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(54) **THIN FILM FORMATION DEVICE AND SEMICONDUCTOR FILM MANUFACTURING METHOD**
DÜNNFILMBILDUNGSEINRICHTUNG UND HALBLEITERFILMHERSTELLUNGSVERFAHREN
DISPOSITIF DE FORMATION DE FILM MINCE ET PROCEDE DE FABRICATION DE FILM DE SEMI-CONDUCTEUR

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- **N. LAYADI; P. R. CABARROCAS; B. DREVILLON; I. SOLOMON: "Real-time spectroscopic ellipsometry study of the growth of amorphous and microcrystalline silicon thin films prepared by alternating silicon deposition and hydrogen plasma treatment", PHYS. REV. B, vol. 52, 1995, pages 5136-5143, XP000542706,**

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Description

TECHNICAL FIELD

[0001] The present invention relates to a thin film forming apparatus for forming a semiconductor film, such as a microcrystalline silicon thin film used for a silicon thin film solar cell, and a method of manufacturing a semiconductor film.

BACKGROUND ART

[0002] An intrinsic (i-type) microcrystalline silicon thin film has been widely used as a photoelectric conversion layer of a silicon thin film solar cell. As a method of manufacturing a microcrystalline silicon thin film, it is general to perform deposition on a substrate by a plasma-enhanced chemical vapor deposition (CVD) method using a mixed gas of silane (SiH_4) and hydrogen (H_2).

[0003] In general, a film forming method called a "highpressure depletion method" has been widely used to deposit the microcrystalline silicon thin film through the plasma CVD method (for example, see Patent Document 1). Specifically, in a high pressure atmosphere, a SiH_4 gas flow rate [SiH_4] is sufficiently reduced (that is, a H_2 gas flow rate [H_2] is sufficiently increased), the flow rate ratio of SiH_4 "[SiH_4]/([SiH_4]+[H_2])" is reduced to about 1% to 5%, and SiH_4 in plasma is depleted. In this way, it is possible to deposit the microcrystalline silicon thin film (conversely, when the flow rate ratio of SiH_4 is high, an amorphous film is deposited). The microcrystalline silicon thin film thus obtained by this method is applied to a photoelectric conversion layer of a solar cell to manufacture a solar cell sample, and the solar cell sample is evaluated. As a result, practical characteristics, such as a photoelectric conversion efficiency of up to about 9%, are obtained.

[0004] As another method of forming the microcrystalline silicon thin film, a film forming method called a layer-by-layer method has been known (for example, see Non-patent Literature 1). In the layer-by-layer method, a plasma CVD apparatus is used to alternately repeat a process of generating SiH_4 plasma in the range of 10 s to 100 s and a process of generating H_2 plasma in the range of 100 s to 600 s plural times to thereby deposit a silicon thin film. Then, the thin film, which is an amorphous state when it is deposited, is continuously exposed to H_2 plasma such that it is crystallized.

[0005] In recent years, a large substrate with a size of 1 m x 1 m or more has been used in order to put a silicon thin film solar cell to practical use and manufacture a solar cell with high productivity and at a low cost. In the formation of the microcrystalline silicon thin film, not only the deposition rate and the quality of a film, but also a large-scale uniform film forming technique for uniformly forming a thin film on a large meter (m)-size substrate become important.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006] Patent Document 1: Japanese Patent Application No. 2001-237187

[0007] Documents WO 2008/052706 A1 (DOW CORNING [US]; ECOLE POLYTECH [FR]; ROCA I CABARROCAS PERE [FR]; BU) 8 May 2008 (2008-05-08), and US 5 956 602 A (ISHIHARA SHUNICHI [JP]) 21 September 1999 (1999-09-21) are pieces of prior art relevant to the present invention.

NON-PATENT LITERATURES

[0008] Non-patent Literature 1: N. Layadi, P. R. Cabarrocas, B. Drevillon, I. Solomon, "Real-time spectroscopic ellipsometry study of the growth of amorphous and microcrystalline silicon thin films prepared by alternating silicon deposition and hydrogen plasma treatment," Phys. Rev. B, vol. 52, pp. 5136-5143 (1995)

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0009] Since the i-type microcrystalline silicon thin film has a relatively low light absorption, it is necessary to increase the thickness of the film to at least 2 μm or more. In the method of depositing the microcrystalline silicon thin film using the plasma CVD method disclosed in Patent Document 1, the flow ratio of SiH_4, that is, "[SiH_4]/([SiH_4]+[H_2])" is adjusted to control crystallinity. Therefore, there is a trade-off relationship between the crystallinity and the deposition rate of the film. That is, in the case of an amorphous film, a high deposition rate is easily obtained. However, when the flow ratio of SiH_4 is reduced for crystallization, there is a problem in that the deposition rate is significantly reduced to about 1 nm/s. For example, a process time of 40 minutes or more is required to deposit a microcrystalline silicon thin film with a thickness of 2.5 μm.

[0010] In the method of forming the microcrystalline silicon thin film using the layer-by-layer method disclosed in Non-patent Literature 1, when switching between a SiH_4 gas used at the time of generating SiH_4 plasma and a H_2 gas used at the time of generating H_2 plasma, the exhaust time is required to exhaust the amount of gas remaining in the supply pipe, thus the net deposition rate is reduced. Non-patent Literature 1 discloses a deposition rate of 0.03 nm/s to 0.06 nm/s as the deposition rate of the microcrystalline silicon thin film in the layer-by-layer method. As such, since the deposition rate is low, it is difficult to improve the throughput of a process of manufacturing a solar cell including a microcrystalline silicon thin film and thus to reduce a manufacturing cost.

[0011] In the method of forming the microcrystalline silicon thin film disclosed in Patent Document 1 or Non-patent Document 1, a technique for uniformly forming a microcrystalline silicon thin film on a large substrate with a size of, for example, 1.4 m x 1.1 m is not considered.

[0012] The invention has been made in order to solve the above-mentioned problems and an object of the invention is to provide an apparatus for forming a thin film and a method of manufacturing a semiconductor film capable of improving the deposition rate while maintaining crystallinity when a semiconductor film, such as a microcrystalline silicon thin film, is deposited.

[0013] In addition, an object of the invention is to provide an apparatus for forming a thin film and a method of manufacturing a semiconductor film capable of uniformly depositing a semiconductor film, such as a microcrystalline silicon thin film, at a high speed, on a large meter-size substrate that is necessary to improve the productivity of a thin film solar cell or reduce manufacturing costs.

MEANS FOR SOLVING PROBLEM

[0014] To achieve the above object, an apparatus for forming a thin film according to the invention includes: a vacuum chamber including a substrate holding unit that holds a substrate and a plasma electrode that is provided so as to face the substrate; a first gas supply unit that continuously supplies a gas containing hydrogen as a main component to the vacuum chamber during deposition; a second gas supply unit that opens or closes a valve to turn on or off the supply of a material gas containing at least one of silicon and germanium to the vacuum chamber during deposition; a high-frequency power source that applies a high frequency voltage to the plasma electrode; a shield box that is connected to a ground so as to surround the plasma electrode outside the vacuum chamber; and a control unit that controls opening or closing of the valve such that the material gas is periodically supplied to the vacuum chamber, and modulates an amplitude of high frequency power supplied to the plasma electrode in synchronization with the opening or closing of the valve, wherein the valve is provided in the shield box.

EFFECT OF THE INVENTION

[0015] According to the invention, when mixed plasma of SiH_4 and H_2 is used to deposit a microcrystalline silicon thin film on a substrate, it is possible to perform modulation on time of the supply of a SiH_4 gas or time of the supply of high frequency power at a high speed. Therefore, it is possible to form a microcrystalline silicon thin film even under the conditions of a high SiH_4 flow ratio where only an amorphous silicon film is obtained by the method according to the related art. As a result, it is possible to improve the throughput of a process of manufacturing a solar cell using a microcrystalline silicon thin film as a photoelectric conversion layer.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

FIG. 1 is a diagram schematically illustrating an example of a structure of a thin film forming apparatus according to a first embodiment of the invention.

FIG. 2 is a diagram illustrating a variation in the flow rates of a H_2 gas and a SiH_4 gas and in the high frequency power of a high-frequency power source over time when a thin film is formed.

FIG. 3 is a diagram illustrating an example of a relationship between a valve opening/closing signal and a variation in SiH emission intensity in a vacuum chamber over time.

FIG. 4 is a diagram schematically illustrating an example of a structure of a thin film forming apparatus according to a second embodiment of the invention.

BEST MODE(S) FOR CARRYING OUT THE INVENTION

[0017] Hereinafter, a thin film forming apparatus and a method of manufacturing a semiconductor film according to exemplary embodiments of the invention will be described in detail with reference to the accompanying drawings. However, the invention is not limited to the embodiments.

First embodiment

[0018] FIG. 1 is a diagram schematically illustrating an example of a structure of a thin film forming apparatus according to a first embodiment of the invention. The thin film forming apparatus is based on a plasma CVD apparatus according to the related art, and includes a substrate stage 12 and a plasma electrode 13 in a vacuum chamber 10 that contains an atmosphere for forming a thin film inside thereof. The plasma electrode 13 and a surface of the substrate stage 12 facing the plasma electrode 13 are arranged in parallel to each other. A gas exhaust pipe 11 is provided in the vacuum chamber 10, and gas in the vacuum chamber 10 is exhausted by a vacuum pump (not shown) connected to the gas exhaust pipe 11 such that the inside of the vacuum chamber 10 is set to a predetermined degree of vacuum.

[0019] The substrate stage 12 is electrically connected to the ground and a substrate 100, which is to be subjected to a deposition process, is mounted on the substrate stage 12. A heater is provided in the substrate stage 12 and a substrate temperature is set to a predetermined value, for example, about 150°C to 250°C during the deposition process. The substrate stage 12 is provided at a lower part of the vacuum chamber 10. The substrate stage 12 corresponds to a substrate holding unit in the claims.

[0020] The plasma electrode 13 includes a cylindrical side portion 131, an upper surface portion 133, which is one end of a cylindrical structure, and the bottom which is opposite to the upper surface portion 133. A gas shower head 132 having a plurality of through holes formed therein is provided in the bottom. In addition, the plasma electrode 13 is fixed in the vacuum chamber 10 such that the gas shower head 132 is parallel to a substrate mounting surface of the substrate stage 12 and is spaced at a predetermined distance from the substrate mounting surface of the substrate stage 12. In this embodiment, the plasma electrode 13 is fixed to the vacuum chamber 10 such that the cylindrical side portion 131 or the upper surface portion 133 is electrically insulated from the vacuum chamber 10 by insulating spacers 14 made of, for example, alumina or Teflon (registered trademark).

[0021] The cylindrical upper surface portion 133 of the plasma electrode 13 is electrically connected to a high-frequency power source 40 via a shield box 20 that is provided so as to correspond to the position of the plasma electrode 13 and an impedance matching box (not shown). In this way, a high frequency voltage is applied to the plasma electrode 13. In general, the oscillating frequency of the high-frequency power source 40 is 13.56 MHz or 27.12 MHz. However, in some cases, a frequency in the range of 30 MHz to 150 MHz, that is, a VHF (Very High Frequency) band is used in order to increase the density of plasma and increase the deposition rate. As such, since a high frequency voltage is applied to the plasma electrode 13, the shield box 20 is connected to the ground at the outside of the vacuum chamber 10 so as to surround the plasma electrode 13, in order to prevent the radiation or leakage of a high frequency.

