As schematically shown in FIG. **7** for example, one embodiment of the disposing means includes an external mount for receiving a solid sample external to the vacuum chamber. The external mount can include a lip flange surface **74**, which generally is defined in stainless steel body **68** and is oriented to face away from the interior of the chamber. Lip flange surface **74** forms part of the exterior surface of the chamber and frames sample port opening **76**. Since lip flange surface **74** is defined in stainless steel body **68**, the external mount is electrically connected to the stainless steel walls defining the counterelectrode surface area exposed to the interior of the vacuum chamber.

As embodied herein and shown schematically in FIG. **7** for example, the external mount can include an external mounting plate in the form of an orifice disk **70**. The external mounting plate is electrically connected, as by metal screws for example, to enclosure body **68**. Moreover, the external mounting plate defines a sample hole in the form of an orifice **71** that is circumscribed by sample port **76** and so controls the exposure of surface **63** of sample **62** to negative glow **106**. Orifice **71** defined in orifice disk **70** desirably can have a circular shape with a diameter on the order of about two to twelve millimeters. An orifice of 2 mm provides a higher

power density, which is desirable to enhance emission intensity. At some point, the orifice becomes too small to be able to accommodate dark spaces. With a 2 mm diameter orifice, a chamber pressure of from about 4 or 5 torr and above, must be maintained. Otherwise, a dark space cannot fit inside the orifice, and consequently no discharge will occur.

A conformable mounting plate sealing gasket in the form of an O-ring **72** is desirably disposed between the interior surface of the periphery of orifice disk **70** and lip flange surface **74** formed around sample port opening **76**. The central opening defined in O-ring **72** is large enough to surround sample port opening **76**. Moreover, the O-ring gasket is able to conform its shape sufficiently under the application of pressure so that a vacuum tight seal is formed between the mounting plate and the exterior of the vacuum chamber enclosure. The O-ring **72** is desirably formed of a rubber soft enough to ensure an excellent seal under vacuum conditions.

In yet further accordance with the apparatus of the present invention, a torque bolt can be provided to bias and secure the sample so as to expose a surface of the sample to the interior of the vacuum chamber. As embodied herein and shown schematically in FIG. **7** for example, a brass torque bolt **78** is disposed outside the vacuum chamber defined by the enclosure. In order to electrically insulate the brass bolt from the sample, a ceramic spacer **80** is desirably disposed between the bolt and the sample **62**.

In still further accordance with the present invention, means are provided to furnish a vacuum tight seal and maintain a less than one dark space separation between the surface forming the vacuum chamber electrode and a surface of the sample exposed to the interior of the vacuum chamber when the sample is secured to the external mount of the enclosure. As embodied herein and shown in FIG. **7** for example, a conformable sample sealing gasket in the form of an O-ring **73** is configured so as to be disposable against and between a first surface and a second surface so as to provide a vacuum tight seal and maintain a less than one dark space separation between the first surface and the second surface when the torque bolt secures the sample against the sample sealing gasket. Desirably, O-ring **73** is disposed between the exterior surface of orifice disk **70** and surface **63** of sample **62**. Accordingly, a separation distance of less than one dark space is maintained between the first surface, which is the sample's surface **63** facing toward the interior of the vacuum chamber, and the second surface, which is the mounting plate surface facing away from the interior of the vacuum chamber, when torque bolt **78** secures sample **62** against sample sealing gasket **73**. A suitable gasket for O-ring **73** is formed of TEFLON TM for example because of higher heat resistant properties of this material than rubber. Pressure is applied to form a vacuum-tight seal between sample **62** and orifice disk **70** and between orifice disk **70** and lip **74** of chamber body **68** by rotation of threaded brass torque bolt **78** against the insulating compression ring formed as spacer **80**. Insulating spacer **80** also functions to prevent bolt **78** from damaging the sample when the bolt is tightened to secure the sample to the external mount.

In some embodiments of the sample securing and dark space maintaining means, the mounting plate, such as orifice disk **70**, can be formed as a unitary part of enclosure body **68**. However, such embodiments would forego the advantages of the interchangeability of mounting plates with differently sized and/or shaped orifices.

In still other embodiments of the sample securing and dark space maintaining means, a sample holder is provided in the form of a mold in which powdered sample material can be compacted and held. The external mounting plate **70** and the flexible gaskets **72** and **73** provide means for disposing the sample relative to the counterelectrode **68** such that application of a predetermined radio frequency electrical potential between sample **62** and counterelectrode **68** in the presence of an inert gas inside the vacuum chamber forms a sustainable glow discharge.

