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(54) **DIELECTRIC BARRIER DISCHARGE PLASMA REACTOR AND METHOD FOR
PLASMA-ENHANCED VAPOR DEPOSITION**

PLASMAREAKTOR MIT DIELEKTRISCHER BARRIEREENTLADUNG UND VERFAHREN ZUR
PLASMAVERSTÄRKTEN DAMPFABSCHIEDUNG

RÉACTEUR PLASMA DE DÉCHARGE À BARRIÈRE DIÉLECTRIQUE ET PROCÉDÉ
D'ÉVAPORATION SOUS VIDE AMÉLIORÉ AU PLASMA

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Description**Field of the invention**

5 **[0001]** The invention is related to a dielectric barrier discharge (DBD) plasma reactor. More specifically, the DBD plasma reactor according to the invention is a device suitable for plasma-enhanced chemical vapor deposition (PECVD) of a coating, for example a crystalline inorganic coating, on a substrate under atmospheric pressure conditions. Examples of crystalline inorganic coatings are V_2O_5 and TiO_2 .

10 **[0002]** The invention is also related to a method for performing PECVD. More precisely, a PECVD method for forming a coating, for example a crystalline inorganic coating, on a substrate under atmospheric pressure conditions.

Description of prior art

15 **[0003]** A known option for forming crystalline inorganic coatings is the use of a two-step process wherein in a first step quasi-amorphous films are deposited followed by a second annealing step. For the first step, a DBD plasma reactor operating at atmospheric pressure and room temperature (e.g. 25°) can for example be used.

20 **[0004]** The DBD plasma reactor is a device that comprises a first electrode, a second electrode separated from the first electrode, and a first dielectric layer located between the first and the second electrode. A plasma area is formed between the first and the second electrode and the substrate is placed in the plasma area. A main gas and generally also a precursor under gaseous form, are introduced between the two electrodes and a power supply is used to apply a voltage, generally an alternating voltage, between the first electrode and the second electrode and create a plasma in the plasma area.

25 **[0005]** After performing this first step of deposition of the coating to the substrate using the DBD plasma reactor, an annealing process needs to be started, i.e. the substrate needs to be heated after deposition until it reaches a sufficiently high temperature for the coating to recrystallize and take a specific crystalline form.

30 **[0006]** American patent application publication number US2005/0236374 discloses a device for processing a welding wire. Figure 3 shows a device for coating the outer surface of a welding wire continuously moving through a tube comprising a dielectric barrier discharge (DBD) plasma reactor wherein a coating material is introduced in vapor form for deposition on the outer surface of the welding wire. As taught by this document, the coating material is an alkali metal. Such coating material doesn't require annealing and therefore doesn't need to be heated after its deposition. Fig 12 shows another embodiment wherein the welding wire passes through a middle portion of the device which does not comprise electrodes and where the wire is heated by a magnetic field generated by a coil arranged coaxially around the wire. Though it is not clear from this document why the welding wire need to be heated before passing through the next portion of the device, it is anyway heated outside of any plasma area. With such a configuration, the substrate (the welding wire) therefore has to be moved outside of the plasma area in order to be heated, which necessarily takes time.

35 **[0007]** Patent document KR101507383B1 discloses a similar arrangement where the coating and heating steps are separated.

[0008] A disadvantage of these approaches is that the overall processing time is long as the annealing step can take hours before completion.

40 **[0009]** Patent document JP2006032303A discloses a capacitive-inductive plasma generation. It has no electrodes and is therefore not capable to produce a DBD plasma.

[0010] Patent document US5510158A discloses a device comprising a DBD reactor. However, the substrate is not placed in the plasma area of the DBD reactor and it is merely by light created by the excited plasma that the substrate is treated.

45 **[0011]** Alternatively, to avoid the annealing step, the substrate could be heated by resistive heating during the deposition. However, this option is often hard to realize in real experimental conditions, as most of the atmospheric plasma deposition is done using high-frequency dielectric barrier discharge, typically in the 1kHz to 100 kHz range. One of the problems is electrical interference between the heating circuit and the plasma circuit, and a further difficulty is related to efficiently heating a substrate when a dielectric is located between the substrate and the electrode. In practice, when using resistive heating, the entire reactor with the electrodes and dielectric is being heated resulting in high power consumption.

50 **[0012]** Hence, there is room for improving DBD plasma reactors for performing PECVD coating on a substrate at atmospheric pressure.

Summary of the invention

55 **[0013]** It is an object of the present invention to provide a new and improved DBD plasma reactor for performing PECVD of a coating, preferably of a crystalline inorganic coating, on a substrate. A further object is to reduce the overall

power consumption of the DBD plasma reactor and reduce the overall processing time for forming the coating.

[0014] The present invention is defined in the appended independent claims. Preferred embodiments are defined in the dependent claims.

[0015] According to a first aspect of the invention, a dielectric barrier discharge (DBD) plasma reactor for plasma enhanced chemical vapor deposition of a coating on a substrate under atmospheric pressure is provided.

[0016] The DBD plasma reactor comprises a first electrode having a first face and a second face opposite to the first face, a second electrode having a third and a fourth face opposite to the third face, the fourth face of the second electrode facing the second face of the first electrode, and wherein the second electrode is separated from the first electrode for forming a plasma area between the second face and the fourth face. The DBD plasma reactor further comprises a first dielectric layer covering the second face of the first electrode and a power supply configured to apply a voltage between the first and second electrode.

[0017] The DBD plasma reactor is characterized in that the plasma reactor further comprises an induction heating coil for heating by induction a substrate when placed in the plasma area and/or for heating a susceptor by induction when placed in the plasma area. The induction heating coil is located outside of the plasma area and the induction heating coil comprises a plurality of windings wound around a central coil axis. In some embodiments, the induction heating coil is for example located such that the first face of the first electrode is facing the induction heating coil or the third face of the second electrode is facing the induction heating coil.

[0018] The DBD plasma reactor is further characterized in that the first electrode and/or second electrode comprises at least a through-hole extending along the central coil axis.

[0019] Advantageously, by providing a through-hole extending along the central coil axis of the induction heating coil, magnetic field lines generated along the coil axis are passing through the through-hole for crossing the first electrode. In this way, when the DBD plasma reactor is in operation, the heating of the first electrode by induction is reduced and when a susceptor is placed on the first dielectric layer, mainly the susceptor is heated by induction. Hence, overall power consumption for heating the substrate is reduced.

[0020] In embodiments, the DBD plasma reactor further comprises, in addition to the first dielectric layer, a second dielectric layer covering the fourth face of the second electrode. Advantageously, with two dielectrics as claimed, the power and formation of streamer discharges is limited.

[0021] In preferred embodiments, at least a central portion of the second face and a central portion of the fourth face are planar and parallel. If for example the second face is planar, this facilitates positioning a susceptor or a substrate on top of the dielectric covering the second face.

[0022] In embodiments, the plurality of windings of the induction heating coil are forming a helix-type coil extending along the central coil axis. Advantageously, magnetic field lines are extending and concentrated along the central coil axis and are passing through the through-hole in the first electrode.

[0023] In further embodiments comprising a helix-type coil, the first electrode comprises a slit for suppressing Eddy currents generated in the first electrode. In some embodiments, the slit is extending from an inner perimeter delimiting the through-hole of the first electrode to an outer perimeter of the first electrode. Advantageously, closed circuits of Eddy currents formed in a plane of the first electrode are broken such that heating of the electrode by Eddy currents is avoided. In some embodiments, the slit is not entirely extending from the inner perimeter to the outer perimeter, but is only extending over a limited distance.

[0024] In other embodiments, the plurality of windings of the induction heating coil are located in a plane for forming a pancake-type coil. Preferably, when using a pancake-type coil, the ratio between a thickness of the first electrode and a skin depth of the first electrode is smaller than 1, preferably smaller than 0.5, more preferably smaller than 0.1. In this way, induction heating of the first electrode is strongly reduced.

[0025] Similarly, in embodiments, the ratio between a thickness (S) of the second electrode and a skin depth (δ) of the second electrode is smaller than 1, preferably smaller than 0.5, more preferably smaller than 0.1. In further embodiments, both the first and second electrode fulfill this condition.

[0026] In preferred embodiments, the induction heating coil comprises a magnetic core, preferably a ferrite core.

[0027] Preferably, the coating is a crystalline inorganic coating, more preferably comprising a transition metal oxide. Indeed, the DBD plasma reactor is especially suited for crystalline coating, such as for example V_2O_5 and TiO_2 , that is performed at atmospheric pressure and room temperature. As during the coating with the DBD plasma reactor according to the invention, the substrate is directly or indirectly heated by the induction heating coil, no additional step of annealing is needed.

[0028] In embodiments, the DBD plasma reactor comprises a gas injection system configured to introduce a gas into the plasma area. In particular embodiments, a precursor in a gaseous form is also injected in the plasma area by the gas injection system.

[0029] In preferred embodiments, the DBD plasma reactor comprises a susceptor, generally arranged on the first dielectric layer.

[0030] A susceptor is to be construed as a piece of material, such as a layer or plate of material configured such that

the substrate can be arranged on the susceptor for forming a thermal contact between the susceptor and the substrate.

[0031] Advantageously, when the DBD plasma reactor is in operation, the susceptor is heated by induction by the induction heating coil and a substrate in thermal contact with the susceptor will be heated by thermal conduction.

[0032] Preferably, the susceptor is made of a metal, more preferably the susceptor is made of a ferromagnetic metal or a ferromagnetic alloy.

[0033] In embodiments, the central coil axis of the induction heating coil is crossing the susceptor.

[0034] According to a second aspect of the invention, a method for forming a coating, preferably a crystalline inorganic coating, on a substrate using PECVD under atmospheric pressure conditions is provided as defined in the appended claims.

Short description of the drawings

[0035] These and further aspects of the invention will be explained in greater detail by way of example and with reference to the accompanying drawings in which:

- Fig.1a to Fig.1d schematically illustrates cross sectional views of examples of embodiments of DBD plasma reactors according to the invention comprising one dielectric layer;
- Fig.2a to Fig.2c schematically illustrates cross sectional views of examples of embodiments of DBD plasma reactors according to the invention comprising two dielectric layers;
- Fig.3a and Fig.3b schematically illustrate the induction of Eddy currents in a metal plate for two different magnetic field orientations;
- Fig.4a is a cross sectional view of an induction heating coil, an electrode and a dielectric layer of a DBD plasma reactor according to the invention;
- Fig.4b is a top view of the electrode shown in Fig.4a;
- Fig.5 is a perspective view of an example of an electrode having a slit and a through-hole;
- Fig.6 is a cross sectional view of an example of a pancake-type coil shown in combination with an electrode and a dielectric layer;
- Fig.7 is a cross section view of an example of a pancake-type coil comprising a magnetic core;
- Fig.8. is a perspective view of an example of pancake type coil having a magnetic core;

[0036] The figures are not drawn to scale. Generally, identical components are denoted by the same reference numerals in the figures.

