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(54) **THIN FILM FORMATION APPARATUS, SPUTTERING CATHODE, AND METHOD OF FORMING THIN FILM**

(71) Applicant: **SHINCRON CO., LTD.**, Kanagawa (JP)

(72) Inventors: **Mitsuhiro Miyauchi**, Kanagawa (JP); **Takanori Murata**, Kanagawa (JP); **Takuya Sugawara**, Kanagawa (JP); **Ichiro Shiono**, Kanagawa (JP); **Yousong Jiang**, Kanagawa (JP); **Tatsuya Hayashi**, Kanagawa (JP); **Ekishu Nagae**, Kanagawa (JP)

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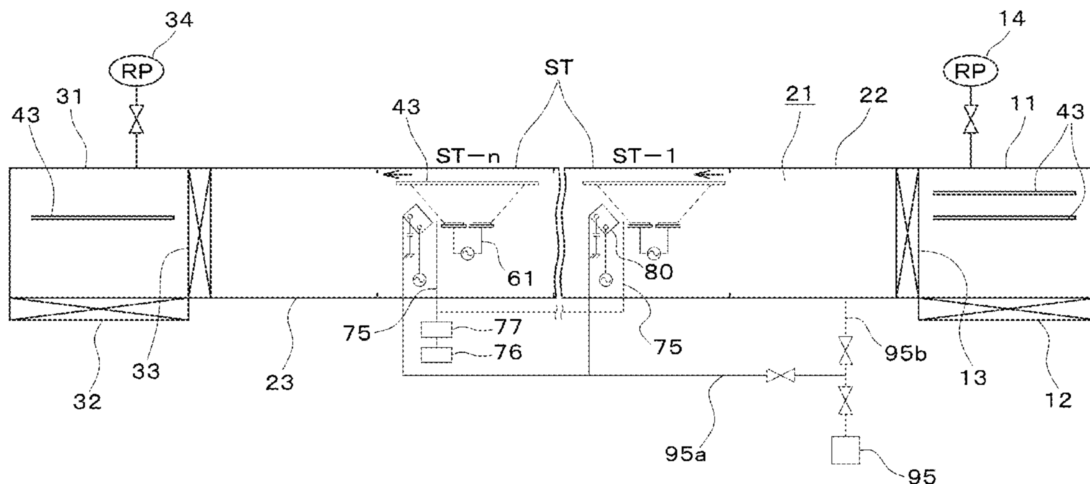
(57) **ABSTRACT**

Provided are a thin film formation apparatus, a sputtering cathode, and a method of forming thin film, capable of forming a multilayer optical film at a high film deposition rate on a large-sized substrate. The thin film formation apparatus forms a thin film of a metal compound on a substrate in a vacuum chamber by sputtering. The vacuum chamber is provided in its inside with targets composed of metal or a conductive metal compound, and an active species source for generating an active species of a reactive gas. The active species source is provided with gas sources for supplying the reactive gas, and an energy source for supplying energy into the vacuum chamber to excite the reactive gas to a plasma state. The energy source is provided between itself and the vacuum chamber with a dielectric window for supplying the energy into the vacuum chamber.