In still further accordance with the apparatus of the present invention, means are provided for applying a radio frequency electromagnetic potential between the counterelectrode, which is exposed to the interior of the vacuum chamber, and the sample to be received by the external mount. As embodied herein and shown schematically in FIG. **7** for example, an RF feedthrough **86** can be electrically attached to the end of a coaxial RF power cable (RG 213/U) **88**, which can be inserted into an elongated cavity **90** defined longitudinally through bolt **78** and spacer **80**. For example, one end of power cable **88** can be connected to an elongated copper conductor rod **92** via a male type-N coaxial connector **94**, wherein the free end of conductor rod **92** can be configured as an electrical terminal **97** with a circular transverse cross-sectional diameter of 3.2 millimeters. A female coaxial connector **96** can be defined at the end of bolt **78** opposite the end of bolt **78** disposed to press against spacer **80**. When male connector **94** is mated to female coaxial connector **96**, the terminal **97** of conductor rod **92** makes contact with the back of sample **62**. Then the RF generator provides the means for applying a radio frequency electromagnetic potential between the counterelectrode **68** and electrical terminal **97**. A circular cylindrical annular glass insulator member **98** can serve as an electrically insulating sheath that surrounds conductor rod **92** and effectively prevents arcing between conductor rod **92** and bolt **78**. In this way, the conductor rod **92** carrying the RF power to the sample **62**, desirably is coaxially shielded completely by bolt **78** excepting only the conductor's terminal point of contact with the sample **62**. Thus, in accordance with the present invention, the conductors carrying the RF power to the sample are completely electrically shielded downstream of the sample and thereby avoid the problems associated with an arrangement such as shown in FIG. **2** of U.S. Pat. No. 4,853,539 to Hall et al with its unshielded contact spring **27**.

What is claimed is:

1. An apparatus for using radio frequency electromagnetic energy to form a glow discharge from a solid sample for use in a mass spectrometer, whether the sample is electrically conducting or nonconducting, and whether the sample is machineable or nonmachineable, the apparatus comprising:

(a) an enclosure,
  i) said enclosure defining a vacuum chamber,
  ii) said enclosure defining an electrically conducting counterelectrode having a surface exposed to the interior of said vacuum chamber;

(b) means for disposing the sample relative to said counterelectrode such that application of a predetermined radio frequency electrical potential between the sample and said counterelectrode in the

presence of an inert gas inside said vacuum chamber forms a sustainable glow discharge;

(c) means for generating a radio frequency electromagnetic potential;

(d) means for electrically connecting to the sample the radio frequency electromagnetic potential generated by said generating means;

(e) means for applying a preselected high direct current voltage to said counterelectrode to aid in providing ions from the glow discharge for subsequent analysis;

(f) means for matching the impedance of said generating means and a combination of said connecting means, said counterelectrode, the sample disposed by said disposing means, said disposing means, and the glow discharge, said impedance matching means being electrically connected in series between said electrically connecting means and said generating means; and

(g) means for blocking direct current flow between said electrically connecting means and said impedance matching means due to said preselected high direct current voltage.

2. An apparatus as in claim **1**, wherein said sample disposing means includes:

i) an annular insulating member configured and disposed with one end connected to said enclosure and defining an elongated opening therethrough; and

ii) a vacuum sealing O-ring configured and disposed about said elongated opening in the vicinity of the end of said annular insulating member opposite said one end connected to said enclosure.

3. An apparatus for using radio frequency electromagnetic energy to form a glow discharge from a solid sample for use in a mass spectrometer, whether the sample is electrically conducting or nonconducting, and whether the sample is machineable or nonmachineable, the apparatus comprising:

(a) an enclosure,

i) said enclosure defining a vacuum chamber,

ii) said enclosure defining an electrically conducting counterelectrode having a surface exposed to the interior of said vacuum chamber;

(b) means for disposing the sample relative to said counterelectrode such that application of a predetermined radio frequency electrical potential between the sample and said counterelectrode in the presence of an inert gas inside said vacuum chamber forms a sustainable glow discharge;

(c) means for generating a radio frequency electromagnetic potential;

(d) means for electrically connecting to the sample the radio frequency electromagnetic potential generated by said generating means;

(e) means for applying a preselected high direct current voltage to said counterelectrode to aid in providing ions from the glow discharge for subsequent analysis;

(f) means for matching the impedance of said generating means and said combination of said connecting means, said counterelectrode, the sample disposed by said disposing means, said disposing means, and the glow discharge, said impedance matching means being electrically connected in series between said electrically connecting means and said generating means; and

(g) mean for blocking direct current flow between said electrically connecting means and said impedance matching means, wherein said connecting means comprises:

i) a first coaxial connector configured to be electrically connected to one end of a radio frequency coaxial cable,

ii) an elongated conductor having a first end and a second end disposed opposite said first end, said first end of said conductor being electrically connected to said first coaxial connector,

iii) an electrically conducting sample holder member having one end configured to receive a sample therein and having an opposite end electrically connected to said second end of said conductor,

iv) an annular insulator member configured and disposed to surround a predetermined length of said conductor extending from said sample holder member toward said first end of said conductor,

v) an adapter member configured and disposed to form a vacuum-tight seal with the exterior surface of an intermediate circumferential portion of said insulator member,

vi) an electrically conducing probe body configured and disposed to surround said conductor and extending between and electrically connecting said first coaxial connector and said adapter member,

vii) an electrically insulating sleeve configured and disposed to surround said conductor and said insulator member and extending between said first coaxial connecter and said adapter member and disposed between said probe body and said annular insulator member, and

viii) an annular cap member configured and disposed with one end forming a vacuum-tight seal with the end of said insulator member disposed farther away from said sample holder member, said annular cap member having a second end configured and disposed to form a vacuum-tight seal with said conductor.