Detailed description of preferred embodiments

[0037] The present disclosure will be described in terms of specific embodiments, which are illustrative of the disclosure and not to be construed as limiting.

[0038] The drawings described are only schematic and are non-limiting.

[0039] Use of the verb "to comprise", as well as the respective conjugations, does not exclude the presence of elements other than those stated.

[0040] Use of the article "a", "an" or "the" preceding an element does not exclude the presence of a plurality of such elements.

[0041] Furthermore, the terms first, second and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequence, either temporally, spatially, in ranking or in any other manner. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the disclosure described herein are capable of operation in other sequences than described or illustrated herein.

DBD plasma reactor, general

[0042] In Fig.1a to Fig.1d and Fig.2a to Fig.2c, examples of embodiments of dielectric barrier discharge (DBD) plasma reactors 1 for plasma enhanced chemical vapor deposition of a coating on a substrate under atmospheric pressure according to the present invention as defined by the claims are shown.

[0043] Such a DBD plasma reactor 1 comprises a first electrode 11 separated from a second electrode 12. The first electrode 11 has a first face 11a and a second face 11b opposite to the first face 11a, and the second electrode 12 has a third 12a and a fourth face 12b, opposite to the third face. As schematically shown on Fig.1a to Fig.1c, Fig.2a and Fig.2b, the fourth face 12b of the second electrode is facing the second face 11b of the first electrode. By separating the first and second electrode, a plasma area 62 between the second face 11b and the fourth face 12b is formed, as

illustrated with a dotted area on the figures mentioned above.

[0044] The first electrode is for example a ground electrode and the second electrode is a high-voltage electrode and a voltage can be applied between the first and second electrode with a power supply 30. In some embodiments, the voltage applied between the first and the second electrode is a direct pulsed voltage. Preferably, the electrodes are

[0045] The fact that the second face 11b and the fourth face 12b are facing each other does not imply that no other elements are placed between the two faces. As further explained below, depending on the specific embodiment, between the second face 11b and the fourth face 12b one or more dielectric layers or additionally a susceptor can for example be placed.

[0046] The DBD plasma reactor 1 shown on Fig.1a and Fig.1b comprises a first dielectric layer 21 covering the second face 11b of the first electrode.

[0047] The DBD plasma reactor according to the invention is characterized in that it comprises an induction heating coil 40 for heating by induction a substrate when placed in the plasma area 62 and/or for heating a susceptor by induction when placed in the plasma area 62. In Fig.1a to Fig.1c, Fig.2a and Fig.2b, reference 100 schematically illustrates a susceptor that is located on top of the first dielectric layer 21. In other embodiments, the substrate is directly positioned on the first dielectric layer 21 without use of a susceptor.

[0048] The induction heating coil is located outside of the plasma area. In the embodiment shown on Fig.1a and Fig.2a, the first face 11a of the first electrode is facing the inducting heating coil 40. In other words, in these examples, the induction heating coil 40 is placed under the first electrode. In other embodiments, as for example shown on Fig.1b, Fig.1c and Fig.2b, the induction heating coil is placed on top of the second electrode. In these examples, the third face 12a of the second electrode is facing the induction heating coil 40.

[0049] The induction heating coil 40 is a coil comprising a plurality of windings wound around a central coil axis X_B . Various embodiments of an induction heating coil will be further discussed below. The induction heating coil is powered by a power supply 50 for providing an alternating current in the coil, typically at a frequency in the kHz range, for example a frequency in range between 1 kHz and 100 kHz.

[0050] The DBD reactor according to the present invention is not limited to embodiments having only one induction heating coil. Indeed, in some embodiments the DBD reactor comprises more than one induction heating coil. For example, as schematically illustrated on Fig.1d and Fig.2c, two induction heating coils 40a and 40b are provided having a common central axis X_B .

[0051] The DBD plasma reactor according to the invention is further characterized in that the first electrode 11 and/or the second electrode 12 comprises a through-hole 15 extending along the central coil axis X_B . In Fig.1a and Fig.2a, examples are shown of embodiments wherein the first electrode comprises a through-hole while Fig.1b shows an example wherein the through-hole is made in the second electrode. In Fig.1c and Fig.2b, examples of embodiments are shown wherein both the first 11 and the second 12 electrode comprise a through-hole 15. The role of the through-hole 15 will be further discussed.

[0052] The DBD plasma reactor of the current invention is not limited to one dielectric layer. For example in Fig.2a and Fig.2b, embodiments of a reactor are shown comprising a second dielectric layer 22 covering the fourth face 12b of the second electrode 12.

[0053] The DBD plasma reactor is suitable to operate under atmospheric pressure, which is to be construed as operating in pressure ranges between 100 torr and 1000 torr. Typically, a DBD plasma reactor comprises a gas injection system configured to introduce gases into the plasma area. For example a main gas, such as e.g. argon, or helium or any other noble gas, can be introduced in the plasma area. The word "main gas" is used in order to distinguish the noble gas from other additional gases that could be introduced in the plasma area. Indeed, in some embodiments, besides the main gas, also a precursor under gaseous form is introduced into the plasma area. In some embodiments, as schematically illustrated on Fig.2a, a chamber 60 is used that is containing at least the first electrode, the second electrode and the induction heating coil. For DBD plasma reactors comprising a chamber, a gas inlet 61 is generally provided to supply gas to the chamber. The arrow on Fig.2a schematically indicates a gas flow direction when entering the chamber.

[0054] In other embodiments, no chamber is required when for example the DBD plasma reactor is located in an atmospheric pressure controlled environment and wherein a gas can directly be introduced in the plasma area.

[0055] The power supply 30 for the electrodes is commercially available and is for example supplying an alternating voltage, e.g. generating an alternating voltage in the kHz range, for example a frequency between 1 and 30 kHz. In other embodiments, the power supply provides a pulsed DC voltage.

[0056] In the embodiment illustrated on Fig.1a, a central portion of the first electrode 11 and a central portion of the second electrode 12 are planar and parallel. In other embodiments, the electrodes do not necessarily have portions that are planar and/or parallel. In further embodiments, the second face of the first electrode and the fourth face of the second electrode are planar and/or parallel.

[0057] Preferably, the first and/or second electrode is/are made of non-magnetic metals.

[0058] The goal of using an induction heating coil as mentioned above is to heat the substrate and/or susceptor and

not to heat the electrode. Indeed, it is well known that Eddy currents induced in a metal by a varying magnetic field can heat the metal. This is schematically illustrated on Fig.3a and Fig.3b, where two exemplary orientations of a magnetic field generated by an induction coil with respect to a metal plate 90 are shown. In Fig.3a, the magnetic field lines are crossing the metal plate 90 transversally, resulting in Eddy currents, indicated by the reference "I" on the figure, flowing in circles in the plane of the metal plate 90. On the other hand, for the configuration shown in Fig.3b, the magnetic field lines pass through the metal plate longitudinally, in a plane parallel with the metal plate. With the latter configuration, the induced Eddy currents will flow through the thickness of the metal plate in small loops as schematically illustrated on Fig.3b. The skin depth δ , being the thickness used by the current to flow, also plays a role when designing the first electrode and/or the susceptor as will be further explained below. The equation defining the skin depth is well known in the art and the skin depth δ depends on the frequency of the varying magnetic field inducing the Eddy currents and on the electrical conductivity and magnetic permeability of the material wherein the Eddy currents are induced.

DBD plasma reactors with susceptor

[0059] In some embodiments, the DBD plasma reactor comprises a susceptor. Indeed, to achieve a good heating of any kind of substrate, either metallic or non-metallic, it is preferred to add a metallic component placed under the substrate that will be uniformly heated by induction. This metallic component is called the "susceptor". This susceptor can be made of any kind of metal, but a ferromagnetic metal like nickel or iron will be far more susceptible to induction heating than a non-ferromagnetic metal like copper or aluminum, due to the contribution of the magnetic permeability to the skin depth and the hysteresis losses. The electric resistance of the conductor is also important as a high resistance metal will heat faster than a low resistance metal due to Joule effect. In induction heating, the skin effect is also an important factor for heating. The susceptor will be a thin sheet or grid of ferromagnetic metal preferably with high resistance. It should withstand a high temperature without oxidation, melting or chemical modification. Suitable materials are Iron, Nickel, Cobalt and any other ferromagnetic alloy with a high Curie temperature and with a reasonable resistance.

[0060] If the substrate is a conducting material, it is not absolutely necessary to use an additional susceptor and the substrate can for example directly be placed on top of the first dielectric layer for being heated by induction by the induction heating coil.

Helix-type of induction coil

[0061] The induction heating coil 40 that is schematically shown on Fig. 1a to Fig. 1c, Fig. 2a and Fig. 2b is a coil wherein the plurality of windings are forming a so-called helix-type coil extending along the central coil axis X_B . This type of coil can also be named solenoid shaped coil. The windings are typically made with Litz wire.

[0062] When such a helix-type coil is placed for example under the first electrode such that the central coil axis is perpendicular to the first electrode, as shown on Fig. 1a and Fig. 2a, the magnetic field lines are similar to the magnetic field lines shown on Fig. 3a, i.e. the magnetic field lines are crossing the first electrode in a direction parallel with the central coil axis. If the first electrode would not have the through-hole 15, the first electrode would be heated by the induced Eddy currents circulating in the first electrode. By providing the through-hole 15 in the first electrode, the magnetic field lines are passing through the through-hole 15, thereby avoiding or reducing induction heating in the first electrode. The person skilled in the art will design the dimension of the opening of the through-hole 15 in accordance with the dimension of the induction heating coil. If the through-hole has a circular opening, the diameter can for example be chosen to be equal or slightly larger than an external diameter of a solenoid shaped coil used as induction coil, as schematically shown on Fig. 1a and Fig. 2a.