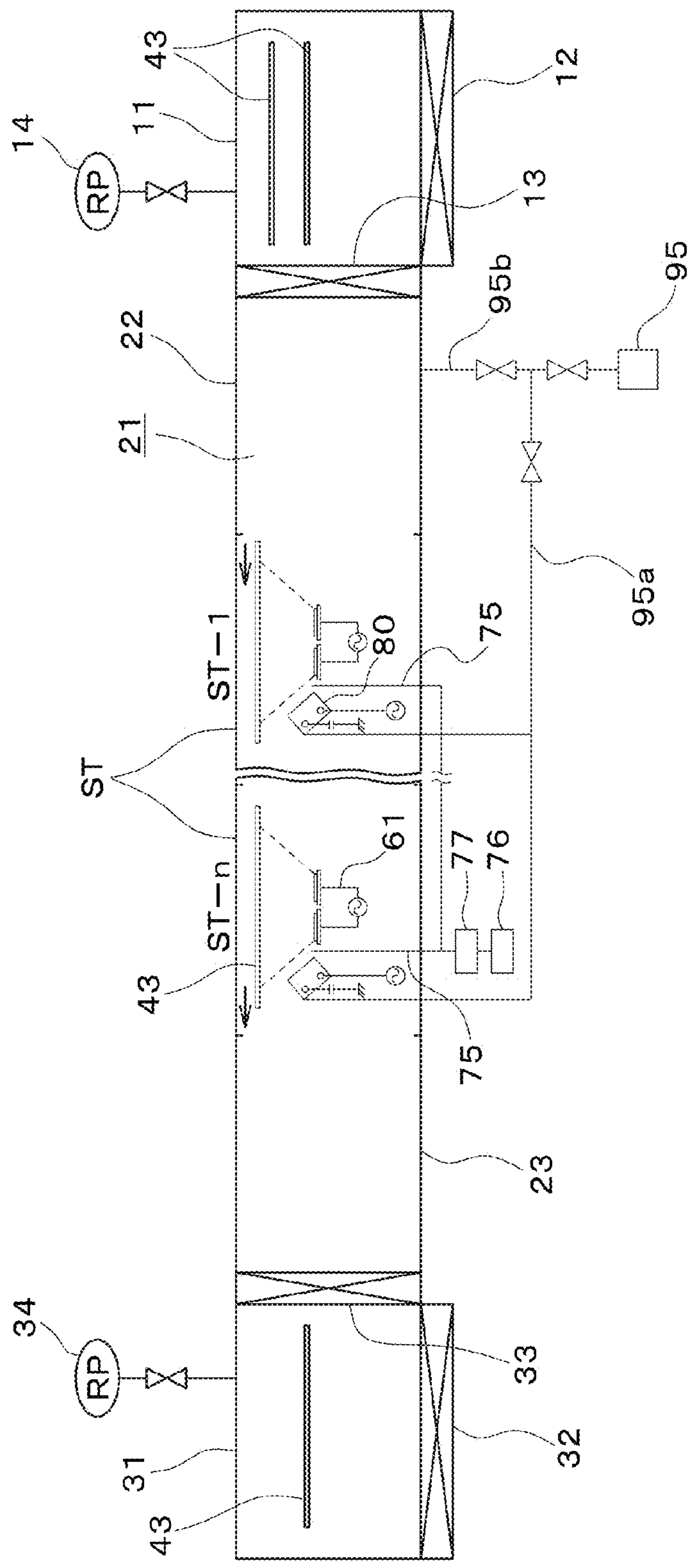


FIG. 1
1
RP
14
11
43
12
13
22
21
95b
95
95a
ST
ST−1
80
75
ST−n
61
77
76
43
75
23
RP
34
33
31
32
43

FIG. 2

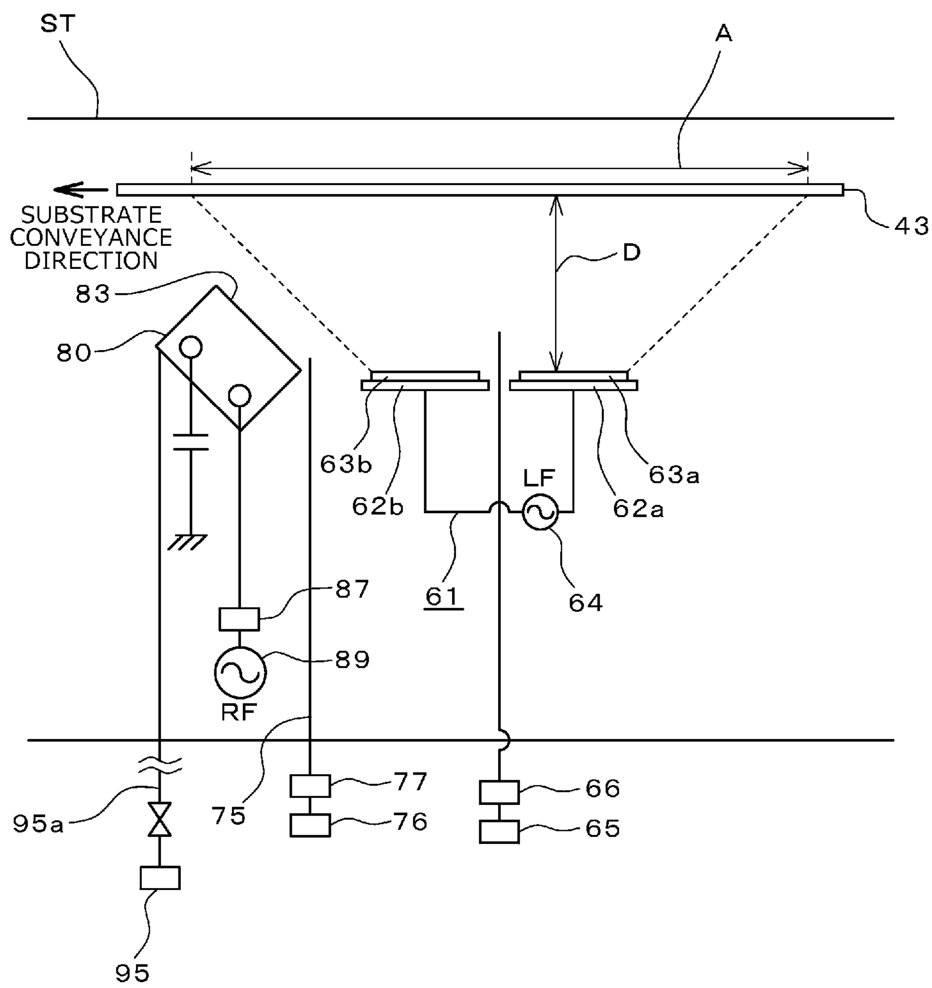


FIG. 3

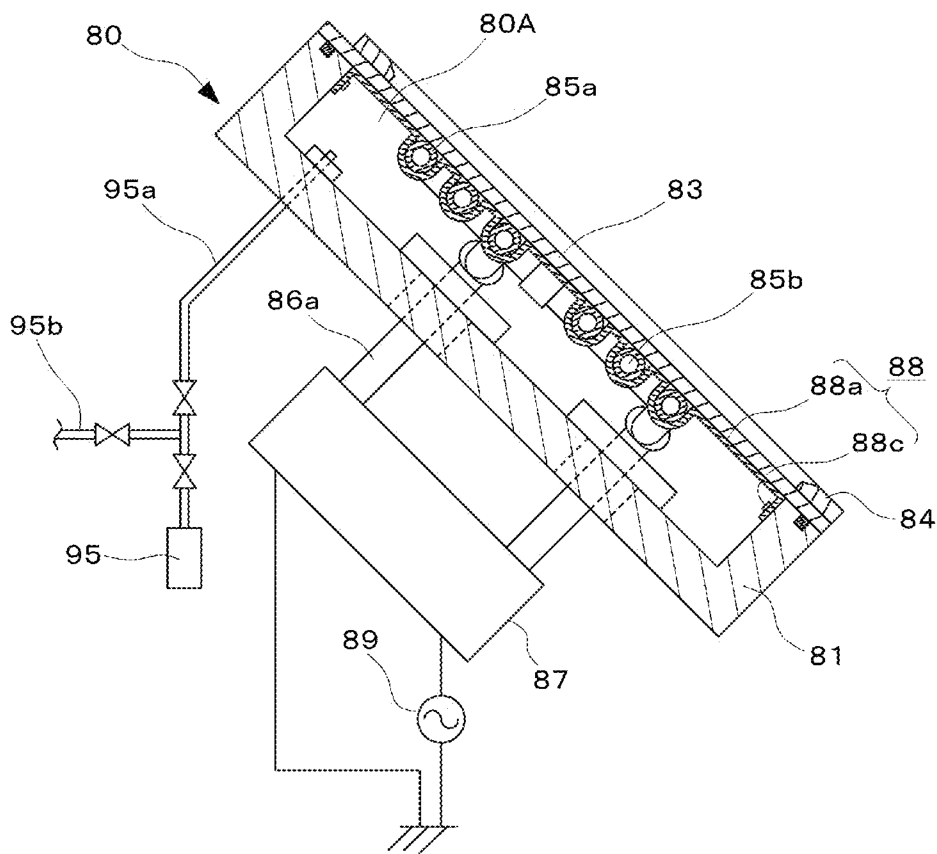
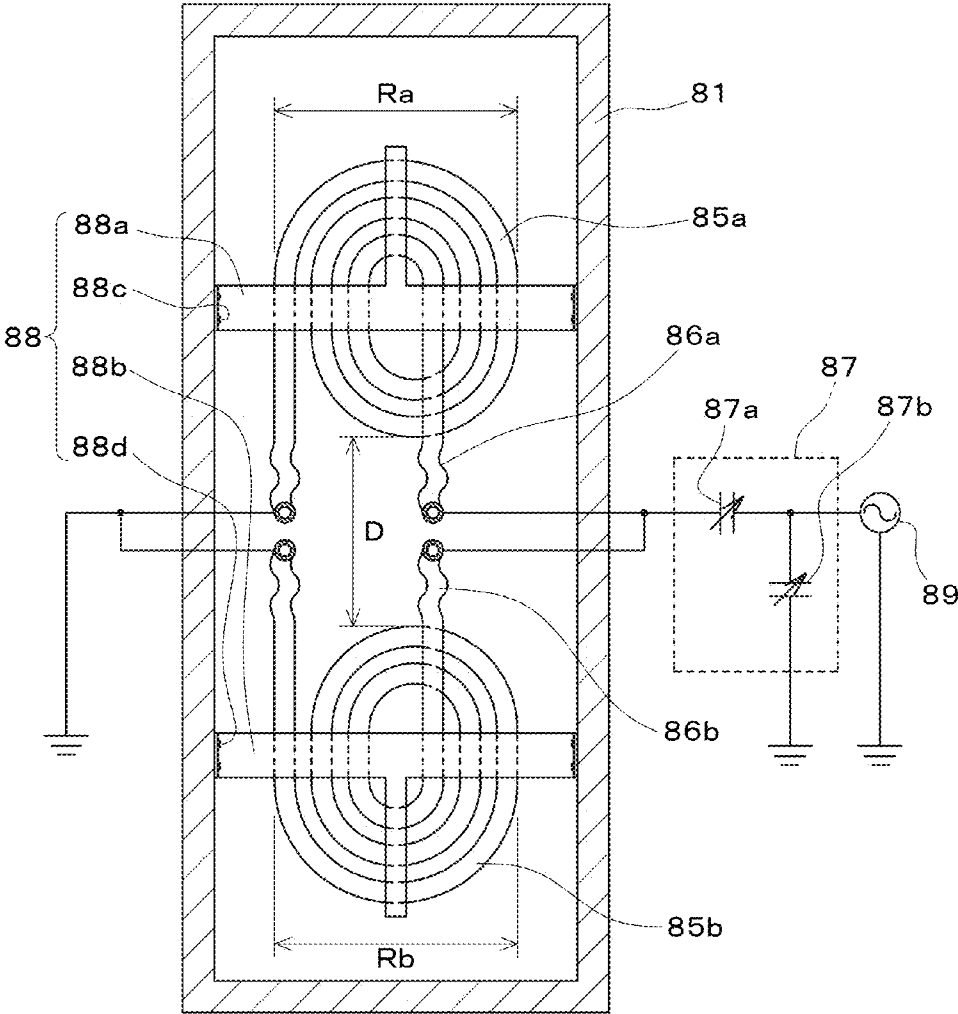