4. An apparatus as in claim **3**, wherein said sample disposing means includes:

an annular insulating member configured and disposed with one end connected to said enclosure and defining an elongated opening therethrough; and

ii) a vacuum sealing O-ring configured and disposed about said elongated opening in the vicinity of the end of said annular insulating member opposite said one end connected to said enclosure and further configured to form a vacuum-tight seal against said insulator member when said insulator member is inserted into said elongated opening; and

iii) wherein said elongated opening is configured so that when the sample is disposed inside said enclosure to sustain a glow discharge on the surface of the sample exposed to said counterelectrode, said O-ring is disposed between said adapter and said sample holder member.

5. An apparatus as in claim **1**, wherein said electrically connecting means comprises:

i) a radio frequency coaxial cable,

ii) a first coaxial connector electrically connected to one end of said radio frequency coaxial cable,

iii) an elongated conductor having a first end and a second end disposed opposite said first end, said first end of said conductor being electrically connected to said first coaxial connector,

iv) a second coaxial connector disposed so that upon engaging said first coaxial connector said second end of said conductor electrically engages the sample during operation of the apparatus,

v) an electrically insulating sheath surrounding said conductor between said first and second ends of said conductor, and

an electrically conducting shield surrounding said conductor upstream of where said terminal contacts the sample.

6. An apparatus as in claim **1**, wherein said sample disposing means includes an external mounting plate and a flexible gasket for sealing the sample against said mounting plate.

7. An apparatus as in claim **1**, further comprising:

(h) an inductive impedance electrically connected as a choke coil to protect said impedance matching means and said radio frequency electromagnetic potential generating means against electronic shorting of said direct current flow blocking means.

8. An apparatus as in claim **1**, further comprising:

(h) an inductive impedance electrically connected in series between said counterelectrode and said means for applying a preselected high direct current voltage to said counterelectrode.

9. An apparatus as in claim **8**, further comprising:

(i) a capacitive impedance electrically connected in parallel between said inductive impedance and said means for applying a preselected high direct current voltage to said counterelectrode.

10. An apparatus as in claim **1**, wherein said high direct current voltage applying means includes a direct current transformer.

11. An apparatus as in claim **1**, wherein said radio frequency electromagnetic potential generating means includes a radio frequency generator capable of generating at least 300 volts at a frequency of at least one megahertz.

12. An apparatus as in claim **1**, wherein said direct current blocking means includes an isolating high voltage capacitance electrically connected in series between said electrically connecting means and said impedance matching means.

13. An apparatus as in claim **1**, wherein said impedance matching means includes a high voltage capacitor electrically connected in series with said radio frequency electromagnetic electric potential generating means.

14. An apparatus as in claim **1**, wherein said means for generating a radio frequency electromagnetic potential includes means for electrically shielding the generated radio frequency electromagnetic potential.

15. An apparatus as in claim **14**, wherein said means for electrically shielding the generated radio frequency electromagnetic potential, comprises:

i) a cylindrically configured electrically conducting shield surrounding said electrically connecting means upstream of where said electrically connecting means electrically connects the radio frequency electromagnetic potential to the sample.

16. An apparatus as in claim **1**, further comprising:

i) a mass spectrometer configured and disposed for receiving matter removed from the glow discharge for subsequent analysis.

17. A method for using radio frequency electromagnetic energy to transform a solid sample, whether the sample is electrically conducting or nonconducting, into a glow discharge source and analyzing the sample with a mass spectrometer, the method comprising the steps of:

(a) enclosing an inert gas within a vacuum chamber defining a counterelectrode having a surface exposed to the interior of said vacuum chamber;

(b) disposing the sample relative to said counterelectrode such that application of a predetermined radio frequency electrical potential between said sample and said counterelectrode in the presence of said inert gas inside said vacuum chamber forms a sustainable glow discharge;

(c) electrically connecting the sample in series to an isolating high voltage capacitance;

(d) electrically connecting in series said isolating high voltage capacitance to a capacitive impedance matching network;

(e) electrically connecting in series to said capacitive impedance matching network, means for generating a radio frequency electromagnetic potential;

(f) applying a radio frequency electromagnetic potential between said counterelectrode and said sample via said isolating high voltage capacitance; and

(g) applying a preselected high direct current voltage to said counterelectrode to accelerate ions from said vacuum chamber to a mass spectrometer for analysis.

18. A method as in claim **17**, further comprising the step of:

(a) electrically connecting an inductance between said capacitive impedance matching network and said isolating high voltage capacitance and between said means for generating a radio frequency electromagnetic potential and said counterelectrode.

19. A method as in claim **17**, further comprising the steps of:

(a) enclosing said vacuum chamber inside a higher vacuum enclosure;

(b) maintaining at electrical ground potential, said impedance matching network and said means for generating a radio frequency electromagnetic potential; and

(c) preventing components maintained at ground electrical potential from bridging between said vacuum chamber and said higher vacuum enclosure.

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