[0022] A H_2 gas supply port 22a for supplying a H_2 gas and a SiH_4 gas supply port 22b for supplying a SiH_4 gas are separately provided in the upper surface portion 133 of the plasma electrode 13, and are connected to a H_2 gas supply pipe 21a for supplying the H_2 gas and a SiH_4 gas supply pipe 21b for supplying the SiH_4 gas, respectively. When plasma is generated, a high frequency voltage and a DC self-bias voltage are simultaneously applied to the upper surface portion 133 of the plasma electrode 13. Therefore, when the gas supply pipes 21a and 21b are made of metal (for example, SUS), the plasma electrode 13 and the gas supply pipes 21a and 21b are electrically insulated from each other. Therefore, gas supply ports that form a gas flow path in an insulator block made of, for example, alumina or Teflon (registered trademark) are used as the gas supply port 22a or 22b. An air-driven-type or electromagnetic gas valve 23a that turns on or off the flow of a H_2 gas from a H_2 gas supply portion (not shown) for supplying the H_2 gas, and a mass flow controller 24a that controls the flow rate of the H_2 gas are provided on the H_2 gas supply pipe 21a. The gas valve 23a is arranged outside the shield box 20.

[0023] An air-driven-type or electromagnetic gas valve 23b that turns on or off the flow of a SiH_4 gas from a SiH_4 gas supply portion (not shown) for supplying the SiH_4 gas, a mass flow controller 24b that controls the flow rate of the SiH_4 gas, and an air-driven-type gas valve 25 that turns on or off the supply of the SiH_4 gas to the vacuum chamber 10 during the formation of a thin film are provided on the SiH_4 gas supply pipe 21b. The gas valve 23b is arranged outside the shield box 20, and the air-driven-type gas valve 25 is arranged close to the SiH_4 gas supply port 22b in the shield box 20. The gas valve 25 is an air driven type, and an air supply pipe 30 that supplies compressed air to the gas valve 25 is provided. An electromagnetic gas valve 31 that turns on or off the supply of the compressed air is provided on the air supply pipe 30 outside the shield box 20.

[0024] When the gas valve 31 is opened or closed, the supply of the compressed air to the gas valve 25 is turned on or off. When the gas valve 31 is turned on to be an open state and the compressed air is supplied to the gas valve 25, the gas valve 25 is turned on (opened) and it is possible to supply the SiH_4 gas flowing through the SiH_4 gas supply pipe 21b into the vacuum chamber 10. When the gas valve 31 is turned off to be a close state and the supply of the compressed air to the gas valve 25 is cut off, the gas valve 25 is turned off (closed) and the supply of the SiH_4 gas flowing through the SiH_4 gas supply pipe 21b into the vacuum chamber 10 is cut off. As such, since the gas valve 25 is opened or closed by the compressed air, it may be possible to rapidly supply the SiH_4 gas into the vacuum chamber 10 or cut off the supply of the SiH_4 gas. In order to turn on or off the supply of the SiH_4 gas as rapidly as possible, it is apparent that the pipe distance between the gas valve 25 and the plasma electrode 13 is preferably as short as possible, for example, 10 cm, 5 cm, ... In addition, it is preferable that the response speed of the gas valve 25 be as quick as possible. For example, the response time, which is from the supply of the compressed air to the event that the gas valve 25 is switched from the closed state to opening state, is preferably equal to or less than 10 ms (milliseconds). In addition, the response time from a closed state to an opened state according to a valve opening/closing signal is preferably equal to or less than 30 ms and more preferably, equal to or less than 15 ms.

[0025] Since a high frequency voltage is applied to the plasma electrode 13 during the formation of a thin film, a high frequency is radiated in the shield box 20. Therefore, the high frequency voltage is also applied to a metal portion of the gas valve 25. However, since the gas valve 25 is an air driven type with no electromagnetic operation, it is possible to prevent an error in the operation of the gas valve 25 or a damage to the gas valve 25. In addition, the supply of the compressed air for driving the gas valve 25 is rapidly performed by the electromagnetic gas valve 31 that is provided outside the shield box 20.

[0026] In the first embodiment, the insulating gas supply port 22b is used to electrically insulate the gas valve 25 from the plasma electrode 13. However, the gas valve 25 is not necessarily insulated from the plasma electrode 13. For example, the air-driven-type gas valve 25 may be directly attached to the upper surface portion 133 of the plasma electrode 13. In this case, there is no problem in the opening/closing operation of the gas valve 25, and it is possible to rapidly turn on or off the supply of the SiH_4 gas into the vacuum chamber 10. However, in this case, it is necessary to provide, for example, an insulating pipe in the middle of the SiH_4 gas pipe 21b in order for electrical insulation.

[0027] In the first embodiment, the air-driven-type valve is given as a representative example of a gas valve that is mechanically opened or closed. However, the gas valve is not limited to the air driven type. For example, a piezoelectric valve that is electrically opened or closed may be used as long as it has a sufficient electromagnetic shielding property.

[0028] An optical window 15 that enables observation of the state of plasma is provided in the side surface of the vacuum chamber 10 at a position corresponding to a space (plasma generation space) between the substrate stage 12 and the plasma electrode 13 where plasma is generated. An emission intensity observing unit 50 for observing the emission intensity (for example, Si: 288 nm and SiH: 414 nm) of light from Si atoms or SiH molecules in the generated plasma is provided in the optical window 15. The emission intensity observing unit 50 includes an interference filter 51 that selects the emission of light from the Si atoms or the SiH molecules from the emission spectrum of the plasma, and a photomultiplier 52 that converts the light emitted from the Si atoms or the SiH molecules selected by the interference filter 51 into an electric signal. In this example, the interference filter 51 is used to select the emission of light from the Si atoms or the SiH molecules. However, a wavelength may be selected by, for example, a spectroscope. In addition, a photodetector (for example, a photodiode) other than the photomultiplier 52 may be used to detect light.

[0029] The thin film forming apparatus further includes a control unit 60 that controls the opening/closing of the gas valve 31 and the operation of the high-frequency power source 40. The control unit 60 supplies a valve opening/closing signal for turning on or off the introduction of the SiH_4 gas into the vacuum chamber 10 at a predetermined period to the gas valve 31. The control unit 60 also supplies a power modulation signal to the high-frequency power source 40 so as to modulate the amplitude of the output of high frequency power supplied to the plasma electrode 13 in synchronization with the tuning-on or turning-off of the supply the SiH_4.

[0030] An emission intensity signal indicating the emission intensity of light from the Si atoms or the SiH molecules observed by the emission intensity observing unit 50 is transmitted to the control unit 60. The control unit 60 calculates the delay time from the output of a valve opening signal toward the gas valve 31 to an actual increase in the light emission intensity of the Si atoms or the SiH molecules. The control unit 60 also calculates the delay time from the output of a valve closing signal toward the gas valve 31 to an actual reduction in the light emission intensity of the Si atoms or the SiH molecules. Thus, the control unit 60 outputs the valve opening/closing signals and the power modulation signal on the basis of the period for which the supply of the SiH_4 gas is turned on or off, which is determined considering the delay time.

[0031] Next, a method of forming a thin film in the thin film forming apparatus having the above-mentioned structure will be described. First, the substrate 100 is placed on the substrate stage 12 in the vacuum chamber 10, and the vacuum chamber 10 is evacuated through the gas exhaust pipe 11 such that the inside of the vacuum chamber 10 is set to a predetermined degree of vacuum. The heater of the substrate stage 12 heats the substrate 100 to a predetermined temperature. In this state, the gas valve 23a provided on the H_2 gas supply pipe 21a is opened to supply a H_2 gas from the H_2 gas supply port 22a to the vacuum chamber 10 at a predetermined flow rate. In this case, the H_2 gas flowing from the H_2 gas supply port 22a into the vacuum chamber 10 flows through the cylindrical plasma electrode 13 and is then supplied to the plasma generation space through the gas shower head 132 provided at a bottom part of the plasma electrode 13.

[0032] For a SiH_4 gas, the gas valve 23b provided on the SiH_4 gas supply pipe 21b is opened and then maintained continuously in the opening state, and the air-driven-type gas valve 25 in the shield box 20 is repeatedly opened and closed with a predetermined period so as to rapidly turn on and off the supply of the SiH_4 gas into the vacuum chamber 10. Specifically, when the valve opening signal is received from the control unit 60, first, the gas valve 31 is operated to be opened, and compressed air is supplied up to the gas valve 25. The gas valve 25 is opened by the action of air pressure and the SiH_4 gas is supplied into the vacuum chamber 10 (plasma generation space) through the gas shower head 132 of the plasma electrode 13. When the valve closing signal is received from the control unit 60, first, the gas valve 31 is operated to be closed and the supply of the compressed air to the gas valve 25 is cut off. When the compressed air is not supplied, the gas valve 25 is closed by the action of air pressure and the supply of the SiH_4 gas into the vacuum chamber 10 is cut off.

[0033] FIG. 2 is a diagram illustrating a variation in the flow rates of the H_2 gas and the SiH_4 gas and in the high frequency power of the high-frequency power source over time during the formation of a thin film. As shown in this figure, the H_2 gas is supplied into the vacuum chamber 10 at a constant flow rate regardless of the time, but the SiH_4 gas is supplied into the vacuum chamber 10 for a period T_{on}, but is not supplied into the vacuum chamber 10 for a period T_{off}. In addition, the high frequency power is applied at an output-level P_{on} to the plasma electrode 13 for the period T_{on}, that is, for the period for which the supply of the SiH_4 gas is on. The high frequency power is also applied at an output level P_{off} (> P_{on}) to the plasma electrode 13 for the period T_{off}, that is, for the period for which the supply of the SiH_4 gas is off.

[0034] The SiH_4 gas is easily dissociated by collision with electrons in plasma. When the density of electrons in plasma is too high, a large amount of SiH_2, SiH, and Si that collide with gas grains and generate particles is generated in addition to SiH_3, which is a precursor of a silicon thin film. This causes the generation of particles in a gas phase. As a result, a defective silicon film with a large number of defects is formed. Therefore, in order to selectively generate preferred SiH_3 molecules, it is effective to set the high frequency power to a low level to reduce plasma density when the supply of the SiH_4 gas is on. It has been known that the H_2 gas is a gaseous species that is less likely to be dissociated. This is because H atoms generated by electron-impact dissociation in plasma is easily recombined in a gas phase, on the wall of the vacuum chamber 10, or on the surface of the electrode and returns to H_2 molecules. Therefore, it is necessary to increase the density of electrons in plasma in order to increase the density of the H atoms in plasma.

[0035] As described above, it is possible to crystallize an amorphous silicon thin film by exposing the amorphous silicon thin film to H_2 plasma. In addition, it has been known that, as the density of H atoms in plasma increases, the time required for crystallization is reduced. Therefore, in order to rapidly crystallize an amorphous silicon film using H_2 plasma, it is necessary to increase the density of H atoms in plasma and the high frequency power for generating plasma may be as high as possible. At the time T_{off} (in FIG. 2, $T_1 < t < T_2$, $T_3 < t < T_4$, ...) when the supply of the SiH_4 gas is off and the surface of the film is crystallized by the H_2 plasma, the high frequency power is set to a high level ($P_{on} < P_{off}$). For this reason, while a thin film is formed, the flow rate of the SiH_4 gas and the output of the high frequency power are controlled as shown in FIG. 2.