FIG. 4



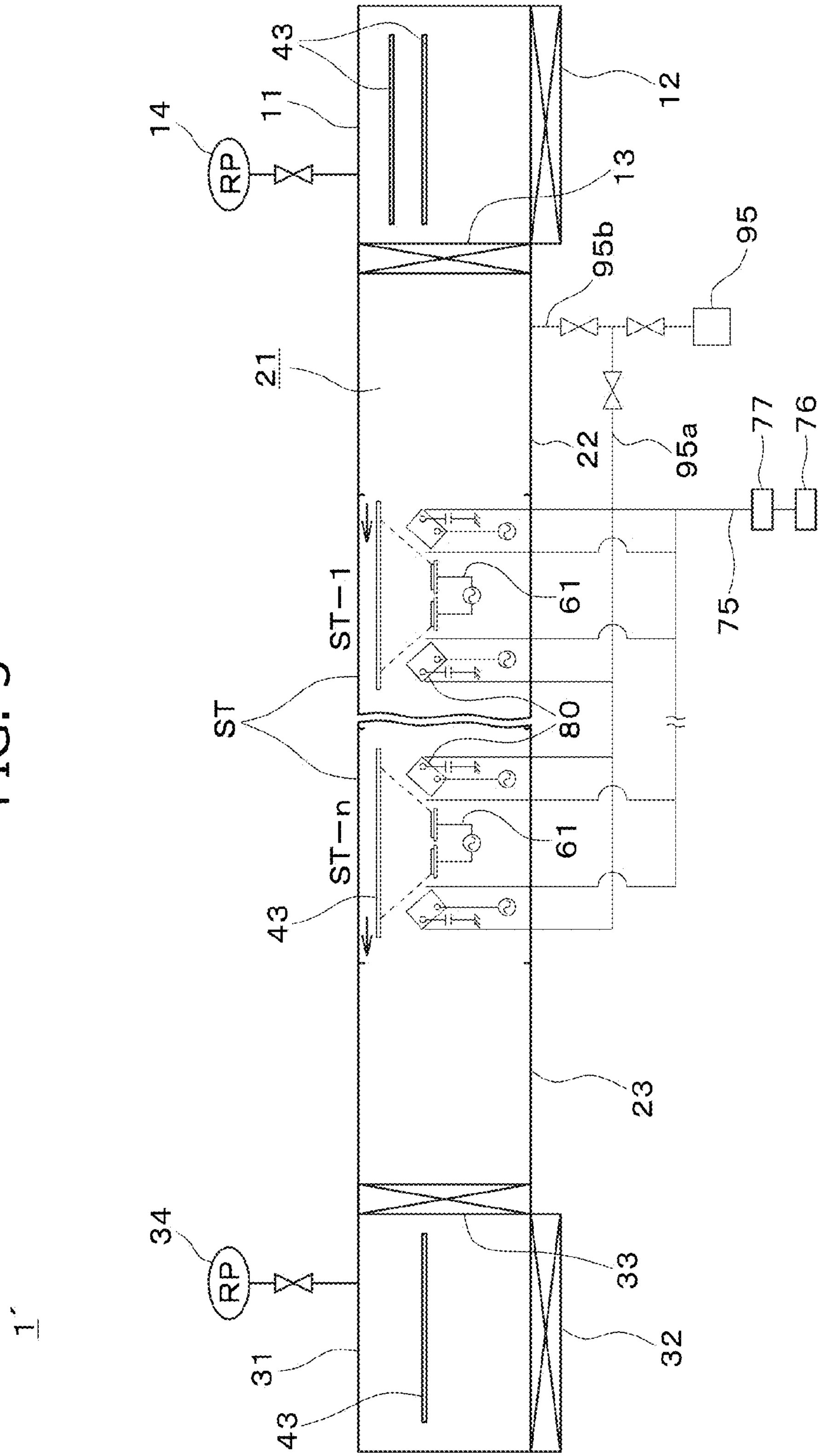


FIG. 5
1´
14
RP
34
RP
11
43
12
13
21
22
23
95
95a
95b
77
76
75
61
80
ST
ST−1
ST−n
31
32
33
43
43

FIG. 6

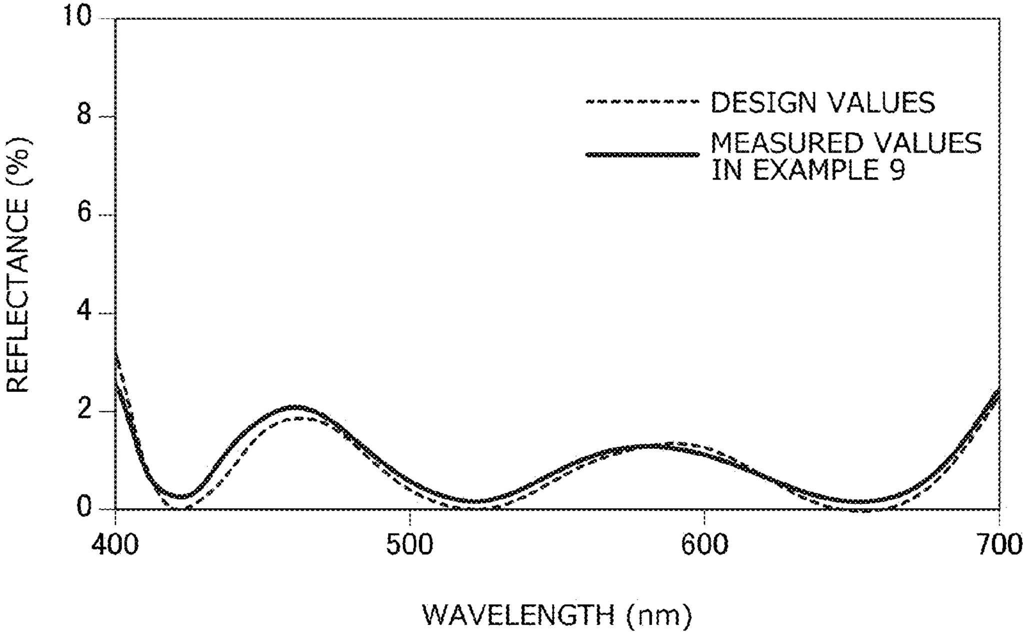


FIG. 7

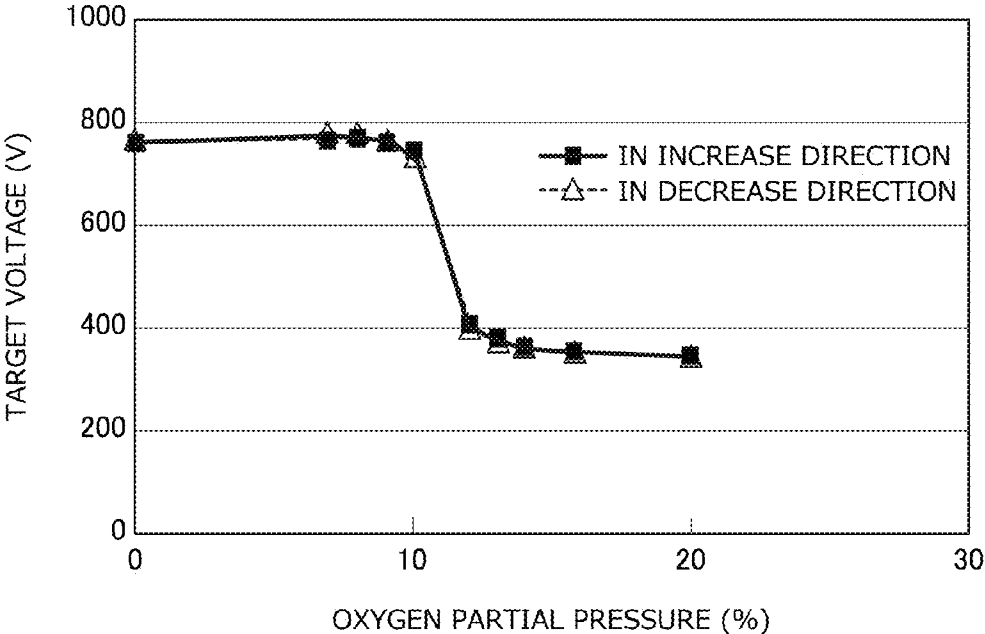
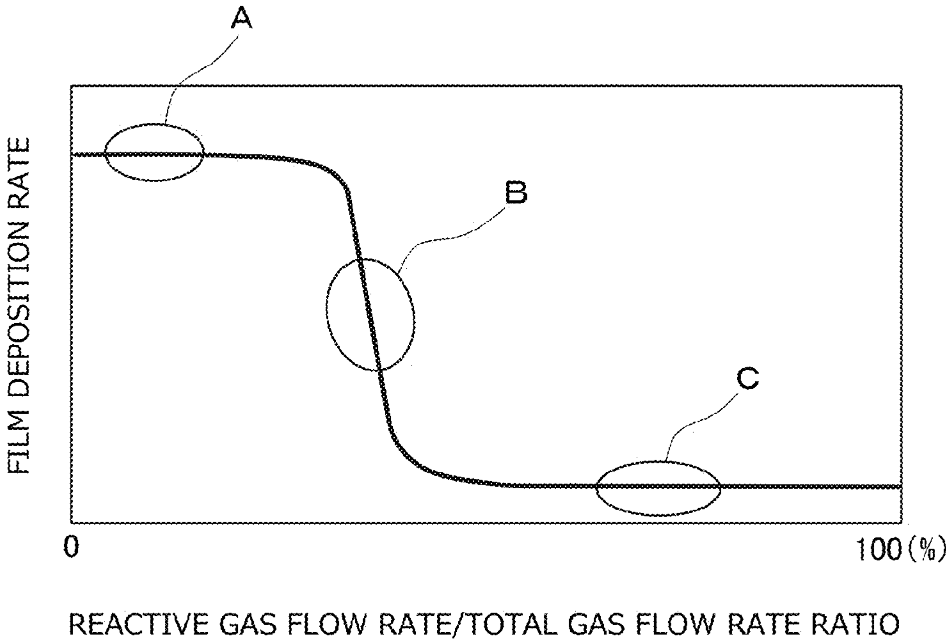


FIG. 8



THIN FILM FORMATION APPARATUS, SPUTTERING CATHODE, AND METHOD OF FORMING THIN FILM

TECHNICAL FIELD

[0001] The present invention relates to a thin film formation apparatus, a sputtering cathode, and a method of forming a thin film and, in particular, to a thin film formation apparatus, a sputtering cathode, and a method of forming a thin film, capable of forming an optical multilayer film on a substrate at a high film deposition rate.

BACKGROUND ART

[0002] As a method of forming a thin film of a metal compound by sputtering, an RF reactive sputtering method, where a thin film is formed by reactive sputtering using a high frequency power source to introduce a reactive gas to a metal compound target or a metal target, a DC reactive sputtering method, where a thin film is formed by reactive sputtering using a DC power supply to introduce a reactive gas to a metal compound target or a metal target, and the like are known.

[0003] A relation between a reactive gas flow rate/total gas flow rate ratio and a film deposition rate (rate of forming thin film) is shown in FIG. **8**. The reactive gas flow rate and the total gas flow rate in FIG. **8** are a gas flow rate measured in the vicinity of the target. In FIG. **8**, a region having the low reactive gas flow rate ratio is called as a metal mode A, in which the film deposition rate is substantially equal to the case where the reactive gas flow rate is zero. In the region of the metal mode, the film deposition rate is insensitive to variations of the reactive gas flow rate values.

[0004] In a region where the reactive gas flow rate ratio is higher than the metal mode, the film deposition rate decreases rapidly as the reactive gas flow rate ratio increases, the region referred to as a transitional region mode B. As the reactive gas flow rate ratio further increases, the film deposition rate is stabilized at a low level, entering a reactive mode C, where the film deposition rate is again insensitive to variations of the reactive gas flow rate values.

[0005] In the above-mentioned RF reactive sputtering method and DC reactive sputtering method, the sputtering is performed in the region of the reactive mode C in the graph of FIG. **8**, resulting in having about ⅕ to ⅒ of the film deposition rate when compared with the case of forming a metal thin film without introducing the reactive gas.

[0006] As a technique for forming an optical multilayer film with high quality while solving the problem of the low film deposition rate observed in the RF reactive sputtering method and the DC reactive sputtering method, there is a known sputtering method, in which a radical source is provided in a vacuum chamber, whereby sputter particles from a metal target, and deposits on a substrate are converted by radicals through oxidation or the like to form metal compounds (e.g., see Patent Document 1).

[0007] In the sputtering method described in Patent Document 1, a film deposition area and a reaction area are separated spatially as well as in a pressure-wise manner in a vacuum chamber, so that after the sputtering is performed with a metal target in the film deposition area, the thus formed metal thin film is brought into contact with an active species of a reactive gas in the reaction area to form a thin film of a metal compound.

[0008] According to the sputtering method described in Patent Document 1, an optical multilayer film can be formed at a high film deposition rate since the film formation is performed in the metal mode A, instead of the reactive mode C in FIG. **8**.

[0009] However, according to the sputtering method of Patent Document 1, the film deposition area where the sputtering is performed and the reaction area where oxidation and nitriding occur by the radicals need to be spatially separated, and further, the high-speed rotation of the substrate is required, thus, a type of sputtering apparatus used in this method is limited to a carousel type rotary drum. This method, therefore, couldn't be applied to an opposed-to-substrate type or in-line type sputtering apparatus. As such, a substrate that can be mounted is limited to the one with a small size, and it has been difficult to form a film on a large-sized substrate.

CITATION LIST

Patent Document

[0010] Patent Document 1: JP 2001-234338 A (Paragraphs 0067-0072 and FIG. 1)

DISCLOSURE OF THE INVENTION

Problem to be Solved by the Invention

[0011] The present invention has been made in view of the above-described problems, and an object of the present invention is to provide a thin film formation apparatus, a sputtering cathode, and a method of forming a thin film, capable of forming an optical multilayer film on a large-sized substrate at a high film deposition rate.

Means for Solving Problem

[0012] As a result of an extensive study on the arrangement of a target and an active species source in a vacuum chamber, the present inventors surprisingly found that it is possible to form a thin film of a metal compound by sputtering in the metal mode or the transitional region mode instead of the reactive mode by arranging an energy source for exciting a reactive gas into a plasma state in a defined position despite that the target and the active species source are not separated spatially or in a pressure-wise manner, but rather arranged to produce mutual electromagnetic and pressure interactions, and were able to complete the present invention.

[0013] That is, the above-mentioned problems can be solved by a thin film formation apparatus for forming a thin film of a metal compound on a substrate in a vacuum chamber by sputtering according to an embodiment of the present invention, wherein the thin film formation apparatus includes in the vacuum chamber a target composed of metal or a conductive metal compound, and an active species source for generating an active species of a reactive gas, arranged to produce mutual electromagnetic and pressure interactions with the target, the active species source includes a gas source for supplying the reactive gas, and an energy source for exciting the reactive gas into a plasma state by supplying an energy within the vacuum chamber, the energy source includes between itself and the vacuum chamber a dielectric window for supplying the energy within the vacuum chamber, and the dielectric window is disposed in parallel with the substrate, or

in such a way as inclining towards the target side at an angle of less than 90° to the substrate.

[0014] In a conventional reactive sputtering, where a target such as metal is sputtered while a reactive gas is introduced, a metal compound is formed on the surface of the target as the introduction rate of the reactive gas increases, so that film formation is performed in the reactive mode with a low film deposition rate. In contrast, in the thin film formation method of the present invention, a metal compound is deposited on a film by sputtering in the metal or transitional region mode instead of the reactive mode, thus an optical multilayer film can be formed at a high film deposition rate.

[0015] That is, because the active species source is arranged to produce mutual electromagnetic and pressure interactions with the target, this configuration creates plasma interactions between a plasma generated by applying a voltage to the target and a plasma generated by the active species source, and thereby increases the plasma density in the area between the target and the substrate. As the result, the amount of the sputtering gas active species such as Ar^+ increases in the vicinity of the target and the sputtering efficiency is improved.

[0016] Further, because of the improvement of the sputtering efficiency, metal or a conductive metal compound is ejected from the target surface before a metal compound is formed on the target surface. Thus, formation of the metal compound is suppressed on the target surface, and the film deposition rate is prevented from being decreased.

[0017] Further, the active species of the reactive gas is generated by the active species source, thus making it possible to achieve a high reaction efficiency using a small amount of the reactive gas. As the result, even if the introduction rate of the reactive gas is reduced, a particle that is not a complete compound and ejected from the target, and a thin film-shaped product that is not a complete compound and formed by the accumulation of such particle on the substrate can be brought into a sufficient reaction. In this way, a thin film of a metal compound can be formed in the metal or transitional region mode.