[0063] The same reasoning can be made for a DBD reactor configuration wherein the induction heating coil is placed on top of the second electrode and wherein the second electrode comprise a through-hole, as shown on Fig. 1b. In alternative embodiments, as shown on Fig. 1c and Fig. 2b, to reduce the heating of both electrodes, a through-hole 15 is provided in each of the two electrodes.

[0064] Remark that the exact location of the induction heating coil outside the plasma area is not important for the current invention, as long as the through-hole is extending along the central coil axis of the induction heating coil.

[0065] Remark also that the dielectric layer 21 partially covering the first electrode is not affecting the magnetic field lines as a dielectric is not a magnetic material. In embodiments, in addition to the provision of the through-hole 15, the induction current in the first electrode can be further reduced or eliminated by providing a slit 14 in the electrode. In preferred embodiments, the slit 14 is extending from an inner perimeter delimiting the through-hole 15 of the first electrode to an outer perimeter of the first electrode 11. The slit breaks the closed electrical circuit when formed in the first electrode such that no circular Eddy currents can circulate. A slit 14 is schematically shown on Fig. 4b for an embodiment wherein the through-hole 15 has a rounded square shape. The two crosses on Fig. 4b schematically illustrate that due to the slit 14 no Eddy currents I can circulate as the closed circuit is broken by the slit 14.

[0066] In embodiments, as illustrated on Fig. 4a, in order to better concentrate the magnetic field in the center of the

induction coil 40, i.e. concentrate the magnetic field lines $\vec{B}$ along the central coil axis, the induction heating coil 40 comprises a magnetic core 41, for example a ferrite core. In this particular embodiment, shown on Fig.4a, in addition to the through-hole 15, additional holes 16,17 are made in the first electrode 11. The location of these additional holes match with corresponding components of the magnetic core 41. The additional holes 16,17 are also shown on Fig.4b which is a top view of the electrode shown on Fig.4a. This is further illustrated on Fig.5 where a perspective view is shown of the first electrode 11 and part of the ferrite core 41 shown on Fig.4a.

Pancake-type of induction coil

[0067] In other embodiments, the DBD plasma reactor is using a pancake-type of induction coil as schematically shown on Fig.6. In Fig.6, the first electrode 11, the first dielectric layer 21 and the induction coil 40 of the pancake-type are shown. A pancake-type of coil, also named flat coil, is a coil wherein the plurality of windings of the coil around a central coil axis X_B are located in a plane. This type of pancake coil allows to generate longitudinal field lines, similar to field lines shown on Fig.3b, in a susceptor arranged on the first dielectric layer 21. However, the magnetic field lines of a pancake-type coil are not completely longitudinal and in the center along the central coil axis X_B , the magnetic field lines are aligned in the direction of the central coil axis X_B and hence these transverse magnetic field lines have to cross through the first electrode before reaching the susceptor. Therefore, for the same reasons as discussed above for the helix-type coil, also for the pancake-type coil, a through-hole 15 extending along the central common coil axis X_B is provided in the first electrode 11 in order to avoid or reduce Eddy currents in the plane of the first electrode induced by a varying transverse magnetic field.

[0068] When a pancake-type coil is used as an induction coil, the heating of the first electrode by Eddy currents resulting from the varying longitudinal magnetic field, as illustrated on Fig.3b, can be strongly reduced or avoided by selecting the thickness S of the first electrode in relation to the skin depth. Indeed, it is known, that if the ratio S/δ between the thickness S of the conductor and the skin depth δ is below 2, the power efficiency of the induction heating drops drastically. This is described in for example the publication "Induction heating of thin slabs and sheets in the rolling line", D. Wohlfahrt and R. Jürgens, in 51st Internationales Wissenschaftliches Kolloquium Technische Universität Ilmenau September 11 - 15, 2006. In other words, if the metal thickness of the first electrode is selected such that the ratio S/δ is well below 2, the induction heating power is nearly zero and the first electrode will not be heated up.

[0069] In embodiments, the ratio between the thickness S of the first electrode and the skin depth δ of the first electrode is smaller than 1, preferably smaller than 0.5, more preferably equal or smaller than 0.1.

[0070] The material selected for the first electrode is important as the material needs to have on the one hand a good conductivity and on the other hand have a low magnetic permeability. Indeed the electrode needs at the same time to be a good conductor for the high voltage and also have a low ratio S/δ , preferably have a skin depth of for example five times or ten time larger than the thickness S of the electrode. Usual non-magnetic metals like copper, aluminum and silver have approximatively the same skin depth and need to be 1 μm thick or thinner to avoid any induction heating with 100 kHz current frequency. Carbon graphite is a good alternative as it has an anisotropic conductivity that reduces the skin depth to some millimeters but keeping a good conductivity.

[0071] In embodiments, as illustrated on Fig.7, the pancake-type of induction coil, also comprises a magnetic core 41, e.g. made of ferrite or another magnetic material, configured such that the magnetic field lines are bent and concentrated in the region where the induction heating is needed, i.e. at the location where the susceptor and/or the substrate are positioned. Magnetic fields lines

$\vec{B}$

resulting from the pancake-induction coil are schematically shown as dotted lines on Fig.7.

Method for plasma-enhanced chemical vapor deposition

[0072] According to a further aspect of the invention, a method for plasma-enhanced chemical vapor deposition of a coating on a substrate under atmospheric pressure using a dielectric barrier discharge plasma reactor as discussed above is provided. Preferably the coating is a crystalline inorganic coating. Generally, two methods can be distinguished, depending on if the substrate is conductive or not.

[0073] As discussed above, if the substrate is conductive, it is not always necessary to use a susceptor. In that case, when the DBD plasma reactor does not comprise a susceptor the method for plasma-enhanced chemical vapor deposition of a coating on a substrate comprises steps of:

- placing a conductive substrate in the plasma area 62, preferably arranging the substrate on the first dielectric layer,

- powering the induction heating coil 40 such that a varying magnetic field is generated in the substrate and the substrate is heated by induction,
- introducing a main gas into the plasma area, preferably additionally introducing a precursor under gaseous form in the plasma area,
- using the power supply 30 for applying a voltage, preferably an alternating voltage, between the first electrode and the second electrode so as to generate a plasma in the plasma area.

[0074] On the other hand, when the DBD plasma reactor comprises a susceptor as discussed above, the method for plasma-enhanced chemical vapor deposition of a coating on a substrate comprises steps of:

- placing a substrate on the susceptor 100 such that a thermal contact is made between the susceptor and the substrate,
- powering the induction heating coil 40 such that a varying magnetic field is generated in the susceptor 100 and the susceptor 100 is heated by induction,
- introducing a main gas into the plasma area, preferably additionally introducing a precursor under gaseous form into the plasma area,
- using the power supply 30 for applying a voltage, preferably an alternating voltage, between the first electrode and the second electrode so as to generate a plasma in the plasma area.

[0075] The methods according to the invention as described above and expressed in the appended claims are not limited by the order of the steps given, in embodiments steps can be performed in a different order or some steps can be performed in parallel.

Claims

1. A dielectric barrier discharge plasma reactor (1) for plasma enhanced chemical vapor deposition of a coating on a substrate under atmospheric pressure, comprising:

- a first electrode (11) having a first face (11a) and a second face (11b) opposite to the first face (11a),
- a second electrode (12) having a third face (12a) and a fourth face (12b) opposite to the third face, the fourth face (12b) of the second electrode facing the second face (11b) of the first electrode, and wherein the second electrode is separated from the first electrode (11) for forming a plasma area (62) between the second face (11b) and the fourth face (12b),
- a first dielectric layer (21) covering the second face (11b) of the first electrode,
- a power supply (30) configured to apply a voltage between the first and second electrode,

characterized in that

the reactor (1) further comprises an induction heating coil (40) for heating by induction the substrate when placed in the plasma area (62) and/or for heating a susceptor by induction when placed in the plasma area (62), said induction heating coil being located outside of said plasma area, and wherein said induction heating coil (40) comprises a plurality of windings (45) wound around a central coil axis (X_B), and **in that** said first electrode (11) and/or said second electrode (12) comprises a through-hole (15) extending along said central coil axis (X_B).

2. A dielectric barrier discharge plasma reactor according to claim 1, further comprising a second dielectric layer (22) covering said fourth face (12b) of the second electrode.

3. A dielectric barrier discharge plasma reactor according to any of the previous claims, wherein at least a central portion of said second face (11b) and a central portion of said fourth face (12b) are planar and parallel.

4. A dielectric barrier discharge plasma reactor according to any of previous claims, wherein said plurality of windings (45) of the induction heating coil (40) are forming a helix-type coil extending along said central coil axis (X_B).

5. A dielectric barrier discharge plasma reactor according to any of claims 1 to 3, wherein said plurality of windings (45) of the induction heating coil (40) are located in a plane so as to form a pancake-type coil.
- 5 6. A dielectric barrier discharge plasma reactor according to claim 5, wherein a ratio between a thickness (S) of the first electrode and a skin depth (δ) of the first electrode and/or a ratio between a thickness (S) of the second electrode and a skin depth (δ) of the second electrode is smaller than 1, preferably smaller than 0.5, more preferably equal or smaller than 0.1.
- 10 7. A dielectric barrier discharge plasma reactor according to any of the previous claims, wherein said induction heating coil (40) comprises a magnetic core (41), preferably a ferrite core.
- 15 8. A dielectric barrier discharge plasma reactor according to any of the previous claims, wherein the first electrode (11) and/or second electrode (12) further comprises a slit (14) for suppressing Eddy currents, preferably said slit is extending from an inner perimeter delimiting the through-hole (15) of the electrode to an outer perimeter of the electrode.
9. A dielectric barrier discharge plasma reactor according to any of the previous claims, wherein said coating is a crystalline inorganic coating, preferably comprising a transition metal oxide.
- 20 10. A dielectric barrier discharge plasma reactor according to any of the previous claims, wherein the first and/or second electrode is/are made of non-magnetic metals.
- 25 11. A dielectric barrier discharge plasma reactor according to any of the previous claims, further comprising a gas injection system configured to introduce a gas into the plasma area.
12. A dielectric barrier discharge plasma reactor according to any of the previous claims, further comprising a chamber containing at least the first electrode, the second electrode and the first dielectric layer, preferably the chamber has a gas inlet (61).
- 30 13. A dielectric barrier discharge plasma reactor according to any of previous claims, further comprising a susceptor (100) arranged on said first dielectric layer (21) .
- 35 14. A method for plasma-enhanced chemical vapor deposition of a coating on a substrate under atmospheric pressure using a dielectric barrier discharge plasma reactor according to any of claims 1 to 13, said method comprising the steps of:
 - placing the substrate on the first dielectric layer or placing a susceptor on the first dielectric layer and placing the substrate on the susceptor (100) such that a thermal contact is made between the susceptor and the substrate;
 - powering the induction heating coil (40) such that a varying magnetic field is generated in said substrate and/or said susceptor,
 - introducing a main gas into the plasma area,
 - using the power supply (30) for applying a voltage between the first electrode and the second electrode so as to generate a plasma in the plasma area.
- 45 15. A method according to claim 14, wherein said coating is a crystalline inorganic coating.