[0036] For the period T_{on}, the SiH_4 gas and the H_2 gas are supplied into the vacuum chamber 10 and SiH_4/H_2 mixed plasma with low electron density including a large number of SiH_3 molecules is generated by the high frequency power P_{on}. An amorphous silicon thin film is formed on the surface of the substrate 100 on the substrate stage 12. Then, when the period T_{on} ends and the period T_{off} starts, only the H_2 gas is supplied into the vacuum chamber 10 and H_2 plasma with high electron density is generated by the high frequency power P_{off} (> P_{on}). The amorphous silicon thin film formed on the substrate 100 is crystallized in a short time.

[0037] As such, it is possible to perform switching between the generation of the SiH_4/H_2 mixed plasma with low electron density that is suitable for the deposition of silicon and the generation of the H_2 plasma with high electron density that is suitable for the crystallization of silicon at a high speed. Therefore, even under the deposition conditions (that is, at a high SiH_4 flow ratio) of the deposition method according to the related art where the deposition rate is high but an amorphous silicon film is formed, it is possible to form a microcrystalline silicon thin film by adjusting the period T_{on} (= $T_1 = T_3 - T_2 = ...$) for which the supply of the SiH_4 gas is on and the period T_{off} (= $T_2 - T_1 = T_4 - T_3 = ...$) for which the supply of the SiH_4 gas is off.

[0038] However, when the time for which the supply of the SiH_4 gas is on or off is relatively short, for example, when T_{on} is shorter than 1 s or T_{off} is shorter than 1 s, it is difficult to modulate the high frequency power in synchronization with the time. Therefore, it is desirable to correctly detect the time delay, which is from the output of the valve opening/closing signal from the control unit 60 toward the gas valve 31 to an actual increase/decrease in the amount of SiH_4 gas flowing into the vacuum chamber 10, and determine the timing at which the amplitude of the high frequency power is modulated, considering the time delay.

[0039] As shown in FIG. 1, the emission intensity observing unit 50 may monitor a variation in the emission intensity of light from the Si atoms or the SiH molecules originating in SiH_4 over time. FIG. 3 is a diagram illustrating an example of a relationship between the valve opening/closing signal and a variation in SiH emission intensity in the vacuum chamber over time. In the valve opening/closing signal, the valve opening timing is t=0, a SiH_4 gas flow rate is 100 sccm, a H_2 gas flow rate is 900 sccm, pressure is 500 Pa, the on time T_{on} of the SiH_4 gas is 100 ms, the off time T_{off} of the SiH_4 gas is 100 ms, and the high frequency power for generating plasma is constantly 300 W. The H_2 gas flow rate is preferably equal to or more than five times the SiH_4 gas flow rate, and more preferably, equal to or more than nine times the SiH_4 gas flow rate, as in this example. As such, since the H_2 gas is continuously supplied, a variation in pressure is small at the on time T_{on} of the SiH_4 gas and the off time T_{off} of the SiH_4 gas. Therefore, manufacturing of a film is stably performed.

[0040] After the valve opening signal is output from the control unit 60 at a time t=0, there is a time delay (= t_1), which is from the time t_1 when SiH emission intensity starts to increase to the actual inflow of the SiH_4 gas into plasma. On the other hand, after the valve closing signal is output from the control unit 60 at a time $t=t_2$, there is a time delay (= t_3-t_2), which is from the time t_3 when SiH emission intensity starts to decrease to the turning-off of the supply of the SiH_4 gas. In this example, the SiH_4 gas is supplied with a time delay of 20 ms or less from the output of the valve opening signal. On the other hand, the supply of the SiH_4 gas is cut off with a time delay of 40 ms or less from the output of the valve closing signal. As such, it is possible to accurately detect the time delay using the monitoring result of the emission intensity observing unit 50. When the on time T_{on} and the off time T_{off} of the SiH_4 gas are set to be shorter than the time delay, it is difficult to turn on or off the actual supply of the SiH_4 gas into the vacuum chamber 10. As a result, it is difficult to form a microcrystalline silicon thin film. Therefore, in the actual thin film forming process, power modulation timing may be determined on the basis of the time delay such that a microcrystalline silicon thin film can be formed. The time delay is calculated for each deposition condition in advance, and a time delay corresponding to the deposition conditions is used to determine the amplitude modulation time of the high frequency power during deposition.

[0041] After the microcrystalline silicon thin film with a predetermined thickness is formed in this way, the gas valve 23a provided on the H_2 gas supply pipe 21a and the gas valve 23b provided on the SiH_4 gas supply pipe 21b are closed, and the heater of the substrate stage 12 is turned off. The vacuum chamber 10 is sufficiently evacuated. Then, the internal pressure of the vacuum chamber 10 returns to atmospheric pressure, and the substrate 100 on the substrate stage 12 is carried out of the vacuum chamber 10. In this way, the thin film forming process ends.

[0042] Finally, the evaluation result of the thin film formed by the thin film forming method will be described. Here, a silicon thin film is formed under the following conditions: a SiH_4 gas flow rate is 100 sccm; a H_2 gas flow rate is 900 sccm (that is, the SiH_4 gas flow ratio = 10%); pressure is 500 Pa; the on time T_{on} of the SiH_4 gas is 100 ms; the off time T_{off} of the SiH_4 gas is 100 ms (that is, a frequency is 5 Hz and a duty ratio is 50%); when the supply of the SiH_4 gas is on, the high frequency power (frequency: 60 MHz) P_{on} for generating plasma is 100 W; when the supply of the SiH_4 gas is off, the high frequency power P_{off} is 500 W; the distance between the plasma electrode 13 and the substrate 100 is 10 mm; and the temperature of the substrate stage 12 is set to 200°C. In this case, the total deposition time for which the high frequency power is supplied is 5 minutes.

[0043] When the silicon thin film was formed under these conditions, a deposition rate of 8.1 nm/s was obtained, and it was possible to perform practical high-speed deposition. In addition, the peak intensity ratio I_c/I_a of the peak I_c of the crystalline silicon thin film at 520 cm^{-1} to the peak I_a of the amorphous silicon thin film at 480 cm^{-1} measured by Raman spectroscopy was 7.2. The peak intensity ratio I_c/I_a indicates the degree of crystallization in the silicon thin film. If the peak intensity ratio I_c/I_a is equal to or more than 5 and equal to or less than 10, the film has sufficient crystallization efficiency for use in a solar cell. Therefore, the microcrystalline silicon thin film formed by the thin film forming method according to the first embodiment has a property that enables the thin film to be used for a solar cell with high photoelectric conversion efficiency.

[0044] According to the first embodiment, while a film is formed by a plasma CVD method, the H_2 gas is supplied into the vacuum chamber 10 at a constant flow rate, the SiH_4 gas is supplied in a manner such that the supply of the SiH_4 gas is rapidly turned on or off with a predetermined period, and the high frequency power whose amplitude is modulated in synchronization with the turning-on or turing-off of the supply of the SiH_4 gas is supplied. Therefore, while the SiH_4 gas is supplied, an amorphous silicon thin film is formed on the substrate 100 at a high speed, and the amorphous silicon thin film is crystallized at a high speed during the period for which the SiH_4 gas is not supplied. This process may be repeatedly performed to form a high-quality microcrystalline silicon thin film at a high speed, as compared with the method of forming a microcrystalline silicon thin film according to the related art.

[0045] The deposition rate in the plasma CVD method according to the related art was about 1 nm/s or less, but the deposition rate in the thin film forming method according to the first embodiment was about 8.1 nm/s. Therefore, it is possible to improve the throughput of a process of manufacturing a photoelectric conversion device, such as a solar cell, using the microcrystalline silicon thin film as a photoelectric conversion layer. In addition, the time required to manufacture the microcrystalline silicon thin film according to the first embodiment is equal to or less than about one eighth of the time required to manufacture the microcrystalline silicon thin film according to the related art. Therefore, it is possible to reduce power required to form the microcrystalline silicon thin film and thus reduce power consumption.

[0046] In the thin film forming method according to the first embodiment, when a microcrystalline silicon film is formed on a relatively small substrate (for example, a substrate with a size of 10 cm x 10 cm), it is possible to form the microcrystalline silicon film with a uniform thickness in an error range of $\pm$10% in the plane of the substrate.

[0047] In the above-mentioned example, parameters, such as a gas flow rate, pressure, and power are fixed. However, the deposition conditions of the microcrystalline silicon film are not limited thereto. The on time T_{on} of the SiH_4 gas is 100 ms and the off time T_{off} thereof is 100 ms. However, the same experiment as described above was performed while changing T_{on} and T_{off}, and the result of the experiment proved that it was preferable to stop the supply of gas at the time when an atom to several silicon layers were formed on the substrate after the supply of the SiH_4 gas started. The detailed setting of the T_{on} or T_{off} time depends on the deposition rate. However, it is possible to obtain the same effect as that in the above-mentioned example under the conditions of a gas supply time in a wide range of 10 ms $\leq T_{on} \leq$ 1 s and an off time in a wide range of 10 ms $\leq T_{off} \leq$ 1 s when a film is formed at a high speed.

[0048] In the method of manufacturing the microcrystalline silicon film according to the first embodiment, H_2 is used as a crystallization acceleration gas and SiH_4 is used as a material gas. However, an inert gas, such as He, Ne, or Ar, may be added to the H_2 gas. For example, the gas preferably includes 50 vol% or more of H_2 as a main component, and more preferably, 80% or more of H_2. In addition, the material gas is not limited to SiH_4. The material gas may be gas including Si, for example, group-IV hydride, such as Si_2H_6, and a dopant gas whose representative examples are diborane (B_2H_6), phosphine (PH_3), and arsine (AsH_3) may be added to the material gas.

[0049] When a microcrystalline silicon germanium (Si_xGe_{1-x}) film other than the microcrystalline silicon film is formed, the same effect as described above is obtained, and it is possible to form the film at a high speed while maintaining high crystallinity. In this case, a mixed gas of SiH_4 and GeH_4 may be used as the material gas. In addition, the emission intensity observing unit 50 may observe light emitted from Si or SiH, or Ge or GeH in plasma.

Second embodiment

[0050] In the thin film forming apparatus and the thin film forming method according to the first embodiment, when the microcrystalline silicon thin film is formed on the substrate 100 with a relatively small size (for example, a substrate with a size of 10 cm x 10 cm), as shown in FIG. 1, it is possible to form a film with a uniform thickness (the uniformity of the thickness of the film in the plane of the substrate is within ±10%) using one air-driven-type gas valve 25 that turns on or off the supply of the SiH_4 gas into the vacuum chamber 10. In addition, it is possible to form a film at a SiH_4 gas flow rate of 100 sccm and a deposition rate of 8.1 nm/s.