[0018] Further, the energy source includes between itself and the vacuum chamber a dielectric window for supplying energy within the vacuum chamber, and the dielectric window is disposed in parallel with the substrate, or in such a way as inclining towards the target side at an angle of less than 90° to the substrate. Thus, it becomes possible to disperse a particle that is not a complete compound and ejected from the target composed of metal or a conductive metal compound by sputtering in the direction toward the substrate, and in the same time, convert a thin film-shaped product that is not a complete compound and formed by the accumulation of the particle that is not a complete compound on the substrate to a complete metal compound. As the result, it becomes unnecessary to separate spatially as well as in a pressure-wise manner between the target and the active species source, and they can be instead arranged to produce mutual electromagnetic and pressure interactions.

[0019] In this configuration, the vacuum chamber may internally include a substrate conveyance section for conveying a substrate, and the active species source may be disposed on at least one of the upstream and downstream sides of the target in the substrate conveyance direction.

[0020] By having the active species source disposed on at least one of the upstream and downstream sides of the target, it becomes possible to disperse a particle that is not a complete compound and ejected from the target composed of metal by sputtering in the direction toward the substrate, and in the same time, convert a thin film-shaped product that is not a complete compound and formed by the accumulation of the particle that is not a complete compound on the substrate to a complete metal compound. It also becomes unnecessary to separate spatially as well as in a pressure-wise manner between the target and the active species source, and they can be instead arranged to produce mutual electromagnetic and pressure interactions.

[0021] In this configuration, the energy source may be a plasma source for generating plasma by inductive coupling and surface wave through the dielectric window.

[0022] Having such configuration makes it possible to appropriately select a positional relation of a radical source relative to the substrate and the target, and readily constitute a thin film formation apparatus capable of forming a film at optimum conditions.

[0023] In this configuration, the active species source may be an inductive coupling type plasma (ICP) radical source.

[0024] Having such configuration makes it possible to achieve a high film deposition rate by large diameter plasma having low pressure and high density.

[0025] In this configuration, the thin film formation apparatus may comprises an in-line type sputtering apparatus having a plurality of film-forming stations including the target and the active species source disposed on at least one of the upstream and downstream sides of the target in the substrate conveyance direction.

[0026] Having such configuration makes it possible to constitute an apparatus for forming a thin film of a metal compound by sputtering with a high film deposition rate in the metal or transitional region mode without a need of adopting a carousel type as before. As the result, it becomes possible to form a thin film of a metal compound on a large-sized substrate with a high film deposition rate without limiting the shape and the size of a substrate.

[0027] In this configuration, the film-forming station may include a detection unit for optically detecting a film deposition rate, and a control unit for controlling the film deposition rate in each film-forming station accordingly by receiving a signal from the corresponding film deposition rate detection unit.

[0028] Having such configuration makes it possible to perform a feedback control of the film deposition rate, for example, by independently controlling a power source and a gas flow rate for sputtering, and a power source and a gas flow rate of the active species source.

[0029] In addition, the thin film formation apparatus preferably includes a sputtering section in the vacuum chamber for sputtering the target and by the sputtering dispersing a particle that is not a complete compound from the target to a substrate, and a composition conversion section in the vacuum chamber for converting the particle to a complete metal compound by contacting the particle with an active species of a reactive gas generated by the active species source, thereby making it possible to form a thin film composed of the complete metal compound on the substrate.

[0030] Having such configuration makes it possible to dispose the target and the active species source to produce mutual electromagnetic and pressure interactions and obviate the need for separating spatially as well as in a pressure-wise

manner between the target and the active species source, thus enabling to provide a thin film formation apparatus with a simple constitution.

[0031] The above-mentioned problems can be solved by a sputtering cathode for forming a thin film of a metal compound on a substrate by sputtering according to an embodiment of the present invention, wherein the sputtering cathode includes a target composed of metal or a conductive metal compound, and an active species source for generating an active species of the reactive gas, arranged to produce mutual electromagnetic and pressure interactions with the target, the active species source includes a gas source for supplying the reactive gas, and an energy source for exciting the reactive gas into a plasma state by supplying energy within the vacuum chamber, the energy source includes a dielectric window for supplying the energy to the outside of the energy source, and the dielectric window is disposed in parallel with the substrate, or in such a way as inclining towards the target side at an angle of less than 90° to the substrate.

[0032] In a conventional reactive sputtering, where a target such as metal is sputtered while a reactive gas is introduced, a metal compound is formed on the surface of the target as the introduction rate of the reactive gas increases, so that film formation is performed in the reactive mode with a low film deposition rate. In contrast, in the thin film formation method of the present invention, a metal compound is deposited on a film by sputtering in the metal or transitional region mode instead of the reactive mode, thus an optical multilayer film can be formed at a high film deposition rate.

[0033] That is, because the active species source is arranged to produce mutual electromagnetic and pressure interactions with the target, this configuration creates plasma interactions between a plasma generated by applying a voltage to the target and a plasma generated by the active species source, and thereby increases the plasma density in the area between the target and the substrate. As the result, the amount of the sputtering gas active species such as Ar^+ increases in the vicinity of the target and the sputtering efficiency is improved.

[0034] Further, because of the improvement of the sputtering efficiency, metal or a conductive metal compound is ejected from the target surface before a metal compound is formed on the target surface. Thus, formation of the metal compound is suppressed on the target surface, and the film deposition rate is prevented from being decreased.

[0035] Further, the active species of the reactive gas is generated by the active species source, thus making it possible to achieve a high reaction efficiency using a small amount of the reactive gas. As the result, even if the introduction rate of the reactive gas is reduced, a particle that is not a complete compound and ejected from the target, and a thin film-shaped product that is not a complete compound and formed by the accumulation of such particle on the substrate can be brought into a sufficient reaction. In this way, a thin film of a metal compound can be formed in the metal or transitional region mode.

[0036] In addition, the target and the active species source may be arranged side by side in the same space of a vacuum chamber in such a way that the sputtering face of the target where erosion occurs and the active species source are arranged to be opposed to the substrate, and the active species source are disposed on at least one of the upstream and downstream sides of the target in the substrate conveyance direction.

[0037] Having such configuration creates plasma interactions between plasma generated by applying a voltage to the target and plasma generated by the active species source, and increases the plasma density in the area between the target and the substrate, so that the amount of Ar^+ increases in the vicinity of the target and the sputtering efficiency can be improved.

[0038] The above-mentioned problems can be solved by a method of forming a thin film according to an embodiment of the present invention, wherein the method comprises a sputtering step for sputtering a target composed of metal or a conductive metal compound and by the sputtering, dispersing a particle that is not a complete compound from the target to a substrate in a vacuum chamber, and a composition conversion step for converting the particle to a complete metal compound by contacting the particle with an active species of a reactive gas generated by an active species source arranged to produce mutual electromagnetic and pressure interactions with the target in the vacuum chamber, thereby enabling to form a thin film composed of the complete metal compound on the substrate.

[0039] In a conventional reactive sputtering, where a target such as metal is sputtered while a reactive gas is introduced, a metal compound is formed on the surface of the target as the introduction rate of the reactive gas increases, so that film formation is performed in the reactive mode with a low film deposition rate. In contrast, in the thin film formation method of the present invention, a metal compound is deposited on a film by sputtering in the metal or transitional region mode instead of the reactive mode, thus an optical multilayer film can be formed at a high film deposition rate.

[0040] That is, because the active species source is arranged to produce mutual electromagnetic and pressure interactions with the target, this configuration creates plasma interactions between a plasma generated by applying a voltage to the target and a plasma generated by the active species source, and thereby increases the plasma density in the area between the target and the substrate. As the result, the amount of the sputtering gas active species such as Ar^+ increases in the vicinity of the target and the sputtering efficiency is improved.

[0041] Further, because of the improvement of the sputtering efficiency, metal or a conductive metal compound is ejected from the target surface before a metal compound is formed on the target surface. Thus, formation of the metal compound is suppressed on the target surface, and the film deposition rate is prevented from being decreased.

[0042] Further, the active species of the reactive gas is generated by the active species source, thus making it possible to achieve a high reaction efficiency using a small amount of the reactive gas. As the result, even if the introduction rate of the reactive gas is reduced, a particle that is not a complete compound and ejected from the target, and a thin film-shaped product that is not a complete compound and formed by the accumulation of such particle on the substrate can be brought into a sufficient reaction, so that a thin film of a metal compound can be formed in the metal or transitional region mode.

[0043] Further, the thin film-shaped product that is not a complete compound and formed by the accumulation of the particle on the substrate is converted to a complete metal compound by contacting with the active species of the reactive gas generated by the active species source arranged to produce mutual electromagnetic and pressure interactions

with the target, thus it becomes possible to arrange the target and the active species source to produce mutual electromagnetic and pressure interactions, and obviate the need for separating spatially as well as in a pressure-wise manner between the target and the active species source, thereby enabling to form a film using a thin film formation apparatus having a simple constitution.

[0044] Additionally, the method of forming a thin film of the present invention may include a film formation repetitive step, in which the sputtering step and the composition conversion step are repeated in parallel a plurality of times after the composition conversion step.

[0045] In such configuration, it is possible to deposit a metal compound to form a film by sputtering performed in the metal or transitional region mode instead of the reactive mode, and produce a thin film of the metal compound having a desired film thickness.

[0046] Before the sputtering step, the method may also include a step of introducing the substrate into an in-line type thin film formation apparatus having a plurality of film-forming stations each including the target and the active species source disposed on at least one of the upstream and downstream sides of the target in the substrate conveyance direction. Then the method may further include an in-station film formation step, where the sputtering step, the composition conversion step, and the film formation repetitive step are carried out in the film-forming stations while the substrate is conveyed at a constant speed, a conveyance step for conveying the substrate to the film-forming stations located on the downstream side in the substrate conveyance direction, and a multiple-station film formation step, where the in-station film formation step and the conveyance step are repeated. After the in-station film formation step is completed in the film-forming station on the most downstream side in the substrate conveyance direction, a discharge step for discharging the substrate to the atmosphere may be performed.

[0047] Having such configuration makes it possible to form a multilayer film composed of a metal compound having a desired number of layers by appropriately selecting the number of the film-forming stations.

Effect of the Invention

[0048] In a conventional reactive sputtering, where a target such as metal is sputtered while a reactive gas is introduced, a metal compound is formed on the surface of the target as the introduction rate of the reactive gas increases, so that film formation is performed in the reactive mode with a low film deposition rate. In contrast, in the thin film formation method of the present invention, a metal compound can be deposited on a film by sputtering in the metal or transitional region mode instead of the reactive mode, thus an optical multilayer film can be formed at a high film deposition rate.