Patentansprüche

- 50 1. Plasmareaktor (1) zur plasmaverstärkten chemischen Gasphasenabscheidung einer Beschichtung auf einem Substrat unter Atmosphärendruck, umfassend:
 - eine erste Elektrode (11) mit einer ersten Fläche (11a) und einer zweiten Fläche (11b) gegenüber der ersten Fläche (11a),
 - 55 • eine zweite Elektrode (12) mit einer dritten Fläche (12a) und einer vierten Fläche (12b) gegenüber der dritten Fläche, wobei die vierte Fläche (12b) der zweiten Elektrode der zweiten Fläche (11b) der ersten Elektrode zugewandt ist, und wobei die zweite Elektrode getrennt von der ersten Elektrode (11) ist zur Bildung einer Plasmafläche (62) zwischen der zweiten Fläche (11b) und der vierten Fläche (12b),

- eine erste dielektrische Schicht (21), die die zweite Fläche (11b) der ersten Elektrode bedeckt,
- eine Stromversorgung (30), das so konfiguriert ist, dass es eine Spannung zwischen der ersten und der zweiten Elektrode anlegt,

5 **dadurch gekennzeichnet das**

der Reaktor (1) umfasst ferner eine Induktionsheizspirale (40) zum Erhitzen des Substrats durch Induktion wenn es im Plasmabereich (62) platziert wird, und/oder zum Erhitzen eines Suszeptors durch Induktion wenn es im Plasmabereich (62) platziert wird, wobei sich die Induktionsheizspule außerhalb des Plasmabereichs befindet und wobei die Induktionsheizspule (40) mehrere Wicklungen (45) umfasst, die um eine zentrale Spulenachse (X_B) gewickelt sind, und in das die erste Elektrode (11) und/oder die zweite Elektrode (12) ein Durchgangsloch (15) umfasst, das sich entlang der zentralen Spulenachse (X_B) erstreckt.

- 15 **2.** Plasmareaktor nach Anspruch 1, der ferner eine zweite dielektrische Schicht (22) umfasst, die die vierte Fläche (12b) der zweiten Elektrode bedeckt.
- 3.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei mindestens ein zentraler Teil der zweiten Fläche (11b) und ein zentraler Teil der vierten Fläche (12b) planar und parallel sind.
- 20 **4.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei die Mehrzahl von Wicklungen (45) der Induktionsheizspule (40) eine Elix-Spule bildet, die sich entlang der zentralen Spulenachse (X_B) erstreckt.
- 5.** Plasmareaktor nach einem der Ansprüche 1 bis 3, wobei die Mehrzahl der Wicklungen (45) der Induktionsheizspirale (40) in einer Ebene angeordnet ist, um eine Pfannkuchenspule zu bilden.
- 25 **6.** Plasmareaktor nach Anspruch 5, wobei ein Verhältnis zwischen einer Dicke (S) der ersten Elektrode und einer Haultiefe (δ) der ersten Elektrode und/oder ein Verhältnis zwischen einer Dicke (S) der zweiten Elektrode und einer Haultiefe (δ) der zweiten Elektrode kleiner als 1, vorzugsweise kleiner als 0.5 ist, besonders bevorzugt gleich oder kleiner als 0.1 ist.
- 7.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei die Induktionsheizspirale (40) einen magnetischen Kern (41), vorzugsweise einen Ferritkern, umfasst.
- 35 **8.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei die erste Elektrode (11) und/oder die zweite Elektrode (12) weiterhin einen Schlitz (14) zur Unterdrückung von Wirbelströmen aufweist, wobei sich der Schlitz vorzugsweise von einem inneren Umfang erstreckt, der das Durchgangsloch (15) der Elektrode an einem äußeren Umfang der Elektrode.
- 9.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei die Beschichtung eine kristalline anorganische Beschichtung ist, die vorzugsweise ein Übergangsmetalloxid enthält.
- 10.** Plasmareaktor nach einem der vorhergehenden Ansprüche, wobei die erste und/oder zweite Elektrode aus nicht-magnetischen Metallen besteht.
- 45 **11.** Plasmareaktor nach einem der vorhergehenden Ansprüche, ferner umfassend ein Gasinjektionssystem, das so konfiguriert ist, dass ein Gas in den Plasmabereich eingeleitet wird.
- 12.** Plasmareaktor nach einem der vorhergehenden Ansprüche, ferner umfassend eine Kammer, die mindestens die erste Elektrode, die zweite Elektrode und die erste dielektrische Schicht enthält, wobei die Kammer vorzugsweise einen Gaseinlass (61) aufweist.
- 50 **13.** Plasmareaktor nach einem der früheren Ansprüche, der ferner einen Suszeptor (100) umfasst, der auf der ersten dielektrischen Schicht (21) angeordnet ist.
- 55 **14.** Verfahren zur plasmaverstärkten chemischen Gasphasenabscheidung einer Beschichtung auf einem Substrat unter Atmosphärendruck unter Verwendung eines Plasmareaktors nach einem der Ansprüche 1 bis 13, wobei das Verfahren die folgenden Schritte umfasst:

- placer des substrats sur la première couche diélectrique ou
- Placer un suscepteur sur la première couche diélectrique et placer des substrats sur le suscepteur (100), de sorte qu'un contact thermique est établi entre le suscepteur et le substrat;
- l'inducteur (40) est alimenté de telle sorte qu'un champ magnétique variable est créé sur le substrat et/ou le suscepteur;
- introduire un gaz principal dans la zone de plasma,
- utiliser l'alimentation (30) pour appliquer une tension entre la première électrode et la seconde électrode, de sorte qu'un plasma est créé dans la zone de plasma.

15. Procédé selon la revendication 14, dans lequel la couche est une couche cristalline inorganique.

Revendications

1. Réacteur plasma à décharge à barrière électrique (1) pour le dépôt chimique en phase vapeur amélioré et par plasma d'un revêtement sur un substrat sous pression atmosphérique, comprenant:

- une première électrode (11) ayant une première face (11a) et une seconde face (11b) opposée à la première face (11a),
- une deuxième électrode (12) ayant une troisième face (12a) et une quatrième face (12b) opposée à la troisième face, la quatrième face (12b) de la deuxième électrode faisant face à la deuxième face (11b) de la première électrode, et dans laquelle la deuxième électrode est séparée de la première électrode (11) pour former une zone de plasma (62) entre la deuxième face (11b) et la quatrième face (12b),
- une première couche diélectrique (21) recouvrant la seconde face (11b) de la première électrode,
- une alimentation (30) configurée pour appliquer une tension entre la première et la deuxième électrode,

caractérisé en ce que

le réacteur (1) comprend en outre une bobine de chauffage par induction (40) pour chauffer par induction le substrat lorsqu'il est placé dans la zone plasma (62) et/ou pour chauffer un suscepteur par induction lorsqu'il est placé dans la zone plasma (62), ladite bobine de chauffage par induction étant située à l'extérieur de ladite zone de plasma, et dans laquelle ladite bobine de chauffage par induction (40) comprend une pluralité d'enroulements (45) enroulés autour d'un axe central de bobine (X_B),
et en ce que ladite première électrode (11) et/ou ladite seconde électrode (12) comprend un trou traversant (15) s'étendant le long dudit axe central de la bobine (X_B).

2. Réacteur plasma à décharge à barrière électrique selon la revendication 1, comprenant en outre une seconde couche diélectrique (22) recouvrant ladite quatrième face (12b) de la seconde électrode.

3. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, dans lequel au moins une partie centrale de ladite deuxième face (11b) et une partie centrale de ladite quatrième face (12b) sont planes et parallèles.

4. Réacteur plasma à décharge à barrière électrique diélectrique selon l'une quelconque des revendications précédentes, dans lequel ladite pluralité d'enroulements (45) de la bobine de chauffage par induction (40) forment une bobine de type à hélice s'étendant le long dudit axe central de bobine (X_B).

5. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications 1 à 3, dans lequel ladite pluralité d'enroulements (45) de la bobine de chauffage par induction (40) sont situés dans un plan de manière à former une bobine de type crêpe.

6. Réacteur plasma à décharge à barrière diélectrique selon la revendication 5, dans lequel un rapport entre une épaisseur (S) de la première électrode et une profondeur de peau (δ) de la première électrode et/ou un rapport entre une épaisseur (S) de la seconde électrode et une profondeur de peau (δ) de la seconde électrode est inférieur à 1, de préférence inférieur à 0.5, de préférence égal ou inférieur à 0.1.

7. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, dans lequel ladite bobine de chauffage par induction (40) comprend un cœur magnétique (41), de préférence un cœur

de ferrite.

8. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, dans lequel la première électrode (11) et/ou la seconde électrode (12) comprend en outre une fente (14) permettant de supprimer les courants de Foucault, de préférence ladite fente s'étendant à partir d'un périmètre intérieur délimitant le trou traversant (15) de l'électrode à un périmètre extérieur de l'électrode.

9. Réacteur plasma à décharge barrière électrique selon l'une quelconque des revendications précédentes, dans lequel ledit revêtement est un revêtement inorganique cristallin, comprenant de préférence un oxyde métallique de transition.

10. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, dans lequel la première et/ou la deuxième électrode est/sont constituée/sont constituée(s) de métaux non magnétiques.

11. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, comprenant en outre un système d'injection de gaz configuré pour introduire un gaz dans la zone du plasma.

12. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications précédentes, comprenant en outre une chambre contenant au moins la première électrode, la deuxième électrode et la première couche diélectrique, de préférence la chambre comporte une entrée de gaz (61).

13. Réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications antérieures, comprenant en outre un suscepteur (100) disposé sur ladite première couche diélectrique (21).