[0051] However, when a film is formed on a large substrate with a size of, for example, 1.4 m x 1.1 m by the apparatus having the above-mentioned structure, the uniformity of the thickness of the film in the plane of the substrate or the crystallinity of the film deteriorates up to ±40%. It is considered that this is because the microcrystalline silicon thin film is thick in the vicinity of the center of the plane, at which the gas valve 25 which supplies the SiH_4 gas is positioned, but the thickness of the microcrystalline silicon thin film significantly decreases toward the periphery of the substrate, which causes spatial nonuniformity in the supply of the SiH_4 gas into the plasma generation space between the plasma electrode 13 and the substrate stage 12.

[0052] In the second embodiment, a thin film forming apparatus and a thin film forming method capable of uniformly forming a microcrystalline silicon thin film on a large meter-size substrate at a high speed will be described.

[0053] FIG. 4 is a diagram schematically illustrating a structure of the vicinity of a SiH_4 gas supply portion of the thin film forming apparatus according to the second embodiment of the invention. The second embodiment is different from the first embodiment in a method of supplying the SiH_4 gas to the plasma electrode 13. Therefore, FIG. 4 shows only the method of supplying the SiH_4 gas. In addition, a H_2 gas supply and introducing portion, such as the H_2 gas supply pipe 21a, a high-frequency power generating and supply portion, such as the high frequency power source 40, and the emission intensity observing unit 50 have the same structure as those in the first embodiment, and thus illustration and description thereof will not be repeated.

[0054] For supplying a H_2 gas and a SiH_4 gas, one H_2 gas supply port (not shown) and a plurality of (in the second embodiment, four) SiH_4 gas supply ports 22b, which are suited to the size of a substrate on which a thin film is formed, are separately provided on an upper surface portion 133 of a plasma electrode 13. SiH_4 gas supply pipes 21b that supply the SiH_4 gas are connected to the SiH_4 gas supply ports 22b, and a mass flow controller 24b that controls the flow rate of the SiH_4 gas from a SiH_4 gas supply portion (not shown) for supplying the SiH_4 gas, and an air-driven-type or electromagnetic gas valve 23b that turns on or off the flow of the SiH_4 are provided on the SiH_4 gas supply pipe 21b outside a shield box 20.

[0055] Inside the shield box 20, the SiH_4 gas supply pipes 21b are connected to a gas storage tank 70 capable of storing a predetermined amount of SiH_4 gas, and respective four SiH_4 gas supply pipes 21b branched off from the gas storage tank 70 are connected to the SiH_4 gas supply ports 22b via air-driven-type gas valves 25a to 25d that turn on or off the supply of the SiH_4 gas to the plasma electrode 13. The gas storage tank 70 has a space capable of storing at least some amount of SiH_4 gas supplied each time the gas valves 25a to 25d are changed from an on state to an off state. In addition, the lengths of the SiH_4 gas supply pipes 21b between the gas storage tank 70 and the gas valves 25a to 25d, which turn on or off the supply of the SiH_4 gas to the plasma electrode 13, are equal to each other. The gas valves 25a to 25d that turn on or off the supply of the SiH_4 gas are directly connected to the SiH_4 gas supply ports 22b in order to maximize the switching speed between the supply of the SiH_4 gas and the cutting-off of the supply of the SiH_4 gas. In addition, the four SiH_4 gas supply ports 22b are regularly arranged in the plane of the plasma electrode 13.

[0056] The gas valves 25a to 25d are an air driven type, and four air supply pipes 30 for supplying compressed air to the gas valves 25a to 25d are provided. Electromagnetic gas valves 31a to 31d that turn on or off the supply of the compressed air are provided to the air supply pipes 30 outside the shield box 20.

[0057] The control unit 60 adjusts the timing of valve opening/closing signals supplied to the gas valves 31a to 31d such that the amounts of SiH_4 gas supplied to the plasma electrode 13 through the SiH_4 gas supply pipes 21b are increased or decreased at the same ratio after the gas valves 25a to 25d of the SiH_4 gas supply pipes 21b are turned on or off. As such, the timing of the valve opening/closing signal is adjusted to reduce a variation in the amount of SiH_4 gas supplied from each of the SiH_4 gas supply pipes 21b over time, thereby reducing nonuniformity in an in-plane distribution during deposition. In addition, the control unit 60 modulates the amplitude of the high frequency power applied to the plasma electrode 13 in synchronization with an increase or decrease in the amount of SiH_4 gas supplied into the vacuum chamber 10.

[0058] Next, a method of supplying the SiH_4 gas in the thin film forming apparatus will be described. When the SiH_4 gas is supplied, the gas valve 23b provided on the SiH_4 gas supply pipe 21b is opened and then maintained in an opened state, and the four gas valves 25a to 25d in the shield box 20 are repeatedly opened and closed with a predetermined period to turn on and off the supply of the SiH_4 gas into the vacuum chamber 10 at a high speed. Specifically, when a signal is received from the control unit 60, first, the gas valves 31a to 31d on the air supply pipes 30 are opened or closed to turn on or off the supply of the compressed air to the gas valves 25a to 25d, respectively.

[0059] For example, when a valve opening signal is output from the control unit 60 and the gas valves 31a to 31d are turned on (opened), the compressed air is supplied to the gas valves 25a to 25d that turn on or off the supply of the SiH_4 gas, and the gas valves 25a to 25d are turned on (opened). Then, the SiH_4 gas stored in the gas storage tank 70 is supplied to the plasma electrode 13 through the SiH_4 gas supply pipes 21b and the SiH_4 gas supply ports 22b, and is then supplied to a plasma generation space through the gas shower head 132. The times from the turning-on of the gas valves 25a to 25d to the arrival of the SiH_4 gas to the gas supply ports 22b are generally different from each other since there is a difference in response speed or operation speed between the gas valves 25a to 25d. Therefore, the control unit 60 makes the transmission timings of the valve opening signals to the gas valves 31a to 31d different from each other such that the SiH_4 gas is simultaneously supplied to all of the SiH_4 gas supply ports 22b.

[0060] On the other hand, when a valve closing signal is output from the control unit 60 and the gas valves 31a to 31d on the gas supply pipes 30 are turned off (closed), the supply of the compressed air to the gas valves 25a to 25d that turn on or off the supply of the SiH_4 gas is cut off and the gas valves 25a to 25d are turned off (closed) by the action of the air pressure. Then, the supply of the SiH_4 gas from the gas storage tank 70 to the plasma electrode 13 through the SiH_4 gas supply pipes 21b is cut off. In this case, the times from the turning-off of the gas valves 25a to 25d to a reduction in the amount of SiH_4 gas from the SiH_4 gas supply ports 22b are generally different from each other since there is a difference in response speed or operation speed between the gas valves 25a to 25d. Therefore, the control unit 60 makes the transmission timings of the valve opening signals to the gas valves 31a to 31d different from each other such that the amount of SiH_4 gas is simultaneously reduced in all of the SiH_4 gas supply ports 22b.

[0061] As such, in the second embodiment, the SiH_4 gas is supplied to the large shower head 132 through a plurality of SiH_4 gas supply pipes 21b and a plurality of gas valves 25a to 25d. Therefore, even when a large shower head 132 is used to form a large meter-size substrate, it is possible to uniformly supply the SiH_4 gas to the plasma generation space.

[0062] In the second embodiment, since the gas storage tank 70 is provided in the middle of the SiH_4 gas supply pipes 21b, it is possible to store a large amount of SiH_4 gas in the gas storage tank 70 during the period for which the gas valves 25a to 25d are turned off. Therefore, it is possible to supply a large amount of SiH_4 gas to the shower head 132 after the gas valves 25a to 25d are turned on. Even when a film is formed on a large meter-size substrate at a high speed, that is, even when a large amount of SiH_4 gas is supplied, it is possible to repeat a process of supplying a large amount of SiH_4 gas since the gas storage tank 70 is provided.

[0063] However, when the time required to turn on or off the supply of the SiH_4 gas is relatively short, for example, when T_{on} is shorter than 1 s or T_{off} is shorter than 1 s, it is difficult to make the supply timing of the SiH_4 gas equal to each other at a plurality of different points. Therefore, in the second embodiment (when there are four gas supply points), it is preferable to correctly detect a variation in the time delay, which is from the simultaneous output of the valve opening/closing signals from the control unit 60 to the gas valves 31a to 31d to an actual increase/decrease in the amount of SiH_4 gas flowing from the gas valves 25a to 25d into the vacuum chamber 10 after the gas valves 25a to 25d on the SiH_4 gas supply pipe 21b are turned on or off. Furthermore, it is preferable to determine the timing of turning on or off the gas valves 31a to 31d for the compressed air, considering the variation in the delay time.

[0064] As shown in FIG. 1, the emission intensity observing unit 50 monitors a variation in the emission intensity of light from the Si atoms or the SiH molecules originating in SiH_4 over time. Next, the monitoring method will be described.

[0065] For example, a H_2 gas is supplied into the vacuum chamber 10 at a predetermined constant flow rate and pressure is controlled to be a predetermined value. Then, high frequency power is supplied to at a predetermined level to generate H_2 plasma. In this state, the control unit 60 outputs the valve opening signal to turn on the gas valve 31a for the compressed air and turn on only the gas valve 25a of the SiH_4 gas supply pipe 21b. Immediately after the SiH_4 gas flows into the H_2 plasma, light is emitted from the Si atoms or the SiH molecules. Therefore, the time difference from when the valve opening signal is output to when the emission intensity of Si or SiH increases is measured and recorded. In addition, the time difference from when the valve closing signal is output from the control unit 60 to when the emission intensity of Si or SiH in the plasma increases is measured and recorded.

[0066] Then, the control unit 60 generates a valve opening signal (or a valve closing signal) for compressed air to turn on (or off) the gas valve 31b for compressed air, and measures and records the time difference from when the gas valve 25b of the SiH_4 gas supply pipe 21b is turned on (or off) to when the emission intensity of Si or SiH increases (or decreases). As such, the time differences are measured and recorded for all of the gas valves 25a to 25d provided in the SiH_4 gas supply pipes 21b by the same method as described above. Then, a variation in the time difference is corrected, and the control unit 60 outputs the valve opening/closing signals to the gas valves 31a to 31d for compressed air such that the SiH_4 gas is supplied to the plasma (or the supply of the SiH_4 gas is cut off) at the same timing. In addition, the control unit 60 performs control such that the SiH_4 gas introduced from the SiH_4 gas supply pipes 21b into the vacuum chamber 10 increases or decreases at the same timing. Therefore, the control unit 60 can modulate the amplitude of the high frequency power applied to the plasma electrode 13 in synchronization with the increase or decrease in the amount of SiH_4 gas flowing into the vacuum chamber 10.

[0067] Finally, an example of the evaluation of a microcrystalline silicon thin film formed on a large glass substrate with a size of 1.4 m x 1.1 m by the above-mentioned method will be described. Here, a silicon thin film is formed under the following conditions: a SiH_4 gas flow rate is 5 slm; a H_2 gas flow rate is 95 slm (that is, SiH_4 gas flow ratio = 5%); pressure is 1000 Pa; the on time T_{on} of the SiH_4 gas is 20 ms; the off time T_{off} of the SiH_4 gas is 80 ms (that is, a frequency is 10 Hz and a duty ratio is 20%); when the supply of the SiH_4 gas is on, the high frequency power (frequency: 27.12 MHz) P_{on} for generating plasma is 1 kW; when the supply of the SiH_4 gas is off, the high frequency power P_{off} is 30 kW; the distance between the plasma electrode 13 and the substrate is 5 mm; and the temperature of the substrate stage 12 is set to 200°C. In this case, the total deposition time for which the high frequency power is supplied is 5 minutes.