[0049] That is, because the active species source is arranged to produce mutual electromagnetic and pressure interactions with the target, this configuration creates plasma interactions between a plasma generated by applying a voltage to the target and a plasma generated by the active species source, and thereby increases the plasma density in the area between the target and the substrate. As the result, the amount of the sputtering gas active species such as Ar^+ increases in the vicinity of the target and the sputtering efficiency is improved.

[0050] Further, because of the improvement of the sputtering efficiency, metal or a conductive metal compound is ejected from the target surface before a metal compound is formed on the target surface. Thus, formation of the metal compound is suppressed on the target surface, and the film deposition rate is prevented from being decreased.

[0051] Further, the active species of the reactive gas is generated by the active species source, thus making it possible to achieve a high reaction efficiency using a small amount of the reactive gas. As the result, even if the introduction rate of the reactive gas is reduced, a particle that is not a complete compound and ejected from the target, and a thin film-shaped product that is not a complete compound and formed by the accumulation of such particle on the substrate can be brought into a sufficient reaction. Thus, a thin film of a metal compound can be formed in the metal or transitional region mode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0052] FIG. **1** is an explanatory diagram illustrating an in-line type sputtering apparatus according to an embodiment of the present invention;

[0053] FIG. **2** is an enlarged explanatory diagram illustrating a configuration of a film-forming station of the in-line type sputtering apparatus according to the embodiment of the present invention;

[0054] FIG. **3** is a schematic explanatory diagram illustrating a radical source according to the embodiment of the present invention;

[0055] FIG. **4** is a schematic explanatory diagram illustrating the radical source according to the embodiment of the present invention;

[0056] FIG. **5** is an explanatory diagram illustrating an in-line type sputtering apparatus according to another embodiment of the present invention;

[0057] FIG. **6** is a graph showing a comparison of reflectance values at the different wavelengths between a multilayer AR film formed in Example 9 and a multilayer AR film in design, where a first layer is Si_3N_4 having the physical film thickness of 123.9 nm, a second layer is SiO_2 having the physical film thickness of 164.3 nm, a third layer is Si_3N_4 having the physical film thickness of 99.5 nm, and a fourth layer is SiO_2 having the physical film thickness of 73.2 nm;

[0058] FIG. **7** is a graph showing a relation between an oxygen partial pressure and a target voltage measured in the in-line type sputtering apparatus according to the embodiment of the present invention under the conditions where oxygen gas flow rate is increased and decreased; and

[0059] FIG. **8** is a graph showing a relation between a reactive gas flow rate/total gas flow rate ratio, and a film deposition rate (rate of forming thin film) in a conventional sputtering.

DETAILED DESCRIPTION OF THE INVENTION

[0060] Hereinafter, embodiments of the present invention will be described with reference to the drawings. The members, the arrangements, and the like described below do not limit the invention of the present application, and may be, of course, modified into various forms in accordance with the spirit of the invention.

[0061] In the specification, an active species of a reactive gas refers to a highly reactive particle generated as a result of reactions such as ionization, dissociation, adhesion, excitation, and the like caused by high-speed electrons colliding

against reactive gas molecules and atoms in plasma, and includes an ion, a radical, an excited species, and the like of a reactive gas.

[0062] The radical of a reactive gas includes a reactive gas radical, in which a molecular ion, an atom, and an inner shell electron of the reactive gas are in an excited state and are more active than a reactive gas molecule.

(Thin Film Formation Apparatus)

[0063] A sputtering apparatus **1** as a thin film formation apparatus of the present embodiment is a so-called load locked type and in-line type sputtering apparatus, and is composed of a load lock chamber **11**, a film deposition chamber **21**, an unloading chamber **31**, and a substrate conveyance device not illustrated.

[0064] The load lock chamber **11** includes a gate valve **12** for making the load lock chamber **11** open to the atmosphere, a gate valve **13** provided between itself and the film deposition chamber **21**, and a rotary pump **14** for evacuating the load lock chamber **11**.

[0065] The unloading chamber **31** includes a gate valve **32** for making the unloading chamber **31** open to the atmosphere, a gate valve **33** provided between itself and the film deposition chamber **21**, and a rotary pump **34** for evacuating the unloading chamber **31**.

[0066] The substrate conveyance device not illustrated is a known substrate conveyance device used in an in-line type sputtering apparatus, and includes a substrate holder not illustrated for holding a substrate **43**, and a substrate conveyance mechanism not illustrated. By the substrate conveyance device, the substrate **43** is introduced from the atmosphere to the load lock chamber **11**, the film deposition chamber **21**, and the unloading chamber **31**, and then conveyed to the atmosphere.

[0067] The substrate **43** is fixed to the substrate holder not illustrated.

[0068] The substrate **43** is a so-called large-sized substrate, such as optical members with a large area, large window glasses for building, large FPDs (flat panel displays), and the like.

[0069] A single substrate **43** may be fixed to the substrate holder not illustrated, or a plurality of substrates, for example, four substrates each having the size of one quarter of the substrate **43**, i.e. the single substrate **43** being horizontally and vertically divided into two equal parts, may be fixed to the substrate holder not illustrated.

[0070] The film deposition chamber **21** includes a plurality of film-forming stations ST (ST**1** to STn) (n is a positive integer) which are connected together, and one end of the film deposition chamber **21** is connected to the load lock chamber **11** via the gate valve **13**, while the other end is connected to the unloading chamber **31** via the gate valve **33**. The bottom part of the film deposition chamber **21** is connected to a pipe **95***b* for exhaust, and the pipe **95***b* is connected to a vacuum pump **95** for evacuating the interior of the film deposition chamber **21**. A configuration is made to adjust the degree of vacuum inside of the film deposition chamber **21** by the vacuum pump **95** and a controller not illustrated.

[0071] The film deposition chamber **21** is a hollow casing body extending in the conveyance direction of the substrate **43**, and includes the plurality of film-forming stations ST (ST**1** to STn) that are connected together between a space part **22** for loading located at the load lock chamber **11** side, and a space part **23** for unloading located at the unloading chamber **31** side.

[0072] The film-forming stations ST are formed as a hollow casing body with both ends open to make a connection to the precedent and following film-forming stations ST, or the space part **22** for loading and the space part **23** for unloading. All film-forming stations ST**1** to STn include in their inside a target mechanism **61**, a radical source **80** as an energy source for an active species source, and a pipe **75** for introducing an reactive gas from a gas cylinder **76** as a gas source.

[0073] The target mechanism **61** is, as shown in FIG. **2**, connected to magnetron sputter electrodes **62***a* and *b* arranged to be opposed to the substrate **43**, and targets **63***a* and *b* held by the magnetron sputter electrodes **62***a* and *b* via a transformer not illustrated, and includes an AC power supply **64** capable of applying an alternating electric field, a gas cylinder **65** for storing a sputtering gas composed of an inert gas such as an argon gas, which serves as an operating gas in sputtering, and a mass flow controller **66** for introducing the sputtering gas stored in the gas cylinder **65**.

[0074] The magnetron sputter electrodes **62***a* and *b* are arranged to be parallel with the substrate **43** held by the substrate holder not illustrated.

[0075] The targets **63***a* and *b* are disposed in such a way that the sputtering surfaces where erosion occurs are arranged to be parallel with the substrate **43**. Erosion in this description refers to a phenomenon where target-constituting elements are sprung out by a sputtering phenomenon leading to a consumption of the target.

[0076] The targets **63***a* and *b* are metal targets, conductive metal compound targets, or composite targets, which are known and generally used in sputtering. Examples of such targets include silicon (Si), niobium (Nb), aluminum (Al), titanium (Ti), zirconium (Zr), tin (Sn), chromium (Cr), tantalum (Ta), tellurium (Te), iron (Fe), magnesium (Mg), hafnium (Hf), nickel-chromium (Ni—Cr), indium-tin (In—Sn), and the like.

[0077] The size of the targets **63***a* and *b* of the present embodiment is 5×27 inches, and a distance D between the targets **63***a* and *b*, and the substrate **43** is 70-400 mm.

[0078] By sputtering the targets **63***a* and *b*, a metal compound is deposited to form a film in a film-forming effective area A shown in FIG. **2**.

[0079] An AC power supply **64** of the present embodiment is constituted of an LF power supply, however, the present invention is not limited thereto, and the AC power supply **64** may be constituted of an RF power supply, a dual frequency RF power supply, and the like.

[0080] In the present embodiment, the degree of vacuum in the film-forming stations ST is adjusted by the vacuum pump **95**, and then an inert gas such as an argon gas is introduced from the gas cylinder **65** by the mass flow controller **66** to adjust a vacuum gas atmosphere of the film-forming stations ST in order to perform a dual magnetron sputtering.

[0081] The dual magnetron sputtering uses a pair of magnetron sputter electrodes **62***a* and *b*, and a pair of targets **63***a* and *b*, both of which are electrically insulated from ground potential. Thus, although it is not illustrated, the magnetron sputter electrodes **62***a* and *b*, and the targets **63***a* and *b* are attached via an insulation material to the sputtering apparatus **1** body that is grounded. Further, the magnetron sputter electrodes **62***a* and *b*, and the targets **63***a* and *b* are also mutually electrically disconnected.

[0082] In this configuration, when an operating gas such as an argon gas is introduced in the vicinity of the targets **63***a* and *b* to adjust a sputtering atmosphere, and a voltage is applied to the magnetron sputter electrodes **62***a* and *b* from the AC power supply **64** via the transformer not illustrated, the targets **63***a* and *b* are constantly applied with an alternating electric field. That is, at a given time point, the target **63***a* becomes a cathode (minus electrode), and the target **63***b* always becomes an anode (plus electrode). At the next time point when the direction of the AC current is reversed, the target **63***b* becomes a cathode, and the target **63***a* becomes an anode. The paired targets **63***a* and *b* alternately become an anode and a cathode in this manner to generate plasma, as the result, the target on a cathode is sputtered to form an ultrathin film of metal on a substrate.

[0083] In the process of sputtering, an incomplete reaction product of metal with low or no conductivity may adhere to an anode. However, when the anode is converted to a cathode by the alternating electric field, the incomplete reaction product of metal is sputtered, and the surface of the target becomes clean again. By repeating this process, a potential state of an anode is stably maintained at all times, thereby preventing variations in plasma potential, which is usually substantially equal to an anode potential. Thus, a metal particle can be stably dispersed to a substrate **43** from targets **63***a* and *b*.

[0084] The targets **63***a* and *b* may contain the same metal, or different metal. When the targets each containing the same metal are used, a thin film containing one metal is formed, while when the targets each containing different metal are used, a thin film of an alloy product is formed.

[0085] The frequency of an AC voltage applying to the targets **63***a* and *b* is preferably 10-120 KHz.

[0086] The radial source **80** consists of an inductive coupling type plasma generator section having a high frequency antenna, and as shown in FIG. **1** and FIG. **2**, each radial source **80** is provided on the downstream side of the target mechanism **61**. As shown in FIG. **3**, the radial source **80** includes a case body **81**, a dielectric plate **83**, a fixed frame **84**, antennas **85***a* and *b*, a fixture **88**, a pipe **95***a*, and a vacuum pump **95**.