14. Procédé de dépôt chimique en phase vapeur amélioré par plasma d'un revêtement sur un substrat sous pression atmosphérique à l'aide d'un réacteur plasma à décharge à barrière électrique selon l'une quelconque des revendications 1 à 13, ledit procédé comprenant les étapes de :

- placer le substrat sur la première couche diélectrique ou placer un suscepteur sur la première couche diélectrique et placer le substrat sur le suscepteur (100) de telle sorte qu'un contact thermique soit établi entre le suscepteur et le substrat;
- alimenter la bobine de chauffage par induction (40) de manière à générer champ magnétique variable dans ledit substrat et/ou ledit suscepteur ;
- introduire un gaz principal dans la zone du plasma ;
- utiliser l'alimentation (30) pour appliquer une tension entre la première électrode et la deuxième électrode de manière à générer un plasma dans la zone du plasma.

15. Procédé selon la revendication 14, dans lequel ledit revêtement est un revêtement inorganique cristallin.

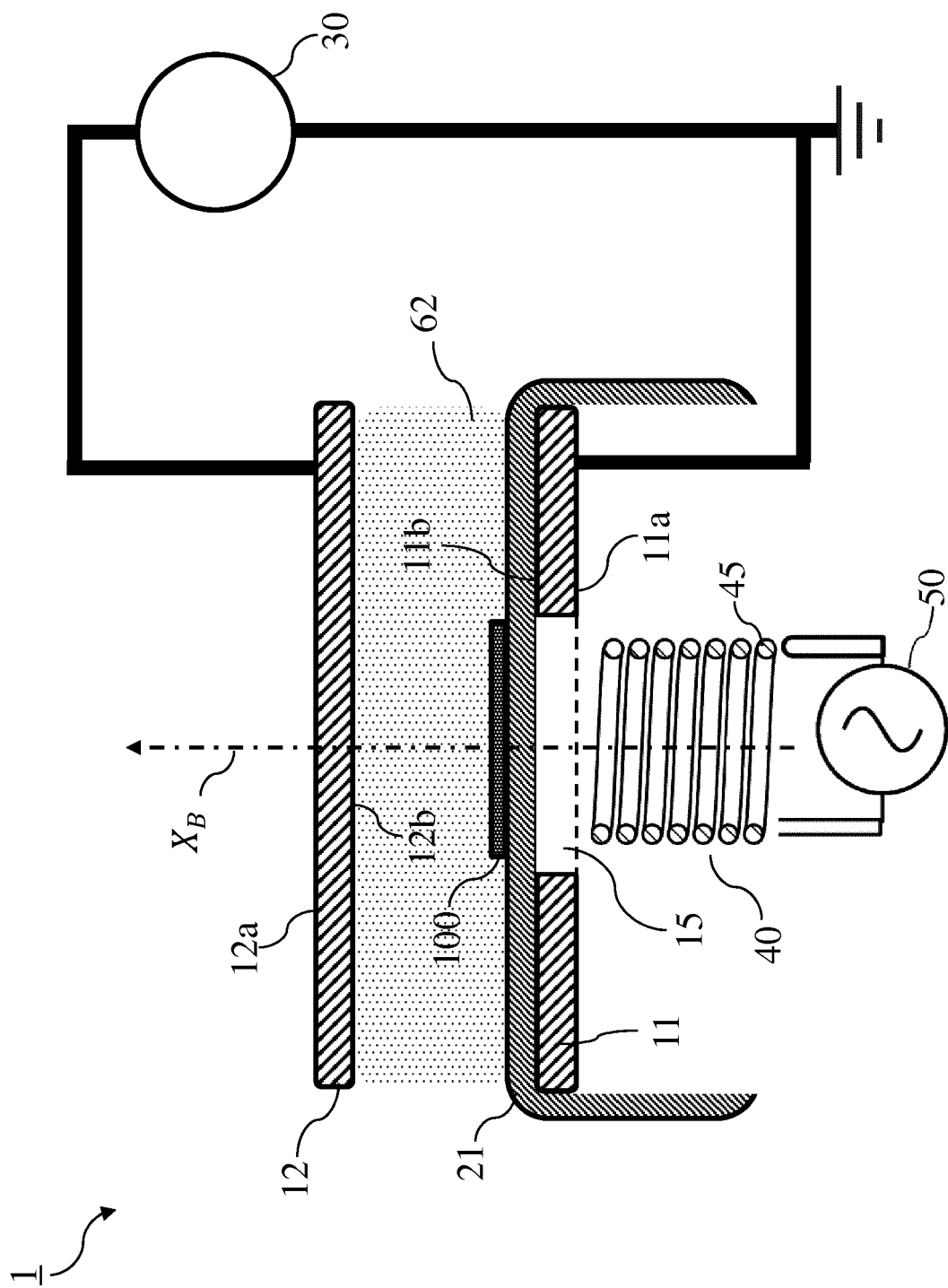


Fig. 1a

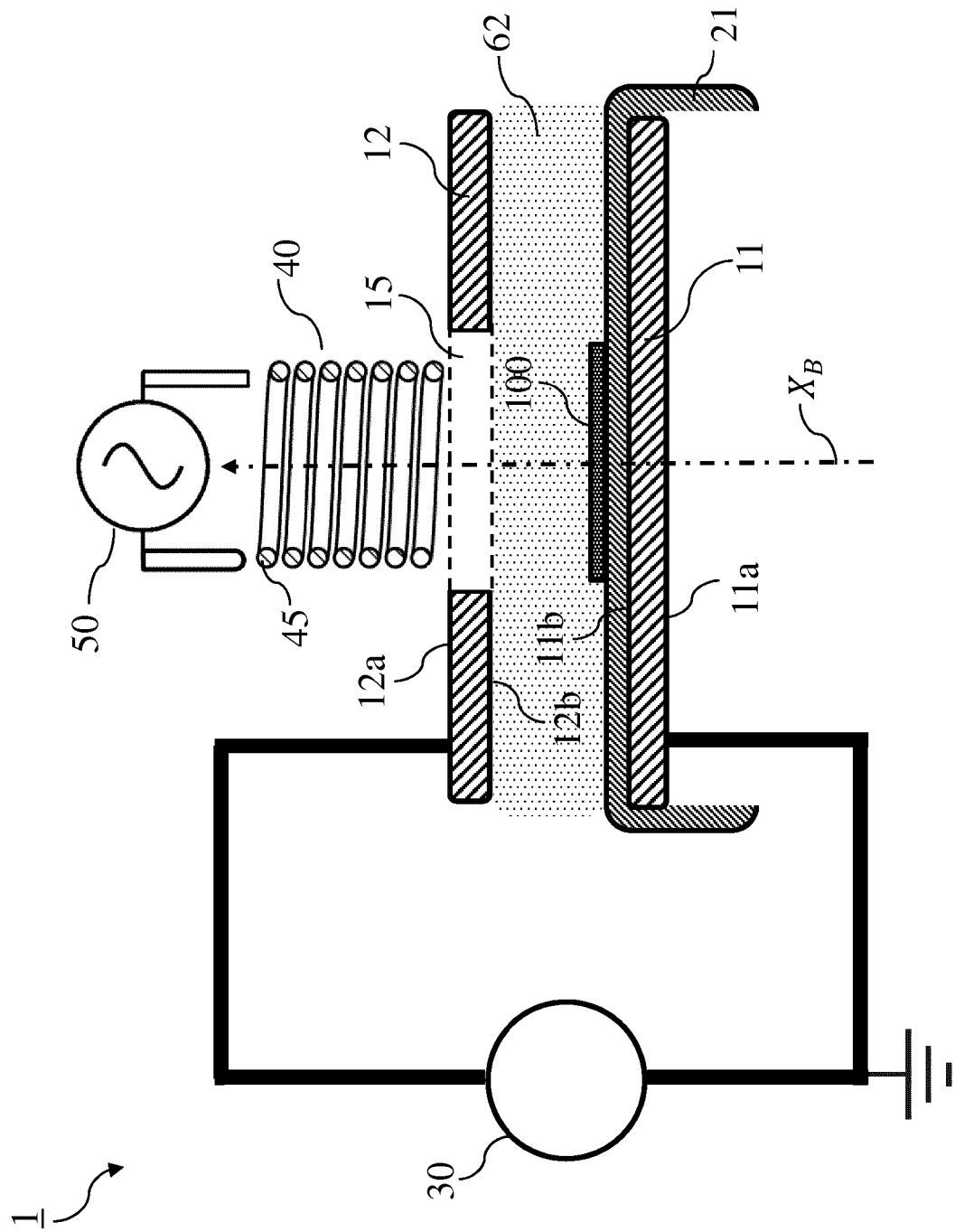


Fig. 1b

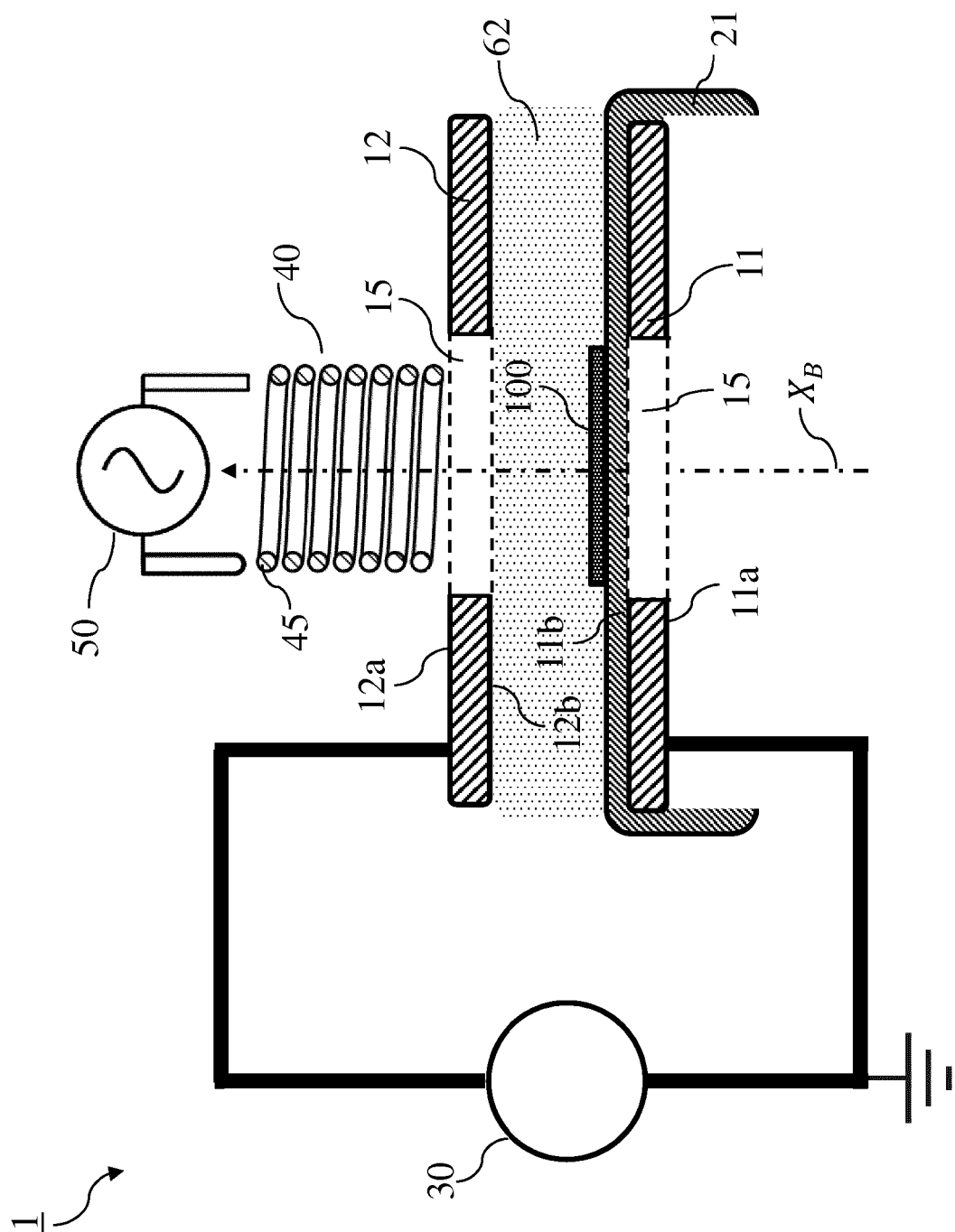


Fig. 1c

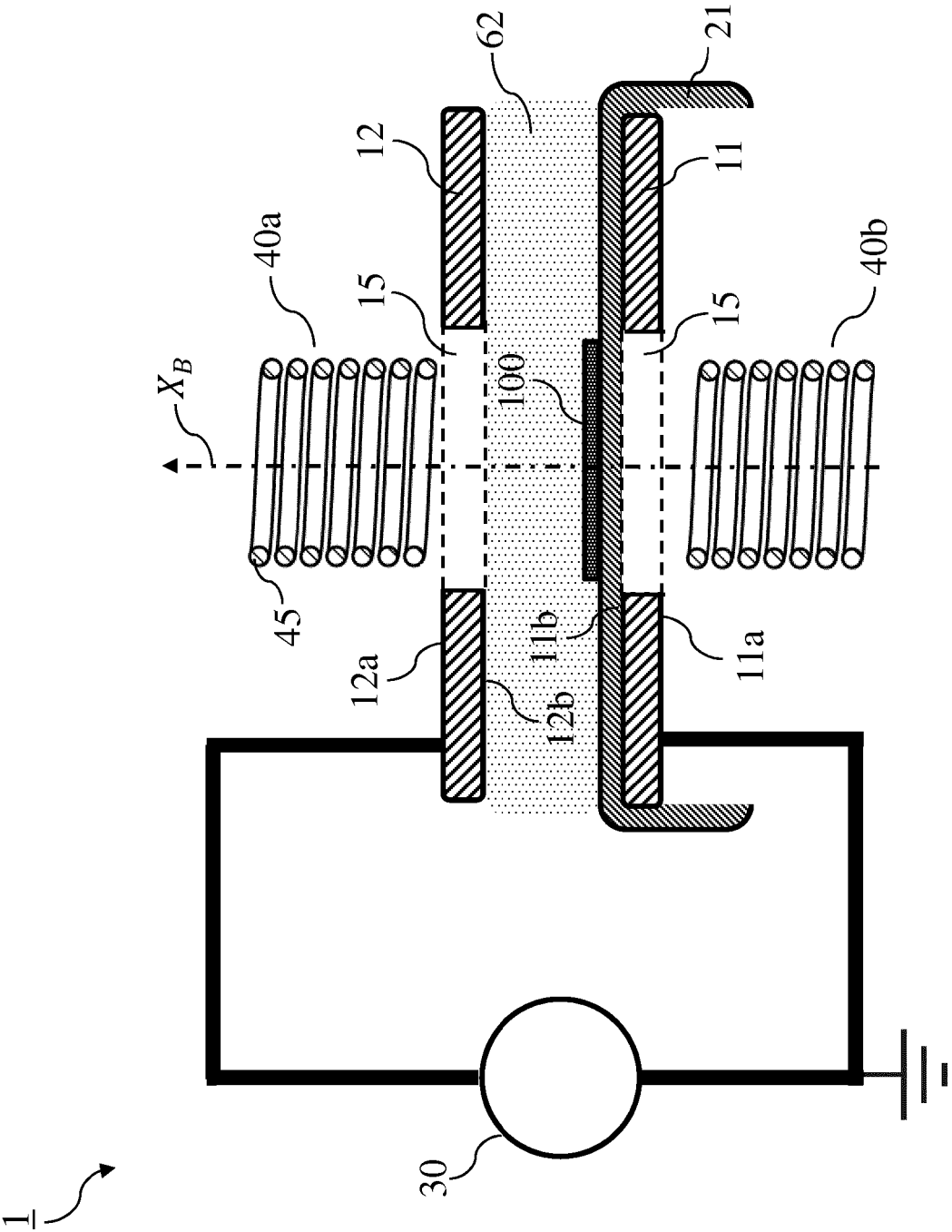
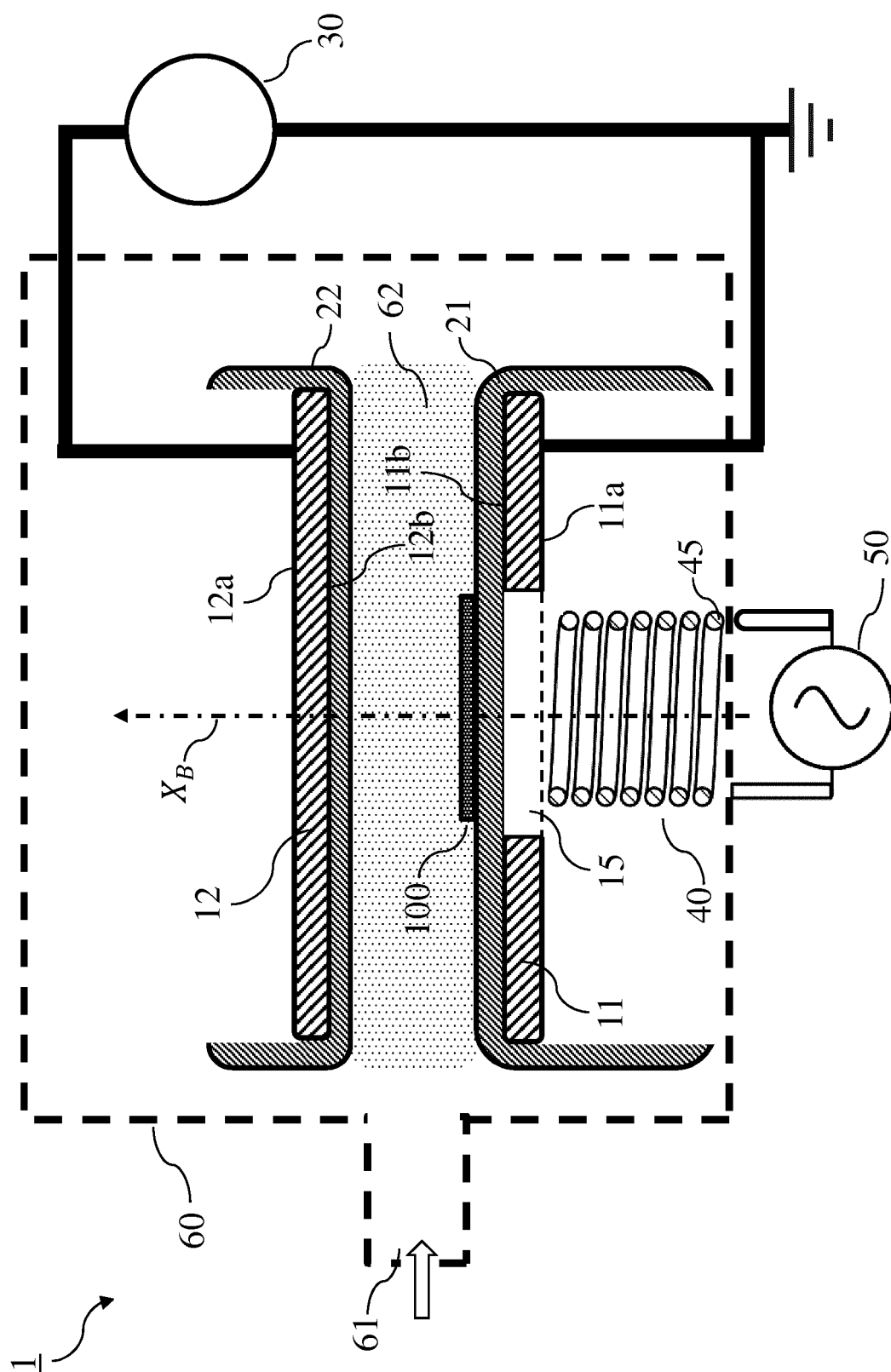