[0068] When deposition of the silicon thin film was performed under these conditions, a deposition rate of 4.2 nm/s was obtained, and uniformity in the plane of the substrate with a size of 1.4 m x 1.1 m was ±8%. Therefore, it was possible to practically form a film with a uniform thickness on a large meter-size substrate at a high speed. In addition, a crystallization ratio calculated by Raman spectroscopy, that is, the peak intensity ratio I_c/I_a of the peak I_c of the crystalline silicon thin film at 520 cm^{-1} to the peak I_a of the amorphous silicon thin film at 480 cm^{-1} was in the range of from 7.9 to 8.3 at a plurality of points in the plane of the substrate. Therefore, it was possible to uniformly form a microcrystalline silicon thin film having a property that enables the film to be used for a solar cell.

[0069] According to the second embodiment, a plurality of SiH_4 gas supply ports 22b for supplying the SiH_4 gas to the shower head is equally provided in the plane of the plasma electrode 13, and the gas storage tank 70 which stores the SiH_4 gas is provided between the SiH_4 gas supply ports 22b and the SiH_4 gas supply portion. In addition, the gas storage tank 70 is connected to the SiH_4 gas supply ports 22b by the SiH_4 gas supply pipes 21a, and the air-driven-type gas valves 25a to 25d are provided on the SiH_4 gas supply pipes 21a at the same distance from the gas storage tank 70. The control unit 60 outputs signals for controlling the turning-on or turning-off of the gas valves 25a to 25d according to a variation in the time delay from the turning-on or turning-off of the gas valves 25a to 25d to an actual increase or decrease in the amount of SiH_4 gas flowing into the vacuum chamber 10. In this way, it is possible to form a microcrystalline silicon film with a uniform thickness on the surface of a large meter-size substrate at a high speed even under the conditions of a high SiH_4 flow rate where only an amorphous silicon thin film is obtained by the method according to the related art. As a result, it is possible to further improve productivity in manufacturing of a solar cell using the microcrystalline silicon thin film as a photoelectric conversion layer or reduce manufacturing costs.

INDUSTRIAL APPLICABILITY

[0070] As described above, the thin film forming method according to the invention is useful to manufacture a solar cell using a microcrystalline silicon thin film as a photoelectric conversion layer. In addition, the thin film forming method according to the invention is useful to manufacture a solar cell using a microcrystalline silicon thin film formed using a large meter-size substrate.

EXPLANATIONS OF LETTERS OR NUMERALS

[0071]

10	Vacuum chamber
11	Gas exhaust pipe
12	Substrate stage
13	Plasma electrode
14	Insulating spacer

15	Optical window
20	Shield box
21a, 21b	Gas supply pipe
22a, 22b	Gas supply port
23a, 23b, 25a to 25d, 31a to 31d	Gas valve
24a, 24b	Mass flow controller
30	Air supply pipe
40	High frequency power source
50	Emission intensity observing unit
51	Interference filter
52	Photomultiplier
60	Control unit
70	Gas storage tank
100	Substrate
131	Side surface portion
132	Gas shower head
133	Upper surface portion

Claims

1. An apparatus for forming a thin film, comprising:

a vacuum chamber (10) including a substrate holding unit (12) that is adapted to hold a substrate (100) and a plasma electrode (13) that is provided so as to face the substrate (100);
a first gas supply unit (21a, 22a, 23a, 24a) that is adapted to continuously supply a gas containing hydrogen as a main component to the vacuum chamber (10) during deposition;
a second gas supply unit (21b, 22b, 23b, 24b) that is adapted to open or close a valve (25; 25a, 25b, 25c, 25d) to turn on or off the supply of a material gas containing at least one of silicon and germanium to the vacuum chamber (10) during deposition;
a high-frequency power source (40) that is adapted to apply a high frequency voltage to the plasma electrode (13); and
a control unit (60) that is adapted to control opening or closing of the valve (25; 25a, 25b, 25c, 25d) such that the material gas is periodically supplied to the vacuum chamber (10), and to modulate an amplitude of high frequency power supplied to the plasma electrode (13) in synchronization with the opening or closing of the valve (25; 25a, 25b, 25c, 25d),
characterized in that
a shield box (20) is provided and is connected to a ground so as to surround the plasma electrode (13) outside the vacuum chamber (10); and
wherein the valve (25; 25a, 25b, 25c, 25d) is provided in the shield box (20).

2. The apparatus for forming a thin film according to claim 1, wherein the valve (25; 25a, 25b, 25c, 25d) is an air valve that is opened or closed by compressed air.

3. The apparatus for forming a thin film according to claim 1, wherein the control unit (60) is adapted to control the high frequency power such that the high frequency power when the supply of the material gas is turned on is lower than the high frequency power when the supply of the material gas is turned off.

4. The apparatus for forming a thin film according to claim 1, further comprising:

an emission intensity observing unit (50) that is adapted to observe light emitted from Si or SiH, or Ge or GeH in plasma generated in a space between the substrate holding unit (12) and the plasma electrode (13),
wherein the control unit (60) is adapted to calculate a deviation of on/off timing of actual supply of the material gas into the vacuum chamber (10) from an instruction of the control unit (60) to open or close the valve (25; 25a, 25b, 25c, 25d) from an observation result of the emission intensity observing unit (50), and to control the valve (25) and the high frequency power source (40) on the basis of a period of the opening and closing of the valve (25; 25a, 25b, 25c, 25d), which is set considering the deviation.

5. The apparatus for forming a thin film according to claim 1, wherein the control unit (60) is adapted to set a time required to open the valve (25; 25a, 25b, 25c, 25d) to be equal to or more than 10 ms and equal to or less than 1 s.

6. The apparatus for forming a thin film according to claim 1, wherein the second gas supply unit includes:

a plurality of material gas supply pipes (21b) that is connected to a plurality of points of the vacuum chamber (10); and
a plurality of the valves (25a, 25b, 25c, 25d) that is provided in the material gas supply pipes (21b), respectively.

7. The apparatus for forming a thin film according to claim 6, wherein the second gas supply unit (21b, 22b, 23b, 24b) further includes a gas storage tank (70) that is adapted to store the material gas from a material gas supply source, the material gas supply pipes (21b) are connected between the gas storage tank (70) and the vacuum chamber (10), and
the valves (25a, 25b; 25c, 25d) are provided on the material gas supply pipes (21b) between the gas storage tank (70) and the vacuum chamber (10).

8. The apparatus for forming a thin film according to claim 6, further comprising:

an emission intensity observing unit (50) that is adapted to observe light emitted from Si or SiH, or Ge or GeH in plasma generated in a space between the substrate holding unit (12) and the plasma electrode (13),
wherein the control unit (60) is adapted to acquire a response time from the opening or closing of the valve (25a, 25b, 25c, 25d) provided on each of the material gas supply pipes (21b) to turning-on or turning-off of the supply of the material gas for each material gas supply pipe based on an observation result of the emission intensity observing unit (50), and
controls opening and closing timing of the pluralityof valves (25a, 25b, 25c, 25d) such that a difference between the response times of the material gas supply pipes (21b) is corrected.

9. A method of manufacturing a semiconductor film in a thin film forming apparatus including the vacuum chamber (10) having the plasma electrode (13) and a shield box (20) that is connected to a ground so as to surround the plasma electrode (13) outside the vacuum chamber (10); and shower head, comprising:

a substrate holding step of holding a substrate (100) so as to face the plasma electrode (13) and the shower head in the vacuum chamber (10) a microcrystalline semiconductor film forming step of intermittently supplying a material gas containing at least one of silicon and germanium while continuously supplying a gas containing hydrogen as a main component to the vacuum chamber (10), and applying different, non-zero, levels of high frequency power to the plasma electrode (13) during a period for which the material gas is supplied and during a period for which the material gas is not supplied in order to generate plasma in a plasma generation space between the plasma electrode (13) and the substrate (100), thereby forming a microcrystalline semiconductor film,
wherein, the microcrystalline semiconductor film forming step, further includes a step of periodically opening or closing a valve (25; 25a, 25b, 25c, 25d) provided in the shield box (20) to supply the material gas from a the shower head (132).

10. The method of manufacturing a semiconductor film according to claim 9, wherein, in the microcrystalline semiconductor film forming step, a time required to intermittently supply the material gas to the plasma generation space is equal to or more than 10 ms and equal to or less than 1 s.

11. The method of manufacturing a semiconductor film according to claim 9, further comprising:

a deviation detecting step of calculating a deviation between output timing of an instruction to open or close the valve (25; 25a, 25b, 25c, 25d) and on or off timing of the supply of the material gas to the plasma generation space, before the microcrystalline semiconductor film forming step,
wherein, in the microcrystalline semiconductor film forming step, a time difference is set between intensity modulation timing of the high frequency power supplied to the plasma electrode (13) and the output timing of the instruction to open or close the valve (25; 25a, 25b, 25c, 25d) on the basis of the deviation.

12. The method of manufacturing a semiconductor film according to claim 11, wherein a plurality of material gas supply paths (21b) is connected to the vacuum chamber (10) via valves (25a, 25b, 25c, 25d) in the shield box (20), and

in the microcrystalline semiconductor film forming step, opening or closing timing of the valve (25a, 25b, 25c, 25d) in each of the material gas supply paths (21b) is individually adjusted with respect to intensity modulation timing of the high frequency power supplied to the plasma electrode (13), on the basis of the deviation of each of the material gas supply paths (21b) calculated in the deviation detecting step.

Patentansprüche

1. Vorrichtung zum Ausbilden eines Dünnfilms, Folgendes umfassend:

   eine Vakuumkammer (10), die eine Substrathalterungseinheit (12) aufweist, die dazu angepasst ist, ein Substrat (100) und eine Plasmaelektrode (13) zu haltern, die dem Substrat (100) zugewandt vorgesehen ist;
   eine erste Gaszufuhreinheit (21a, 22a, 23a, 24a), die dazu angepasst ist, kontinuierlich ein Gas, das Wasserstoff als Hauptbestandteil enthält, der Vakuumkammer (10) während einer Abscheidung zuzuführen;
   eine zweite Gaszufuhreinheit (21b, 22b, 23b, 24b), die dazu angepasst ist, ein Ventil (25; 25a, 25b, 25c, 25d) zu öffnen oder zu schließen, um die Zufuhr eines Materialgases, das Silicium und/oder Germanium enthält, zur Vakuumkammer (10) während einer Abscheidung ein- oder auszuschalten;
   eine Hochfrequenzenergiequelle (40), die dazu angepasst ist, eine Hochfrequenzspannung an die Plasmaelektrode (13) anzulegen; und
   eine Steuereinheit (60), die dazu angepasst ist, ein Öffnen oder Schließen des Ventils (25; 25a, 25b, 25c, 25d) so zu steuern, dass das Materialgas der Vakuumkammer (10) periodisch zugeführt wird, und eine Amplitude der der Plasmaelektrode (13) zugeführten Hochfrequenzenergie synchron mit dem Öffnen oder Schließen des Ventils (25; 25a, 25b, 25c, 25d) zu modulieren,
   dadurch gekennzeichnet, dass
   ein Abschirmkasten (20) vorgesehen und mit einer Masse verbunden ist, so dass die Plasmaelektrode (13) außerhalb der Vakuumkammer (10) umgeben ist; und
   wobei das Ventil (25; 25a, 25b, 25c, 25d) im Abschirmkasten (20) vorgesehen ist.

2. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 1, wobei es sich bei dem Ventil (25; 25a, 25b, 25c, 25d) um ein Luftventil handelt, das durch Druckluft geöffnet oder geschlossen wird.

3. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 1, wobei die Steuereinheit (60) dazu angepasst ist, die Hochfrequenzenergie so zu steuern, dass die Hochfrequenzenergie, wenn die Zufuhr des Materialgases eingeschaltet ist, niedriger ist als die Hochfrequenzenergie, wenn die Zufuhr des Materialgases ausgeschaltet ist.

4. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 1, darüber hinaus umfassend:

   eine Emissionsstärkenbeobachtungseinheit (50), die dazu angepasst ist, Licht zu beobachten, das ausgehend von Si oder SiH oder Ge oder GeH in Plasma emittiert wird, das in einem Raum zwischen der Substrathalterungseinheit (12) und der Plasmaelektrode (13) entsteht,
   wobei die Steuereinheit (60) dazu angepasst ist, eine Abweichung eines Ein-/Ausschaltzeitpunkts einer tatsächlichen Zufuhr des Materialgases in die Vakuumkammer (10) ausgehend von einer Instruktion der Steuereinheit (60) zu berechnen, das Ventil (25; 25a, 25b, 25c, 25d) ausgehend von einem Beobachtungsergebnis der Emissionsstärkenbeobachtungseinheit (50) zu öffnen oder zu schließen, und das Ventil (25) und die Hochfrequenzenergiequelle (40) auf Grundlage einer Zeitdauer des Öffnens und Schließens des Ventils (25; 25a, 25b, 25c, 25d) zu steuern, die unter Berücksichtigung der Abweichung eingestellt ist.

5. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 1, wobei die Steuereinheit (60) dazu angepasst ist, eine Zeit, die zum Öffnen des Ventils (25; 25a, 25b, 25c, 25d) erforderlich ist, auf gleich oder mehr als 10 ms oder weniger als 1 s einzustellen.

6. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 1, wobei die zweite Gaszufuhreinheit umfasst:

   mehrere Materialgaszufuhrrohre (21b), die an mehrere Stellen der Vakuumkammer (10) angeschlossen sind; und
   mehrere Ventile (25a, 25b, 25c, 25d), die jeweils in den Materialgaszufuhrrohren (21b) vorgesehen sind.

7. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 6, wobei die zweite Gaszufuhreinheit (21b, 22b, 23b,

24b) darüber hinaus einen Gasspeicherbehälter (70) umfasst, der dazu angepasst, das Materialgas aus einer Materialgaszufuhrquelle zu speichern,
die Materialgaszufuhrrohe (21b) zwischen dem Gasspeicherbehälter (70) und der Vakuumkammer (10) angeschlossen sind, und
die Ventile (25a, 25b, 25c, 25d) an den Materialgaszufuhrrohren (21b) zwischen dem Gasspeicherbehälter (70) und der Vakuumkammer (10) vorgesehen sind.

8. Vorrichtung zum Ausbilden eines Dünnfilms nach Anspruch 6, darüber hinaus umfassend:

eine Emissionsstärkenbeobachtungseinheit (50), die dazu angepasst ist, Licht zu beobachten, das ausgehend von Si oder SiH oder Ge oder GeH in Plasma emittiert wird, das in einem Raum zwischen der Substrathalterungseinheit (12) und der Plasmaelektrode (13) entsteht,
wobei die Steuereinheit (60) dazu angepasst ist, eine Ansprechzeit ausgehend vom Öffnen oder Schließen des Ventils (25a, 25b, 25c, 25d) zu erfassen, das an jedem der Materialgaszufuhrrohre (21b) vorgesehen ist, um die Zufuhr des Materialgases für jedes Materialgaszufuhrrohr auf Grundlage eines Beobachtungsergebnisses der Emissionsstärkenbeobachtungseinheit (50) ein- oder auszuschalten, und
einen Öffnungs- und Schließzeitpunkt der mehreren Ventile (25a, 25b, 25c, 25d) so steuert, dass eine Differenz zwischen den Ansprechzeiten der Materialgaszufuhrrohre (21b) korrigiert wird.

9. Verfahren zum Herstellen einer Halbleiterschicht in einer Dünnfilmausbildungsvorrichtung, die die Vakuumkammer (10) mit der Plasmaelektrode (13) und einem Abschirmkasten (2), der die Plasmaelektrode (13) außerhalb der Vakuumkammer (10) umgebend an Masse angeschlossen ist; und einen Sprühkopf aufweist, Folgendes umfassend:

einen Substrathalterungsschritt, um ein Substrat (100) der Plasmaelektrode (13) und dem Sprühkopf in der Vakuumkammer (10) zugewandt zu haltern, einen Ausbildungsschritt für eine mikrokristalline Halbleiterschicht, um ein Materialgas, das Silicium und/oder Germanium enthält, intermittierend zuzuführen, während ein Gas, das Wasserstoff als Hauptbestandteil enthält, der Vakuumkammer (10) kontinuierlich zugeführt wird, und um verschiedene, nicht Null betragende Hochfrequenzenergiepegel an die Plasmaelektrode (13) während eines Zeitraums, über den das Materialgas zugeführt wird, und während eines Zeitraums anzulegen, über den das Materialgas nicht zugeführt wird, um Plasma in einem Plasmaentstehungsraum zwischen der Plasmaelektrode (13) und dem Substrat (100) entstehen zu lassen, wodurch eine mikrokristalline Halbleiterschicht ausgebildet wird,
wobei der Ausbildungsschritt für eine mikrokristalline Halbleiterschicht darüber hinaus einen Schritt umfasst, ein im Abschirmkasten (20) vorgesehenes Ventil (25; 25a, 25b, 25c, 25d) periodisch zu öffnen oder zu schließen, um das Materialgas aus dem Sprühkopf (132) zuzuführen.

10. Verfahren zum Herstellen einer Halbleiterschicht nach Anspruch 9, wobei im Ausbildungsschritt für eine mikrokristalline Halbleiterschicht eine Zeit, die erforderlich ist, um das Materialgas dem Plasmaentstehungsraum intermittierend zuzuführen, gleich oder mehr als 10 ms oder gleich oder weniger als 1 s ist.

11. Verfahren zum Herstellen einer Halbleiterschicht nach Anspruch 9, darüber hinaus umfassend:

einen Abweichungserfassungsschritt zum Berechnen einer Abweichung zwischen einem Ausgabezeitpunkt einer Instruktion, das Ventil (25; 25a, 25b, 25c, 25d) zu öffnen oder zu schließen, und einem Ein- oder Ausschaltzeitpunkt der Zufuhr das Materialgases zum Plasmaentstehungsraum vor dem Ausbildungsschritt für eine mikrokristalline Halbleiterschicht,
wobei im Ausbildungsschritt für eine mikrokristalline Halbleiterschicht eine Zeitdifferenz zwischen einem Stärkenmodulationszeitpunkt der Hochfrequenzenergie, die der Plasmaelektrode (13) zugeführt wird, und dem Ausgabezeitpunkt der Instruktion, das Ventil (25; 25a, 25b, 25c, 25d) zu öffnen oder zu schließen, auf Grundlage der Abweichung eingestellt wird.

12. Verfahren zum Herstellen einer Halbleiterschicht nach Anspruch 11, wobei mehrere Materialgaszufuhrwege (21b) über Ventile (25a, 25b, 25c, 25d) im Abschirmkasten (20) an die Vakuumkammer (10) angeschlossen sind, und
im Ausbildungsschritt für eine mikrokristalline Halbleiterschicht ein Öffnungs- oder Schließzeitpunkt des Ventils (25a, 25b, 25c, 25d) in jedem der Materialgaszufuhrwege (21b) einzeln im Hinblick auf einen Stärkenmodulationszeitpunkt der Hochfrequenzenergie, die der Plasmaelektrode (13) zugeführt wird, auf Grundlage der im Abweichungserfassungsschritt berechneten Abweichung jedes der Materialgaszufuhrwege (21b) eingestellt wird.

Revendications

1. Appareil destiné à former un film mince, comprenant :

   une chambre à vide (10) incluant une unité de maintien de substrat (12) qui est apte à maintenir un substrat (100) et une électrode à plasma (13) qui est disposée de façon à faire face au substrat (100) ;
   une première unité de fourniture de gaz (21a, 22a, 23a, 24a) qui est apte à fournir continuellement un gaz contenant de l'hydrogène en tant que composant principal à la chambre à vide (10) pendant le dépôt ;
   une deuxième unité de fourniture de gaz (21b, 22b, 23b, 24b) qui est apte à ouvrir ou fermer une vanne (25 ; 25a, 25b, 25c, 25d) pour brancher ou couper la fourniture d'un gaz de matériau contenant au moins l'un du silicium et du germanium à la chambre à vide (10) pendant le dépôt ;
   une source de puissance haute fréquence (40) qui est apte à appliquer une tension haute fréquence à l'électrode à plasma (13) ; et
   une unité de commande (60) qui est apte à commander l'ouverture ou la fermeture de la vanne (25 ; 25a, 25b, 25c, 25d) de telle sorte que le gaz de matériau soit périodiquement fourni à la chambre à vide (10), et à moduler une amplitude de puissance haute fréquence fournie à l'électrode à plasma (13) en synchronisation avec l'ouverture ou la fermeture de la vanne (25 ; 25a, 25b, 25c, 25d),
   caractérisé en ce que
   un boîtier de protection (20) est disposé et est connecté à une terre de façon à entourer l'électrode à plasma (13) à l'extérieur de la chambre à vide (10) ; et sachant que la vanne (25 ; 25a, 25b, 25c, 25d) est disposée dans le boîtier de protection (20).

2. L'appareil destiné à former un film mince selon la revendication 1, dans lequel la vanne (25 ; 25a, 25b, 25c, 25d) est une vanne à air qui s'ouvre ou se ferme par air comprimé.

3. L'appareil destiné à former un film mince selon la revendication 1, dans lequel l'unité de commande (60) est apte à commander la puissance haute fréquence de telle sorte que la puissance haute fréquence, lorsque la fourniture du gaz de matériau est branchée, soit inférieure à la puissance haute fréquence lorsque la fourniture du gaz de matériau est coupée.

4. L'appareil destiné à former un film mince selon la revendication 1, comprenant en outre :

   une unité d'observation d'intensité d'émission (50) qui est apte à observer de la lumière émise à partir de Si ou SiH, ou Ge ou GeH dans du plasma généré dans un espace entre l'unité de maintien de substrat (12) et l'électrode à plasma (13),
   sachant que l'unité de commande (60) est apte à calculer un écart de temporisation de branchement/coupure de fourniture effective du gaz de matériau dans la chambre à vide (10) à partir d'une instruction de l'unité de commande (60) pour ouvrir ou fermer la vanne (25 ; 25a, 25b, 25c, 25d) à partir d'un résultat d'observation de l'unité d'observation d'intensité d'émission (50), et à commander la vanne (25) et la source de puissance haute fréquence (40) en fonction d'une période de l'ouverture et de la fermeture de la vanne (25 ; 25a, 25b, 25c, 25d), qui est définie compte tenu de l'écart.