[0087] As shown in FIG. **3**, the case body **81** is an approximately rectangular container made of stainless steel, having an opening portion in one face. The dielectric plate **83** is fixed to the container to close the opening, thereby constituting a dielectric window. The internal space of the case body **81** closed by the dielectric window constitutes an antenna storage chamber **80**A.

[0088] The antenna storage chamber **80**A is partitioned from the film-forming stations ST by the dielectric plate **83** to form a space independently from the film-forming stations ST. The dielectric plate **83** is a known dielectric having a plate-like shape, and is made of quartz in the present embodiment.

[0089] The fixed frame **84** is a rectangular frame. The fixed frame **84** and the case body **81** are connected by bolts not illustrated in such a way that the dielectric plate **83** is held and fixed by the fixed frame **84** and the case body **81**.

[0090] The antennas **85***a* and *b* are disposed in the antenna storage chamber **80**A.

[0091] The antennas **85***a* and *b* consist of spiral coil electrodes in which the surface of round tubes made of copper is coated with silver, and are disposed in the antenna storage chamber **80**A in such a way that the spiral face of the electrodes is arranged in parallel with the bottom surface of the case body **81** and the dielectric plate **83**.

[0092] The antennas **85***a* and *b* are connected in parallel with a high frequency power source **89**. Further, as shown in FIG. **4**, the antennas **85***a* and *b* are connected via conductive wires **86***a* and *b*, respectively to a matching box **87** having variable capacitors **87***a* and *b*, and further connected to the high frequency power source **89**.

[0093] The fixture **88** is composed of fixing plates **88***a* and *b*, which are plates having grooves to which the antennas **85***a* and *b* can be fitted, and fixing bolts **88***c* and *d*.

[0094] The antennas **85***a* and *b* are respectively fitted into the fixing plates **88***a* and *b*, and fixed to the case body **81** by the fixing bolts **88***c* and *d*. A plurality of bolt holes are formed to the case body **81** in the up to down direction, and the fixing plates **88***a* and *b* are fixed to the case body **81** using some of the bolt holes.

[0095] In order to insulate the fixing plates **88***a* and *b* from the antennas **85***a* and *b*, an insulating material is installed at least in contact faces between the antennas **85***a* and *b*, and the fixing plates **88***a* and *b*.

[0096] As shown in FIG. **3**, the bottom surface of the case body **81** is provided with the pipe **95***a* for exhaust, and connected to the vacuum pump **95** via valves. This configuration makes it possible to evacuate the inside of the antenna storage chamber **80**A through the operation of the valves by using the vacuum pump **95** for evacuating the film-forming stations ST. It should be noted that FIG. **1** only shows a portion of the pipe **95** connecting to some radical sources **80**.

[0097] In the present embodiment, as shown in FIG. **3** and FIG. **4**, an inductive coupling type plasma source having spiral antennas in a flat spiral shape is used, however, different types of inductive coupling type plasma source may also be used. Examples of the different types include the one in which high-frequency current is applied to a coil having a cylindrical helical antenna wound on a glass tube in a spiral manner, and the one in which an antenna is inserted to the inside of plasma.

[0098] Further, other plasma sources in which plasma is generated by inductive coupling and surface wave through a dielectric window may be used, and examples of such plasma sources include electron cyclotron resonance plasma (ECP) source, helicon wave excited plasma (HWP) source, microwave-excited surface wave plasma (SWP) source, and the like.

[0099] Instead of using the inductive-coupling type plasma source, a capacitance-coupling type plasma source may also be used, in which a plate-shaped electrode is disposed within the antenna storage chamber **80**A and applied with high frequency power of 100 KHz-50 MHz to generate plasma.

[0100] Further, a plasma source generating plasma in which inductive-coupling type plasma and capacitance-coupling type plasma are mixed may also be used.

[0101] In the film-forming statins ST, as shown in FIG. **3**, a pipe **75** is provided between the radical source **80** and the substrate **43**, and is connected to a gas cylinder **76** for supplying an reactive gas via a mass flow controller **77**. This configuration makes it possible to supply the reactive gas to an area between the radical source **80** and the substrate **43**.

[0102] In the present embodiment, oxygen gases, such as oxygen (O_2), ozone (O_3), and dinitrogen oxide (N_2O), nitrogen gases, such as nitrogen (N_2), carbon gases, such as methane (CH_4), fluorine gases, such as fluorine (F_2) and carbon tetrafluoride (CF_4), and the like may be used as a reactive gas.

[0103] In the present embodiment, the mass flow controller **66** for introducing the sputtering gas, and the mass flow

controller **77** for introducing the reactive gas are independently installed. Having such configuration makes it possible to perform a feedback control of the film deposition rate by independently controlling a power and a gas flow rate of the sputtering, and a power and a gas flow rate of the active species source while monitoring a film deposition rate and the like.

[0104] As shown in FIG. **2**, the radical source **80** is inclined toward the substrate **43** in such a way that the surface plane of the dielectric plate **83**, i.e. the surface plane of the dielectric window formed by the dielectric plate **83** faces the center area of the substrate **43**. The angle between the surface plane of the dielectric plate **83** and the substrate **43** is in the range of 0°≤ and <90°. In another words, the dielectric plate **83** is arranged in parallel with the targets **63***a* and *b*, or in such a way as inclining towards the substrate **43** held by the substrate holder not illustrated at an angle of 0°≤ and <90°, so that the outside of the film-forming stations ST becomes closer to the substrate **43**. The preferable angle between the surface plane of the dielectric plate **83** and the substrate **43** is 0°-60° for obtaining the highest film deposition rate.

[0105] Further, each film-forming station ST includes an optical film-forming rate controller not illustrated, and thus can control a film-forming rate to adjust the thicknesses of a film by modifying sputtering conditions in each film-forming station ST using the optical film-forming rate controller.

[0106] The optical film-forming rate controller not illustrated includes an optical film thickness meter not illustrated for measuring the thin film thickness formed on the substrate **43**, and a controller unit not illustrated for adjusting gas flow rates by controlling mass flow controllers **66** and **67** on the basis of film thickness measurement results obtained by the optical film thickness meter.

[0107] As the optical film thickness meter, a transmission type optical film thickness meter that measures light transmitting through an optical thin film upon being emitted from a projector is used. However, a reflection type optical film thickness meter may also be used, in which the film thickness is measured by using an interference phenomenon caused by a phase difference occurring between the light reflected on the surface of an optical thin film, and the light reflected on an interface between a substrate and an optical film due to their having different light paths.

[0108] During sputtering, the optical film thickness meter not illustrated monitors the thickness of a thin film being formed on the substrate **43** in each film-forming station ST, and if the optical film thickness meter detects a decrease in a film deposition rate, then it performs a control to return the film deposition rate to the original level by increasing current capacity of the AC power supply **64** and the high frequency power source **89**.

[0109] The radical source **80** of the present embodiment induces a reactive gas stored in the reactive gas cylinder **76** to the film-forming stations ST via the mass flow controller **77** while keeping the pressure in the antenna storage chamber **80**A lower than that in the film-forming stations ST. The antennas **85***a* and *b* are supplied with a voltage of 13.56 MHz from the high frequency power source **89** in order to flow a high-frequency current. In this manner, the generation of plasma is suppressed in the antenna storage chamber **80**A, and the antennas **85***a* and *b* supplied with the voltage from the high frequency power source **89** generate an induced electric field within the film-forming stations ST, thereby generating plasma of the reactive gas.

[0110] In each film-forming station ST, the target mechanism **61** is provided in the center of the film-forming stations ST in the substrate conveyance direction, and a single radial source **80** is provided on the downstream side of the target mechanism **61** in the substrate conveyance direction.

[0111] The number of the film-forming stations ST (ST**1** to STn) constituting the film deposition chamber **21** is determined to be greater than or equal to the number of layers in a multilayer film to be formed. If the number of the film-forming stations ST to be installed is equal to the number of layers in a multilayer film to be formed, each film-forming station ST forms one layer of the multilayer film. If the number of the film-forming stations ST to be installed is greater than the number of layers in a multilayer film to be formed, at least one layer of the multilayer film is formed by a plurality of the film-forming stations ST.

[0112] The space part **22** for loading and the space part **23** for unloading have the same configuration as the film-forming stations ST except that the target mechanism **61** or the radical source **80** is not provided within the space part **22** or **23**.

[0113] In the present embodiment, only one radical source **80** is disposed on the downstream side of the target mechanism **61**, however, like a sputtering apparatus **1'** in FIG. **5**, a pair of radical sources **80** may be disposed on both the upstream and downstream sides of the target mechanism **61** to interpose the target mechanism **61**. Other configuration of the sputtering apparatus **1'** is the same as in the sputtering apparatus **1**, thus the description thereof will be omitted.

[0114] A single radical source may be also disposed on the downstream side of the target mechanism **61**.

(Method of Foaming Thin Film)

[0115] A method of foaming a thin film using a sputtering apparatus **1** of the present embodiment will be described below.

[0116] First, the inside of the film deposition chamber **21** is evacuated. Then, a prescribed number of substrates **43** with a large size are prepared by mounting them on the substrate folders not illustrated. The prescribed number of substrates are introduced into the load lock chamber **11** of the sputtering apparatus **1** by opening the gate valve **12**, and then the gate valve **12** is closed. The load lock chamber **11** in an atmospheric state is evacuated until the degree of vacuum becomes equivalent to that in the film deposition chamber **21**.

[0117] Next, the target mechanism **61** and the radical source **80** in each film-forming station ST are put in operation to start the sputtering, while a first substrate **43** is introduced into the space part **22** for loading in the film deposition chamber **21** by opening the gate valve **13**.

[0118] While the substrates **43** are moved at constant speed toward the film-forming station STn by a substrate conveyance mechanism not illustrated, film deposition is sequentially performed in the film-forming stations in the order of ST**1** to STn.

[0119] In each film-forming station ST**1** to STn, a thin film of a metal compound is formed as follows.

[0120] When the substrate **43** is conveyed by the substrate conveyance mechanism and introduced in the first film-forming station ST**1**, the substrate **43** is gradually introduced in a film-forming effective area A shown in FIG. **2** from the upstream side in the substrate conveyance direction.

[0121] When the substrate **43** enters the film-forming effective area A, first in the sputtering step, metal particles are

beaten out from the targets **63***a* and *b* by sputtering and dispersed toward the substrate **43** in an area surrounded by the film-forming effective area A, and the targets **63***a* and *b*.

[0122] Next, some of dispersed metal particles are converted to incomplete reaction products of metal by radicals of a reactive gas generated in the radical source **80** while the dispersed metal particles travel from the targets **63***a* and *b* to the substrate **43**. These metal particles and incomplete reaction products of metal are equivalent to a particle that is not a complete compound falling under the embodiments.