Fig. 1d



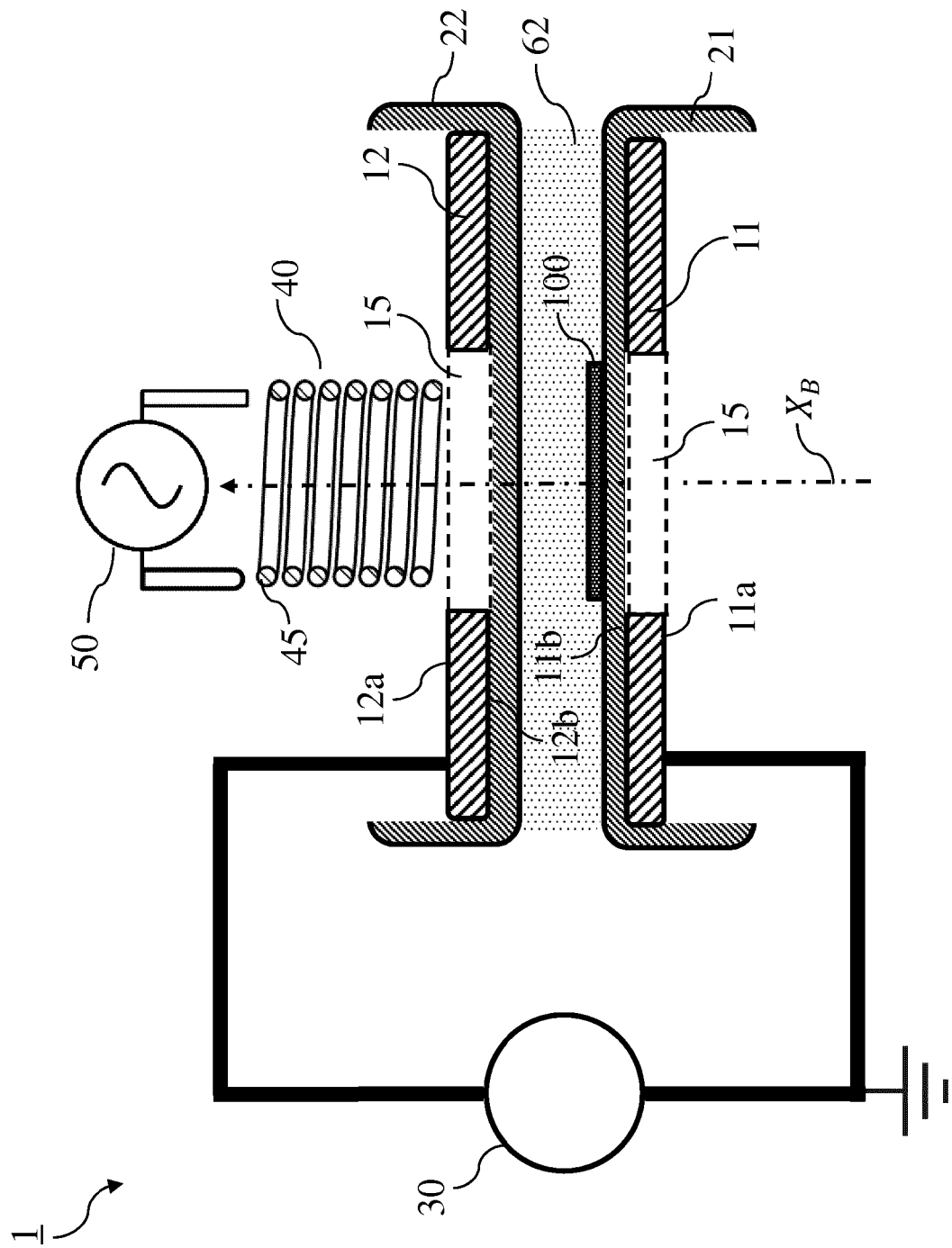


Fig. 2b

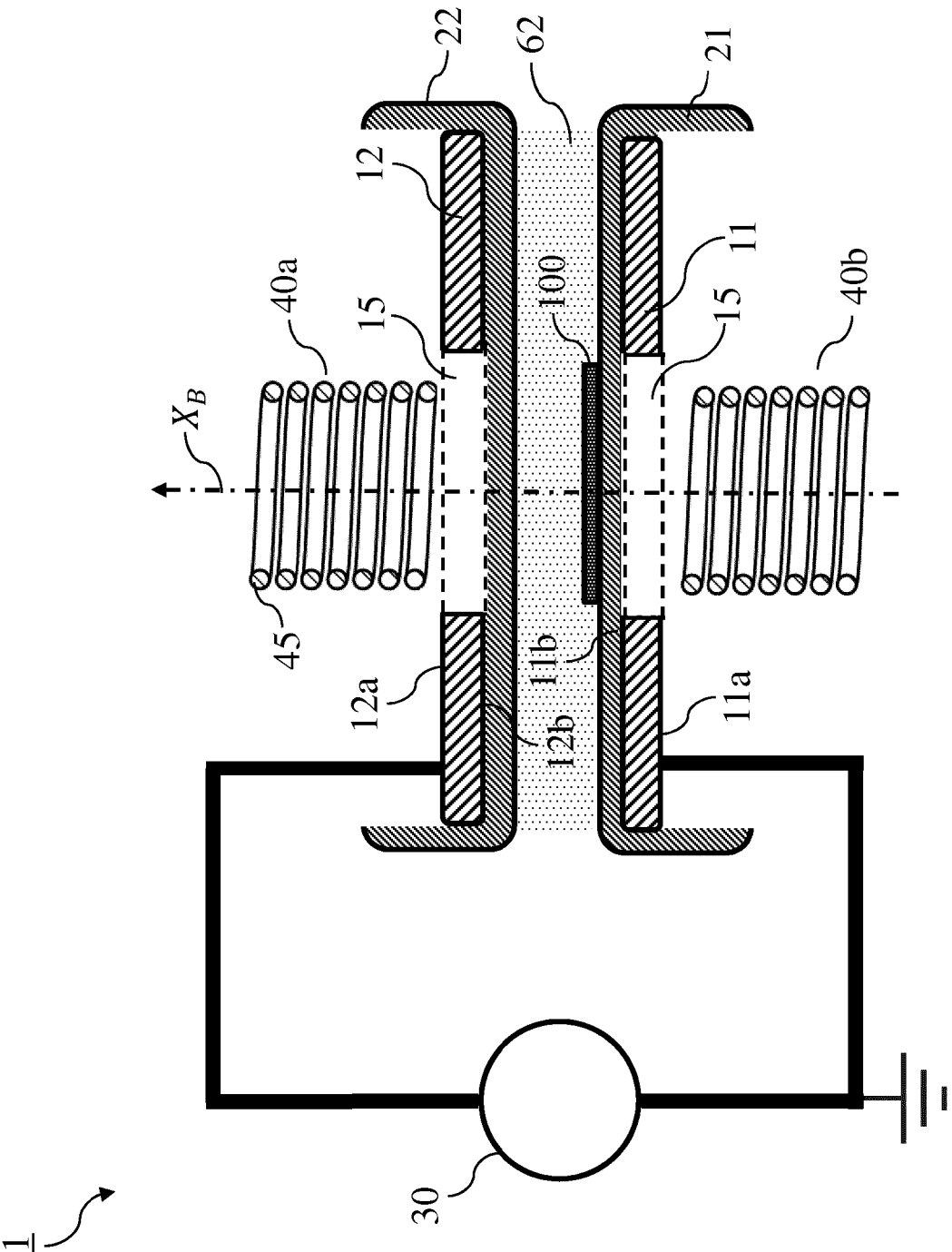


Fig. 2c

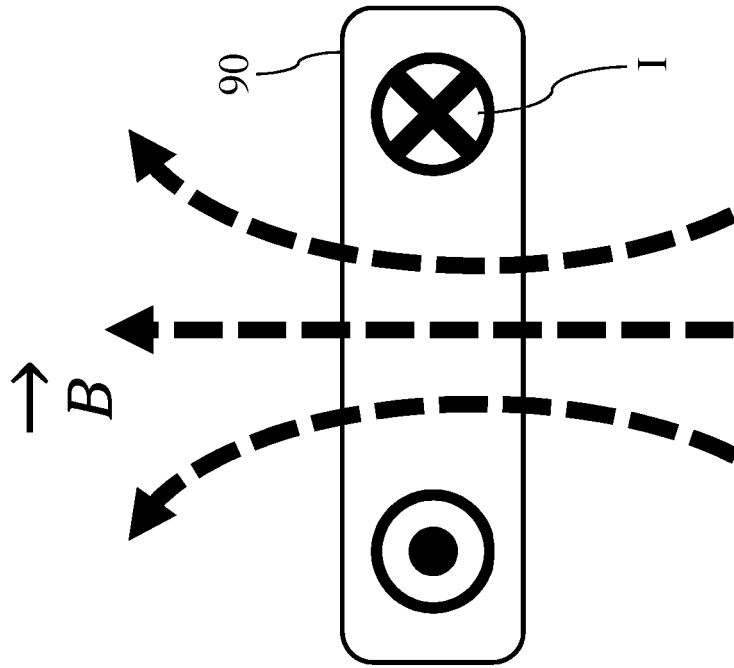


Fig. 3a

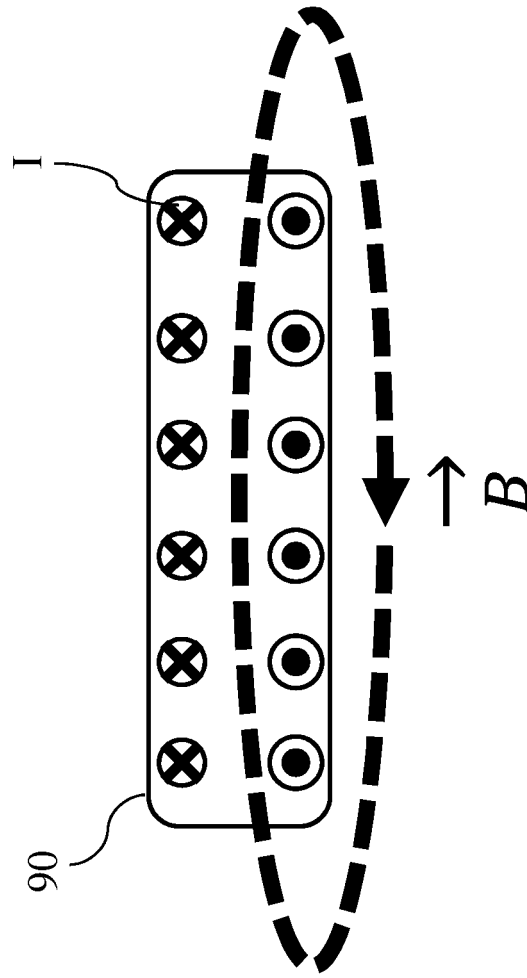


Fig. 3b

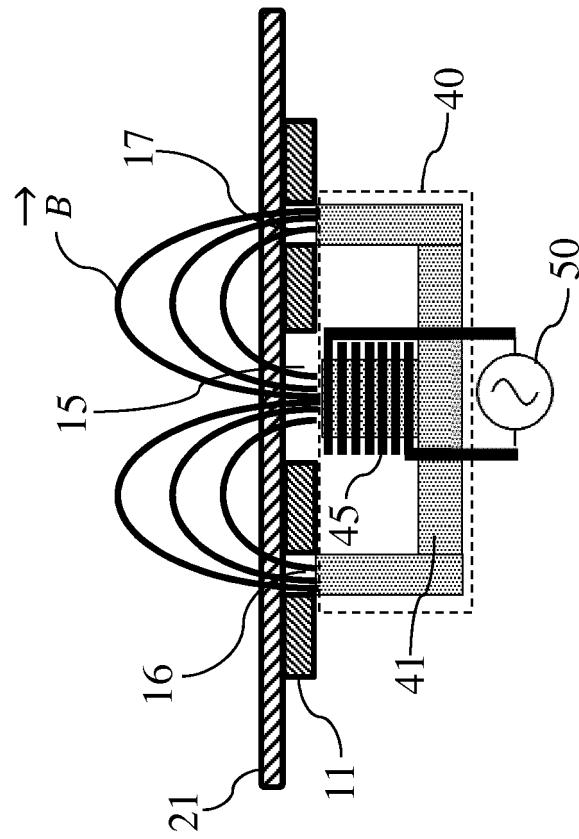


Fig. 4a

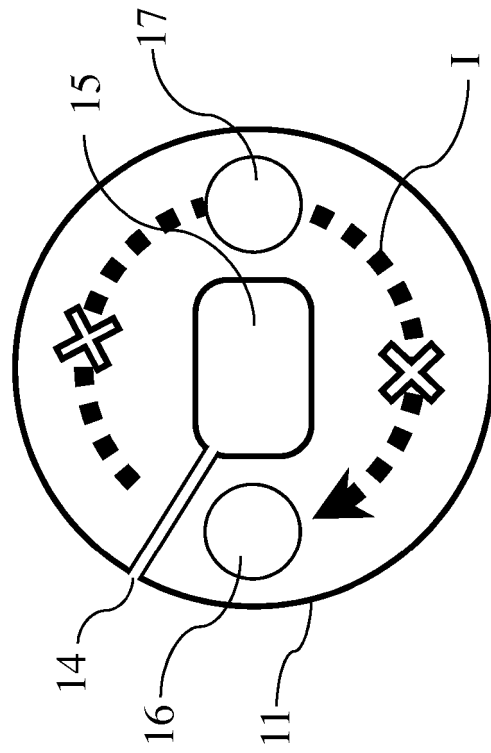