5. L'appareil destiné à former un film mince selon la revendication 1, dans lequel l'unité de commande (60) est apte à définir un temps nécessaire pour ouvrir la vanne (25 ; 25a, 25b, 25c, 25d) pour qu'il soit égal ou supérieur à 10 ms et égal ou inférieur à 1 s.

6. L'appareil destiné à former un film mince selon la revendication 1, dans lequel la deuxième unité de fourniture de gaz inclut :

   une pluralité de tuyaux de fourniture de gaz de matériau (21b) qui est connectée à une pluralité de points de la chambre à vide (10) ; et
   une pluralité des vannes (25a, 25b, 25c, 25d) qui est disposée dans les tuyaux de fourniture de gaz de matériau (21b), respectivement.

7. L'appareil destiné à former un film mince selon la revendication 6, dans lequel la deuxième unité de fourniture de gaz (21b, 22b, 23b, 24b) inclut en outre un réservoir de stockage de gaz (70) qui est apte à stocker le gaz de matériau à partir d'une source de fourniture de gaz de matériau,
   les tuyaux de fourniture de gaz de matériau (21b) sont connectés entre le réservoir de stockage de gaz (70) et la

chambre à vide (10), et
les vannes (25a, 25b, 25c, 25d) sont disposées sur les tuyaux de fourniture de gaz de matériau (21b) entre le réservoir de stockage de gaz (70) et la chambre à vide (10).

8. L'appareil destiné à former un film mince selon la revendication 6, comprenant en outre :

une unité d'observation d'intensité d'émission (50) qui est apte à observer de la lumière émise à partir de Si ou SiH, ou Ge ou GeH dans du plasma généré dans un espace entre l'unité de maintien de substrat (12) et l'électrode à plasma (13),
sachant que l'unité de commande (60) est apte à acquérir un temps de réponse depuis l'ouverture ou la fermeture de la vanne (25a, 25b, 25c, 25d) disposée sur chacun des tuyaux de fourniture de gaz de matériau (21b) pour brancher ou couper la fourniture du gaz de matériau pour chaque tuyau de fourniture de gaz de matériau en fonction d'un résultat d'observation de l'unité d'observation d'intensité d'émission (50), et
commande une temporalité d'ouverture et de fermeture de la pluralité de vannes (25a, 25b, 25c, 25d) de telle sorte qu'une différence entre les temps de réponse des tuyaux de fourniture de gaz de matériau (21b) soit corrigée.

9. Procédé de fabrication d'un film semiconducteur dans un appareil de formation de film mince incluant la chambre à vide (10) comportant l'électrode à plasma (13) et un boîtier de protection (20) qui est connecté à une terre de façon à entourer l'électrode à plasma (13) à l'extérieur de la chambre à vide (10) ; et une tête de pulvérisation, comprenant :

une étape de maintien de substrat consistant à maintenir un substrat (100) de façon à faire face à l'électrode à plasma (13) et à la tête de pulvérisation dans la chambre à vide (10), une étape de formation de film semiconducteur microcristallin consistant à fournir par intermittence un gaz de matériau contenant au moins l'un du silicium et du germanium tout en fournissant continuellement un gaz contenant de l'hydrogène en tant que composant principal à la chambre à vide (10), et en appliquant différents niveaux, non égaux à zéro, de puissance haute fréquence à l'électrode à plasma (13) pendant une période pendant laquelle le gaz de matériau est fourni et pendant une période pendant laquelle le gaz de matériau n'est pas fourni afin de générer du plasma dans un espace de génération de plasma entre l'électrode à plasma (13) et le substrat (100), formant de la sorte un film semiconducteur microcristallin,
sachant que l'étape de formation de film semiconducteur microcristallin comprend en outre une étape consistant à ouvrir ou fermer périodiquement une vanne (25 ; 25a, 25b, 25c, 25d) disposée dans le boîtier de protection (20) pour fournir le gaz de matériau depuis la tête de pulvérisation (132).

10. Le procédé de fabrication d'un film semiconducteur selon la revendication 9, dans lequel, dans l'étape de formation de film semiconducteur microcristallin, un temps nécessaire pour fournir par intermittence le gaz de matériau à l'espace de génération de plasma est égal ou supérieur à 10 ms et égal ou inférieur à 1 s.

11. Le procédé de fabrication d'un film semiconducteur selon la revendication 9, comprenant en outre :

une étape de détection d'écart consistant à calculer un écart entre une temporalité de sortie d'une instruction d'ouverture ou de fermeture de la vanne (25 ; 25a, 25b, 25c, 25d) et une temporalité de branchement ou de coupure de la fourniture du gaz de matériau à l'espace de génération de plasma, avant l'étape de formation de film semiconducteur microcristallin,
sachant que, dans l'étape de formation de film semiconducteur microcristallin, une différence de temps est définie entre une temporalité de modulation d'intensité de la puissance haute fréquence fournie à l'électrode à plasma (13) et la temporalité de sortie de l'instruction d'ouverture ou de fermeture de la vanne (25 ; 25a, 25b, 25c, 25d) en fonction de l'écart.

12. Le procédé de fabrication d'un film semiconducteur selon la revendication 11, dans lequel une pluralité de chemins de fourniture de gaz de matériau (21b) est connectée à la chambre à vide (10) via des vannes (25a, 25b, 25c, 25d) dans le boîtier de protection (20), et
dans l'étape de formation de film semiconducteur microcristallin, la temporalité d'ouverture ou de fermeture de la vanne (25a, 25b, 25c, 25d) dans chacun des chemins de fourniture de gaz de matériau (21b) est réglée individuellement par rapport à la temporalité de modulation d'intensité de la puissance haute fréquence fournie à l'électrode à plasma (13), en fonction de l'écart de chacun des chemins de fourniture de gaz de matériau (21b) calculé dans l'étape de détection d'écart.

FIG.1

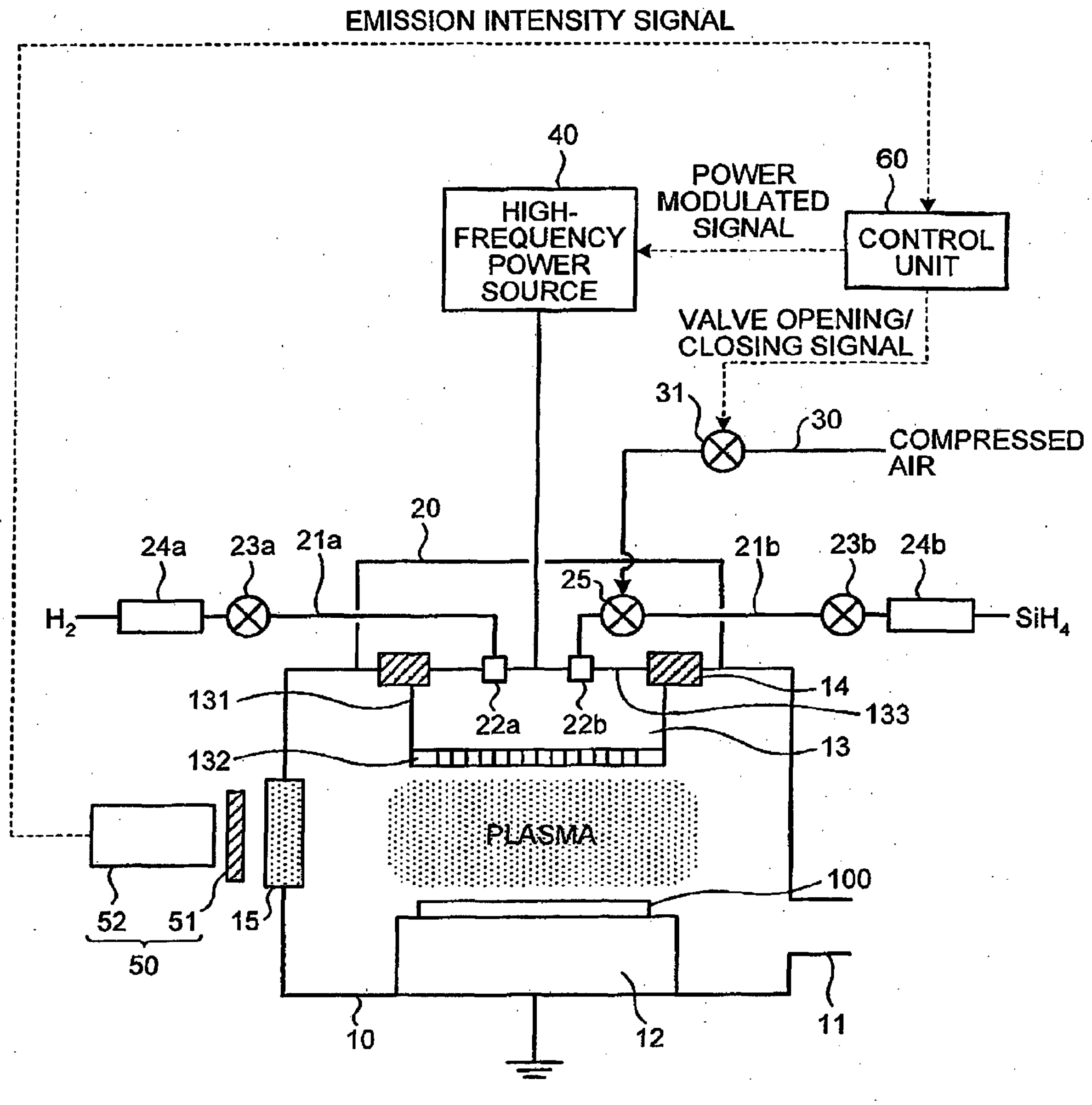

EMISSION INTENSITY SIGNAL
40
HIGH-FREQUENCY POWER SOURCE
POWER MODULATED SIGNAL
60
CONTROL UNIT
VALVE OPENING/ CLOSING SIGNAL
31
30
COMPRESSED AIR
20
24a
23a
21a
H2
25
21b
23b
24b
SiH4
14
133
131
22a
22b
13
132
PLASMA
100
52
51
15
50
10
12
11