[0123] Then, the metal particles and the incomplete reaction products of metal are deposited on the substrate **43** to form a thin film-shaped product that is not a complete compound.

[0124] In the following composition conversion step, the thin film-shaped product that is not a complete compound on the substrate **43** is converted to a complete compound of metal by radicals of a reactive gas generated in the radical source **80**.

[0125] While the substrate **43** is passing through the film-forming effective area A, the sputtering step and the composition conversion step are executed repeatedly in parallel, so that a thin film of a metal compound is formed on the substrate **43** by the time the substrate **43** is discharged from the film-forming effective area A.

[0126] In the second and subsequent film-forming stations ST**2** to STn, the same steps are performed as in the film-forming station ST**1**, and a thin film composed of a complete compound of metal is formed in each station.

[0127] If a combination of metal in the targets **63***a* and *b* is the same between adjacent film-forming stations STi and STi+m (i and m each denotes a positive integer), the adjacent film-forming stations STi and STi+m form a thin film having an identical layer. That is, one layer of a thin film is formed by a plurality of film-forming stations STi and STi+m.

[0128] On the other hand, if a combination of metal in the targets **63***a* and *b* is different between adjacent film-forming stations STi and STi+m (i and m each denotes a positive integer), the adjacent film-forming stations STi and STi+m form a thin film having multiple layers.

[0129] During the sputtering by the targets **63***a* and *b*, and the radical formation of the reactive gas by the radical source **80**, the film deposition rate is controlled by an optical film deposition rate control mechanism not illustrated. The film deposition rate control mechanism adjusts the gas flow rates by regulating the mass flow controllers **66** and **77** based on the data of the amount of the metal, the gases, and the metal compounds detected by an optical fiber not illustrated, thereby controlling the film deposition rates to a desired value. As such, the film thickness is controlled in the film-forming stations ST.

[0130] After the film formation and reaction are completed in the film-forming stations ST, the substrate **43** is introduced into the space part **23** for unloading. The space part **23** for unloading is evacuated in advance until the degree of vacuum becomes equivalent to that in the film deposition chamber **21**. The substrate **43** is introduced into the unloading chamber **31** by opening the gate valve **33** and stored in the unloading chamber **31** after closing the gate valve **33**.

[0131] Next, an upcoming substrate **43** stored in the load lock chamber **11** is introduced into the film deposition chamber **21**, and after completing the same film formation and reaction, introduced and stored in the unloading chamber **31** in the same manner. After completing the same treatments on all substrates **43** stored in the load lock chamber **11**, the unloading chamber is switched to an atmospheric state and then all the substrates **43** are taken out in the atmosphere by opening the gate valve **32** to finish the film formation.

[0132] By performing the above-described method, a multilayer film of a metal compound having the number of layers according to the number of the film-forming stations ST and the kinds of metal and reactive gases is formed.

[0133] If different kinds of metal and reactive gases are used in all film-forming stations ST that are adjacent to each other, a multilayer film has the number of layers equivalent to the number of the film-forming stations ST. If the same kinds of metal and reactive gases are used in the film-forming stations ST that are adjacent to each other, these adjacent film-forming stations ST all together form one layer of a film.

EXAMPLES

[0134] The present invention is explained below in greater detail through Examples.

Test Example 1

[0135] In the present Test Example, a radical source **80** was disposed in such a way that the surface plane of a dielectric plate **83** was in parallel with a substrate **43** as well as targets **63***a* and *b*. In Examples 1 to 4, a distance D between the substrate **43**, and the targets **63***a* and *b* in a film-forming statins ST was respectively set to 40 mm, 70 mm, 200 mm, and 400 mm for forming a film. Then, film deposition rates and obtained films were compared among those Examples.

[0136] In the present Test example, a sputtering apparatus **1** having a single film-forming station ST was used to form a single layer film of silicon oxide on a large-sized glass substrate having a size of 600 cm×400 cm by the method of forming a thin film according to the embodiment described above.

[0137] In the film-forming station ST**1**, a silicon target was used as the targets **63***a* and *b*, and an argon gas was supplied at 800 sccm from a gas cylinder **65** as a sputtering gas. As a reactive gas, oxygen (O_2) gas was introduced at 80 sccm and converted to a radical by a radical source **80**.

[0138] Other specific conditions and results are shown in Table 1.

TABLE 1

	Distance D (mm)	Angle of radical source (deg.)	Target LF Power (kW)	Radical source RF Power (kW)	Film deposition rate (nm · m/min)	Index of refraction @550 nm	Absorption coefficient
Example 1	40	0	7.0	4.5	85.8	1.48	5.8×10^{-3}
Example 2	70	0	7.0	4.5	70.9	1.48	4.6×10^{-4}
Example 3	200	0	7.0	3	63.4	1.48	1.8×10^{-4}
Example 4	400	0	7.0	2.5	26.1	1.47	1.7×10^{-4}

[0139] Based on the results in Table 1, it was found that when the distance D was 40 mm, absorption coefficient of a formed film ended up being high over 10^{-3}. This may be because if the distance D is too short, the film deposition rate becomes too high for a reaction to keep up and the absorption occurs.

[0140] As optical thin film requires the absorption coefficient in a range of 10^{-4} to obtain a sufficient transmittance, it was found that the distance D needed to be longer than 40 mm.

Test Example 2

[0141] In the present Test Example, the distance D between the substrate **43**, and the targets **63***a* and *b* in the film-forming statins ST was set to 200 mm, and the radical source **80** was disposed in such a way that the surface plane of the dielectric plate **83** was inclined toward the targets **63***a* and *b* side at an angle of 0°, 30°, and 60° to the substrate **43** to form a film in Examples 3, 5, and 6, respectively. Then, film deposition rates and obtained films were compared among those Examples.

[0142] Specific conditions and results are shown in Table 2. Other conditions of the present Test Example were the same as those in the Test Example 1.

TABLE 2

	Distance D (mm)	Angle of radical source (deg.)	Target LF Power (kW)	Radical source RF Power (kW)	Film deposition rate (nm* m/min)	Index of refraction @550 nm	Absorption coefficient
Example 3	200	0	7.0	3	63.4	1.48	1.8×10^{-4}
Example 5	200	30	8.0	3	70.9	1.48	1.7×10^{-4}
Example 6	200	60	8.0	3	67.1	1.48	3.0×10^{-4}

[0143] The results in Table 2 showed that the film deposition rate was higher in the case where the surface plane of the dielectric plate **83** was inclined at an angle of 30° and 60° to the substrate **43** than the case where the surface plane was not inclined. Therefore, it was found that if the radical source was inclined toward the targets **63***a* and *b* side, the reactivity came to improve while the absorption coefficient was kept to an appropriate level, thus making it possible to increase a target power and further improve the film deposition rate.

Test Example 3

[0144] In the present Test Example, a film was formed in a sputtering apparatus **1** having a single film-forming station ST. Film deposition rates and obtained films were compared between the case where one radical source **80** was provided and the case where a pair of radical sources **80** were provided on both the upstream and downstream sides of the targets **63***a* and *b* to interpose them.

[0145] Specific conditions and results are shown in Table 3. Other conditions of the present Test Example were the same as those in the Test Example 1.

TABLE 3

	Distance D (mm)	Angle of radical source (deg.)	Target LF Power (kW)	Radical source RF Power (kW)	Film deposition rate (nm* m/min)	Index of refraction @550 nm	Absorption coefficient
Example 5	200	30	8.0	3	70.9	1.48	1.7×10^{-4}
Example 7	200	30	9.0	3 × 2	78.3	1.48	1.7×10^{-4}

[0146] The results in Table 3 showed that the film deposition rate was higher by around 10 percent in the case where the pair of radical sources **80** were provided than the case where one radical source **80** was provided, while the absorption coefficient values were substantially the same between them. Therefore it was found that if the pair of radical sources **80** were provided, the reactivity came to improve while the absorption coefficient was kept to an appropriate level, thus making it possible to increase a target power and further improve the film deposition rate.

Test Example 4

[0147] In the present Test Example, a multilayer AR film was formed using the sputtering apparatus **1** according to the embodiment described above to compare film-forming conditions and obtained films between Example 8, where each layer is formed by a single station ST and Example 9, where each layer is formed by a plurality of stations ST.

[0148] In Examples 8 and 9, the multilayer AR film was designed as follows: a first layer is Si_3N_4 having physical film thickness of 123.9 nm, a second layer is SiO_2 having physical film thickness of 164.3 nm, a third layer is Si_3N_4 having physical film thickness of 99.5 nm, and a fourth layer is SiO_2 having physical film thickness of 73.2 nm.

[0149] In Example 8, a sputtering apparatus **1** having four film-forming stations ST was used, and in each film-forming station ST**1** to ST**4**, a silicon target was used as targets **63***a* and *b*, and an argon gas was supplied at 800 sccm from a gas cylinder **65** as a sputtering gas. Further, as a reactive gas, nitrogen gas (N_2) at 140 sccm was introduced in the film-forming stations S**1** and S**3**, and oxygen (O_2) gas at 60 sccm was introduced, and these gases were converted to radicals by a radical source **80**. The film-forming stations ST**1-4** respectively formed Si_3N_4, SiO_2, Si_3N_4, and SiO_2 films.

[0150] Additionally, a substrate conveying speed was set to 4.4 mm/s, the distance D to 200 mm, and the angle between the dielectric plate **83** and the substrate **43** to 30°.

[0151] Other specific conditions and results of Example 8 are shown in Table 4.

TABLE 4

	Film composition	Physical film thickness (nm)	Target LF Power (kW)	Radical source RF Power (kW)	Radical source gas species	Radical source gas flow rate (sccm)
ST1	Si_3N_4	123.9	13.0	3	N_2	140
ST2	SiO_2	164.3	5.6	3	O_2	60
ST3	Si_3N_4	99.5	10.4	3	N_2	140
ST4	SiO_2	73.2	2.5	3	O_2	40

[0152] In Example 9, a sputtering apparatus **1** having seven film-forming stations ST was used. In the film-forming stations ST**1**-**6**, each pair of adjacent film-forming stations ST formed a film having the same composition, so that all together three layers, Si_3N_4, SiO_2, and Si_3N_4, were formed, while in the film-forming station ST**7**, a SiO_2 film was formed on the top of the stack by the single film-forming station ST. Film thickness of each four layer in an obtained film was designed to be equal to the corresponding each four layer in Example 8.

[0153] Additionally, the substrate conveying speed was set to 8.7 mm/s, the distance D to 200 mm, and the angle between the dielectric plate **83** and the substrate **43** to 30°.

[0154] Other specific conditions and results of Example 9 are shown in Table 5.