Fig. 4b

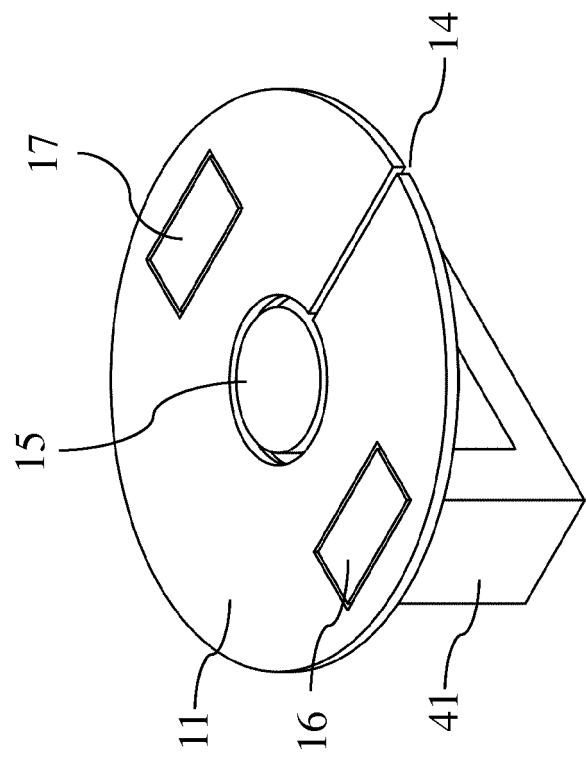


Fig. 5

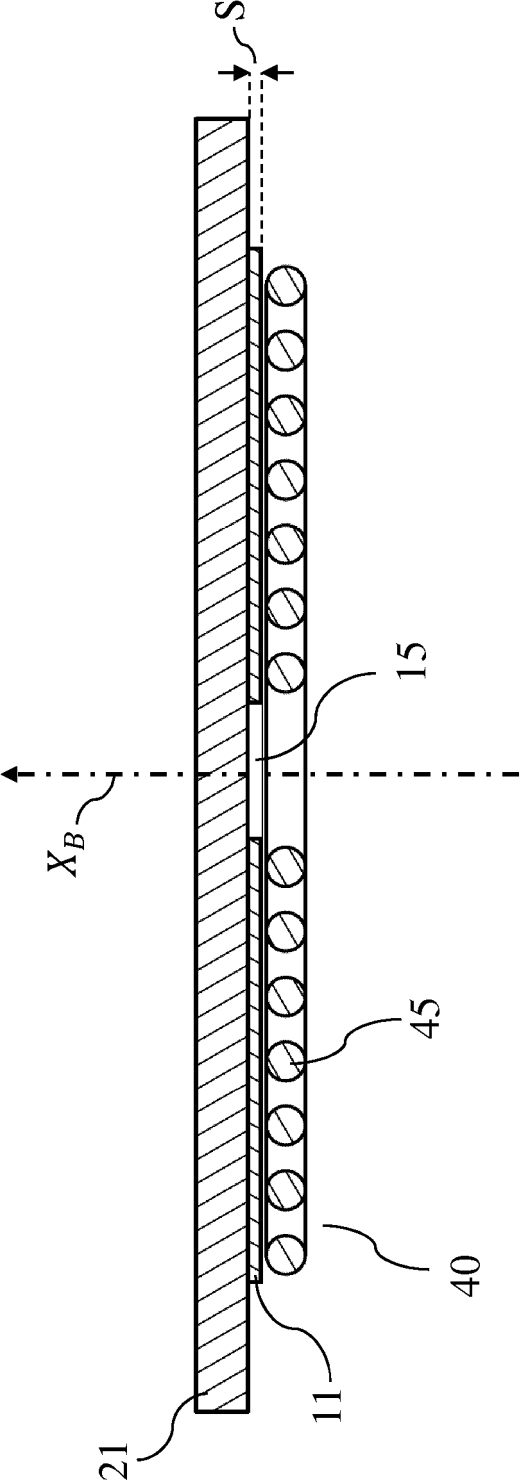


Fig. 6

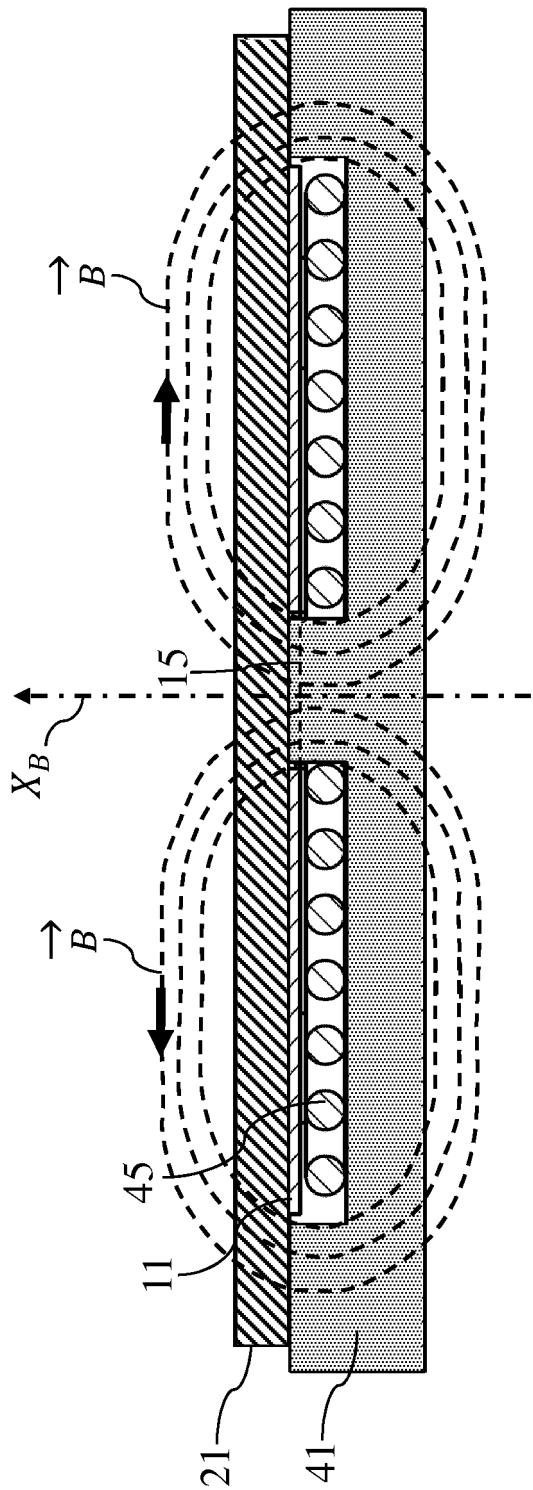


Fig. 7

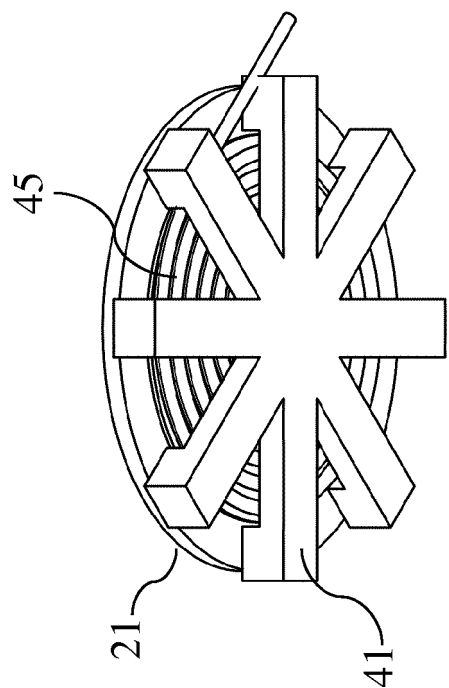


Fig. 8

REFERENCES CITED IN THE DESCRIPTION

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