FIG.2

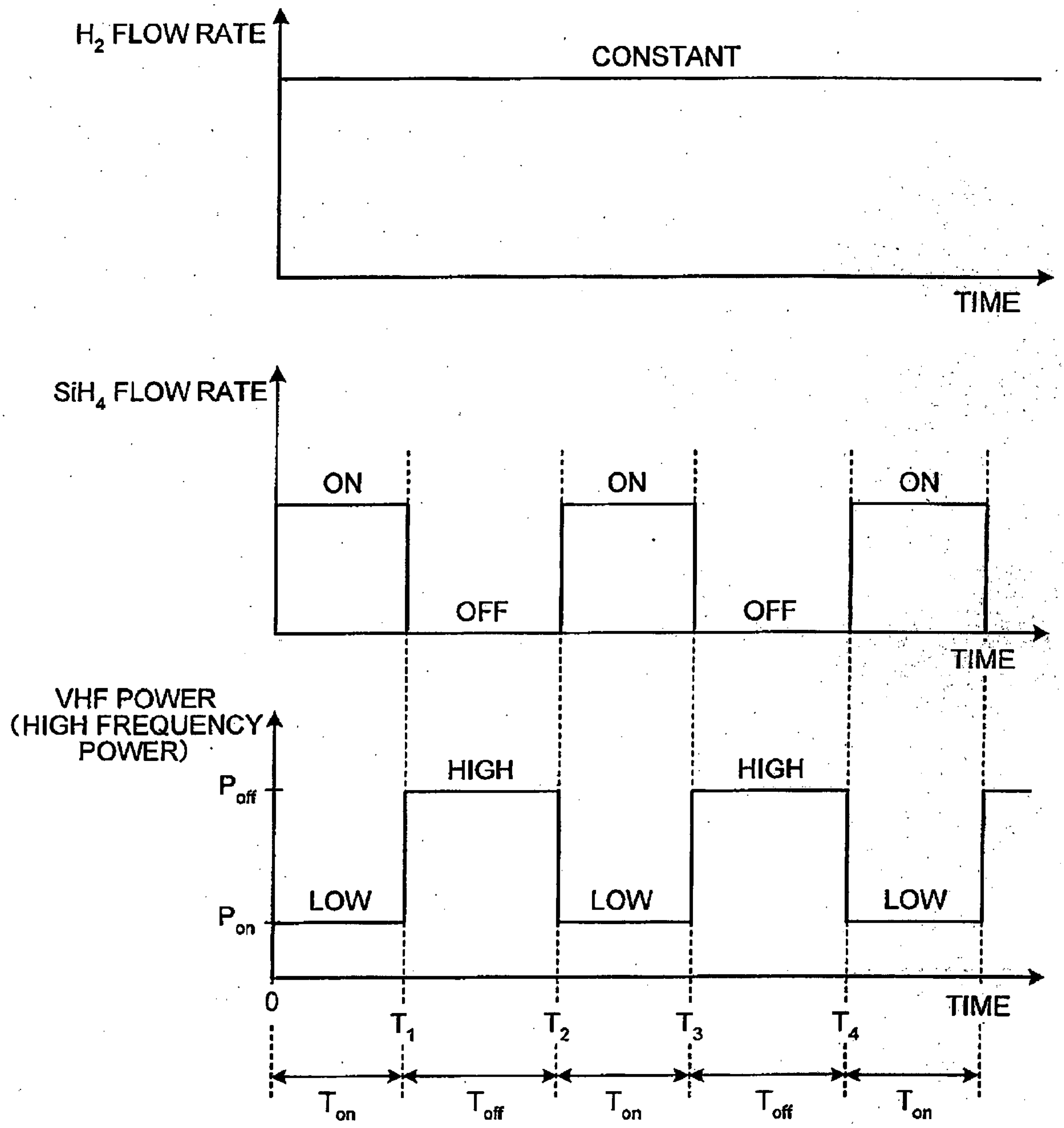

H2 FLOW RATE
CONSTANT
TIME
SiH4 FLOW RATE
ON
OFF
ON
OFF
ON
TIME
VHF POWER (HIGH FREQUENCY POWER)
Poff
Pon
HIGH
HIGH
LOW
LOW
LOW
0
T1
T2
T3
T4
TIME
Ton
Toff
Ton
Toff
Ton

FIG.3

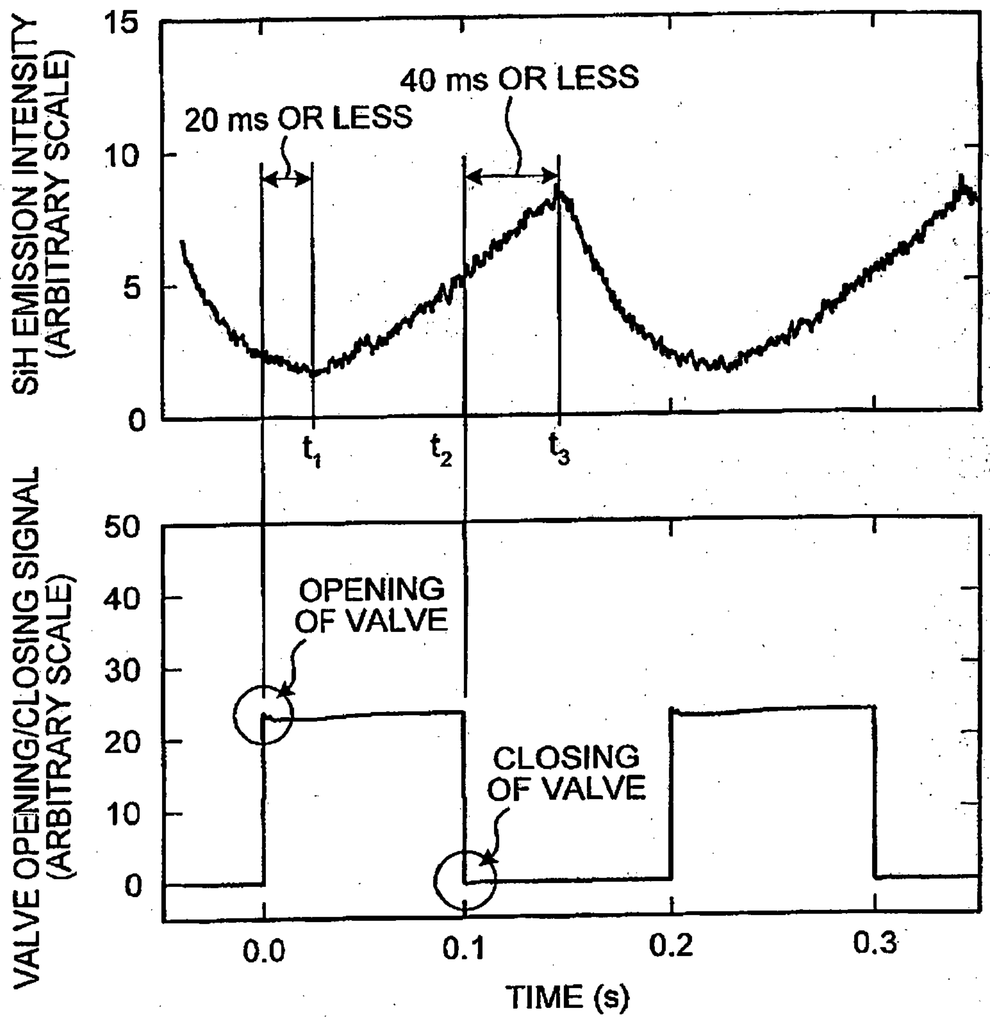
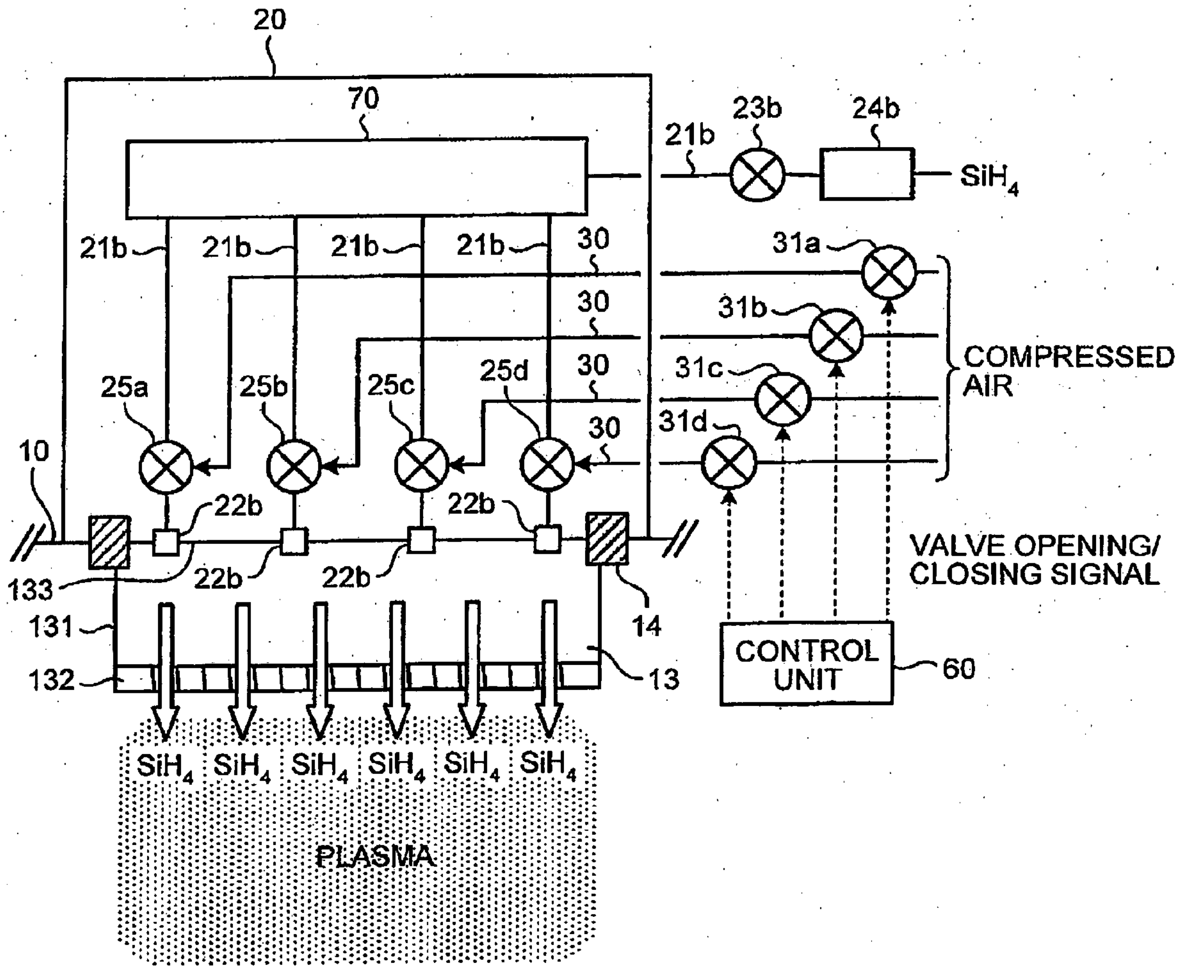

SiH EMISSION INTENSITY (ARBITRARY SCALE)
15
10
5
0
40 ms OR LESS
20 ms OR LESS
t1
t2
t3
VALVE OPENING/CLOSING SIGNAL (ARBITRARY SCALE)
50
40
30
20
10
0
OPENING OF VALVE
CLOSING OF VALVE
0.0
0.1
0.2
0.3
TIME (s)

FIG.4


20
70
21b
23b
24b
SiH4
21b
21b
21b
21b
30
31a
30
31b
COMPRESSED AIR
25a
25b
25c
25d
30
31c
30
31d
10
22b
22b
133
22b
22b
VALVE OPENING/ CLOSING SIGNAL
131
14
132
13
CONTROL UNIT
60
SiH4 SiH4 SiH4 SiH4 SiH4 SiH4
PLASMA

REFERENCES CITED IN THE DESCRIPTION

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