TABLE 5

	Film composition	Physical film thickness (nm)	Target LF Power (kW)	Radical source RF Power (kW)	Radical source gas species	Radical source gas flow rate (sccm)
ST1	Si_3N_4	62.0	13.0	3	N_2	140
ST2	Si_3N_4	62.0	13.0	3	N_2	140
ST3	SiO_2	82.2	5.6	3	O_2	60
ST4	SiO_2	82.2	5.6	3	O_2	60
ST5	Si_3N_4	49.8	10.4	3	N_2	120
ST6	Si_3N_4	49.8	10.4	3	N_2	120
ST7	SiO_2	73.2	5.0	3	O_2	60

[0155] In Test Example 4, it was found that the film thickness of each layer is approximately the same between Example 9, where the plurality of film-forming stations ST were used to form one layer of the film, and Example 8, where the single film-forming station ST was used to form one layer of the film. Further, the substrate conveying speed in Example 9 was approximately twice as fast as that in Example 8, however, since the first three layers were formed by two film-forming stations ST in Example 9, the total time required for forming a film per one substrate **43** was the same between Example 9 and Example 8.

[0156] However, the substrate conveying speed in Example 9 is faster than that in Example 8, and there are more film-forming stations ST in the sputtering apparatus **1** in Example 9, thus when the substrates **43** are continuously conveyed into the sputtering apparatus **1** in an in-line manner, the maximum number of the substrates **43** residing in the sputtering apparatus **1** becomes higher and the productivity is improved.

[0157] FIG. **6** is a graph showing a comparison of reflectance values at the different wavelengths between a multilayer AR film formed in Example 9 and a multilayer AR film in design, where a first layer is Si_3N_4 having the physical film thickness of 123.9 nm, a second layer is SiO_2 having the physical film thickness of 164.3 nm, a third layer is Si_3N_4 having the physical film thickness of 99.5 nm, and a fourth layer is SiO_2 having the physical film thickness of 73.2 nm.

[0158] As shown in FIG. **6**, it was found that the multilayer AR film formed in Example 9 had optical properties close to those in a film design.

Test Example 5

[0159] In the present Test Example, the conditions used were the same as those in Test Example 3 except for an oxygen gas flow rate. A target voltage was measured when the oxygen gas flow rate was at 0, 60, 70, 80, 90, 110, 120, 130, 150, and 200 sccm in a situation where the oxygen gas flow rate was increased from 0 sccm to 200 sccm, and a situation where the oxygen gas flow rate was decreased from 200 sccm to 0 sccm to confirm if the target voltage exhibited variable paths over oxygen partial pressures in the above situations, i.e. if so-called a hysteresis phenomenon occurs.

[0160] Table 6 shows data on the oxygen gas flow rate, the oxygen partial pressure, and the target voltage on oxygen increase and decrease, while FIG. **7** shows a graph depicting a relation between the oxygen partial pressure and the target voltage on oxygen increase and decrease.

TABLE 6

O_2 gas flow rate (sccm)	O_2 gas partial pressure (%)	Target voltage on oxygen increase (V)	Target voltage on oxygen decrease (V)
0	0.0	762	767
60	7.0	767	773
70	8.0	772	777
80	9.1	767	770
90	10.1	750	735
110	12.1	411	404
120	13.0	386	378
130	14.0	369	366
150	15.8	357	356
200	20.0	349	349

[0161] FIG. **7** showed that the target voltage exhibited substantially the same variable paths over the oxygen partial pressures whether the oxygen flow rate is increased or decreased, and it was found that the hysteresis phenomenon seen during a reactive sputtering didn't occur.

[0162] Therefore, it was found that unlike the reactive sputtering, it was easy to control the film deposition rate by adjusting the oxygen flow rate in sputtering using the sputtering apparatus **1** of the present Example by the method according to the embodiment described above.

REFERENCE NUMERALS

[0163] A film-forming effective area A
[0164] D distance
[0165] ST, ST**1**-*n* film-forming station
[0166] **1** sputtering apparatus
[0167] **11** load lock chamber
[0168] **12**, **13**, **32**, **33** gate valve
[0169] **14**, **34** rotary pump
[0170] **21** film deposition chamber
[0171] **22** space part for loading
[0172] **23** space part for unloading
[0173] **31** unloading chamber
[0174] **43** substrate

[0175] **61** target mechanism
[0176] **62***a*, **62***b* magnetron sputter electrode
[0177] **63***a*, **63***b* target
[0178] **64** AC power supply
[0179] **65**, **76** gas cylinder
[0180] **66**, **77** mass flow controller
[0181] **75**, **95***a*, **95***b* pipe
[0182] **80** radical source
[0183] **80**A antenna storage chamber
[0184] **81** case body
[0185] **83** dielectric plate
[0186] **84** fixed frame
[0187] **85***a*, **85***b* antenna
[0188] **86***a*, **86***b* conductive wire
[0189] **87** matching box
[0190] **87***a*, **87***b* variable capacitor
[0191] **88** fixture
[0192] **88***a*, **88***b* fixing plate
[0193] **88***c*, **88***d* fixing bolt
[0194] **89** high frequency power source
[0195] **95** vacuum pump

1. A thin film formation apparatus for forming a thin film of a metal compound on a substrate in a vacuum chamber by sputtering, the apparatus comprising:
a target, provided in the vacuum chamber, composed of metal or a conductive metal compound, and
an active species source, provided in the vacuum chamber, for generating an active species of a reactive gas that is arranged to produce mutual electromagnetic and pressure interactions with the target,
wherein:
the active species source comprises
a gas source for supplying the reactive gas, and
an energy source for supplying energy into the vacuum chamber to excite the reactive gas to a plasma state;
the target that is arranged to be opposed to the substrate;
the energy source comprises between itself and the vacuum chamber a dielectric window for supplying the energy into the vacuum chamber; and
the dielectric window is arranged in parallel with the substrate, or in such a way as inclining towards the target side at an angle of less than 90° to the substrate.

2. The thin film formation apparatus according to claim **1**, wherein:
a substrate conveyance section for conveying the substrate is provided within the vacuum chamber; and
the active species source is provided on at least one of upstream and downstream sides of the target in a substrate conveyance direction.

3. The thin film formation apparatus according to claim **1**, wherein the energy source is a plasma source for generating plasma by inductive coupling and surface wave through the dielectric window.

4. The thin film formation apparatus according to claim **1**, wherein the active species source is an inductive coupling type plasma (ICP) radical source.

5. The thin film formation apparatus according to claim **2**, further comprising an in-line type sputtering apparatus having a plurality of film-forming stations each comprising the target and the active species source disposed on at least one of the upstream and downstream sides of the target in the substrate conveyance direction.

6. The thin film formation apparatus according to claim **5**, wherein the film-forming stations each comprises:
a detection unit for optically detecting a film deposition rate; and
a control unit for controlling the film deposition rate in each film-forming station accordingly by receiving a signal from the corresponding film deposition rate detection unit.

7. The thin film formation apparatus according to claim **1**, further comprising:
a sputtering section for sputtering the target and by the sputtering, dispersing a particle that is not a complete compound from the target to a substrate in the vacuum chamber; and
a composition conversion section for converting the particle to a complete metal compound by contacting the particle with an active species of a reactive gas generated by the active species source in the vacuum chamber, thereby being capable of forming a thin film composed of the complete metal compound on the substrate.

8. A sputtering cathode for forming a thin film of a metal compound on a substrate by sputtering, comprising:
a target composed of metal or a conductive metal compound; and
an active species source for generating an active species of a reactive gas that is arranged to produce mutual electromagnetic and pressure interactions with the target,
wherein
the active species source comprises
a gas source for supplying the reactive gas, and
an energy source for supplying energy into a vacuum chamber to excite the reactive gas to a plasma state,
the target that is arranged to be opposed to the substrate,
the energy source comprising a dielectric window for supplying the energy to an outside of the energy source,
the dielectric window being arranged in parallel with the substrate, or in such a way as inclining towards a target side at an angle of less than 90° to the substrate.

9. The sputtering cathode according to claim **8**,
wherein the target and the active species source are disposed side by side in a same space of a vacuum chamber in such a way that a sputtering face of the target where erosion occurs and the active species source are arranged to be opposed to the substrate, and the active species source are disposed on at least one of upstream and downstream sides of the target in a substrate conveyance direction.

10. A method of forming a thin film comprising:
a sputtering step for sputtering a target composed of metal or a conductive metal compound, the target being arranged to be opposed to a substrate, and by the sputtering, dispersing a particle that is not a complete compound from the target to the substrate in a vacuum chamber; and
a composition conversion step for converting the particle to a complete metal compound in the vacuum chamber by providing a dielectric window for supplying the energy into the vacuum chamber that is arranged in parallel with the substrate, or in such a way as including towards the target side at an angle of less than 90° to the substrate, and by contacting the particle with an active species of a reactive gas generated by an active species source for generating the active species of the reactive gas that is arranged to produce mutual electromagnetic and pres-

sure interactions with the target, thereby forming a thin film composed of the complete metal compound on the substrate.

11. The method of forming a thin film according to claim **10**, further comprising, after the composition conversion step, a film formation repetitive step where the sputtering step and the composition conversion step are repeated in parallel a plurality of times.

12. The method of forming a thin film according to claim **10**, further comprising:

before the sputtering step, a step of introducing the substrate into an in-line type thin film formation apparatus having a plurality of film-forming stations each including the target and the active species source disposed on at least one of the upstream and downstream sides of the target in a substrate conveyance direction;

an in-station film formation step, where the sputtering step, the composition conversion step, and the film formation repetitive step are carried out in the film-forming stations while the substrate is conveyed at a constant speed;

a conveyance step for conveying the substrate to the film-forming stations on the downstream side in a substrate conveyance direction;

a multiple-station film formation step, where the in-station film formation step and the conveyance step are repeated; and

a discharge step for discharging the substrate to the atmosphere after the in-station film formation step is completed in the film-forming station on a most downstream side in the substrate conveyance direction.

13. The thin film formation apparatus according to claim **1**, wherein the dielectric window is arranged in such a way as inclining towards the target side at an angle of more than or equal to 30° to the substrate which is arranged to be opposed to the energy source in a direction perpendicular to a forwarding direction of the substrate.

14. The thin film formation apparatus according to claim **1**, wherein:

a substrate conveyance section for conveying the substrate is provided within the vacuum chamber; and

the active species source is provided on upstream and downstream sides of the target in a substrate conveyance direction.

15. The thin film formation apparatus according to claim **1**, further comprising:

a mass flow controller for introducing the sputtering gas, and a mass flow controller for introducing the reactive gas, which are independently installed;

a detection unit for optically detecting a film deposition rate; and

a control unit that receives a signal from the detection unit, and independently controls at least a power of the sputtering, the mass flow controller for introducing the sputtering gas, a power of the active species source and the mass flow controller for introducing the reactive gas, thereby controlling the film deposition rate.

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