

Apparatus for the generation of fluorine gasField of the Invention

This invention relates to an apparatus that generates fluorine gas (referred to below as a fluorine gas generator). More particularly, this invention relates to a fluorine gas generator that is disposed in the gas supply system of a semiconductor processing system. Semiconductor processing refers in this context to the various processes carried out in order to fabricate semiconductor devices and/or semiconductor device-connecting structures (e.g., interconnects, electrodes) on the substrate undergoing the processing (the target substrate) by the formation of semiconductor, dielectric, and conductive layers in specific patterns on the target substrate, such as a semiconductor wafer or LCD substrate.

Description of the Prior Art

A variety of semiconductor processes, such as film formation, etching, and diffusion, are carried out on the target substrate, e.g., a semiconductor wafer or LCD substrate, during the fabrication of semiconductor devices. The semiconductor processing systems used to carry out these treatments employ fluorine-type gases as process gases in a variety of applications, such as for the etching of silicon films and silicon oxide films and to clean the interior of process compartments. Fluorine gas has been receiving attention as a new etching gas and cleaning gas, but it is generally not produced at the actual site of semiconductor device fabrication because its safety and reliability issues have not been completely addressed.

Electrolytic cell-based apparatuses are known for the production of fluorine gas at gas production plants. A fluorine gas generator of this type is disclosed, for example, in Japanese Laid Open Patent Application (PCT) Number Hei 9-505853 (505,853/1997). In the therein disclosed apparatus, a separation means extending from the top into the molten salt functions to partition the interior of the electrolytic cell into a central anode compartment and a surrounding cathode compartment. Two probes that end at different heights are disposed within the anode compartment. These two probes function as surface level gauges in order to

effect ON/OFF control of the current fed between the anode and cathode. Thus, this apparatus controls the generation of fluorine gas by detecting the surface level of the molten salt.

Another prior art fluorine gas generator is schematically illustrated in Figure 3. This apparatus has an improved structure for controlling the feed of fluorine gas from the electrolytic cell. In this particular apparatus, the fluorine gas generated at the anode 114 side of an electrolytic cell 112 is continuously fed through a conduit 120 into an intermediate capacitor 116 and is temporarily stored therein. When the capacitor 116 reaches a certain specified pressure, a switching valve 122 disposed between a compressor 118 and the capacitor 116 is temporarily opened and a certain specified amount of the fluorine gas is suctioned into the compressor 118. The valve 122 is repeatedly operated in order to raise the pressure of the secondary buffer tank 124 to a specified value.

Problems to Be Solved by the Invention

During their investigations the inventors discovered that several safety and reliability problems occur, vide infra, when the fluorine gas generator illustrated in Figure 3 is operated for long periods of time. The absence of a solution to these problems makes it quite difficult from a practical standpoint to incorporate and use the fluorine gas generator in an automated production system, for example, in systems for fabricating semiconductor devices.

Embodiments of the invention were developed in view of the aforementioned problems with the prior art. Embodiments can provide a fluorine gas generator that is capable of very safe and highly reliable operation even during long-term operations. Embodiments can provide an apparatus that can produce fluorine gas both on-site and on-demand. As used herein, on-site means that the fluorine gas generator is combined or assembled with the particular main process apparatus, for example, the main process apparatus of a semiconductor processing system. On-demand means that the gas can be supplied, with accompanying control of its required components, with a timing that responds to the requirements of the main process apparatus.

Means Solving the Problems

In accordance with a first aspect of the present invention there is provided an apparatus for the generation of fluorine gas, that is characteristically provided with an electrolytic cell that carries out the electrolysis of hydrogen fluoride in an electrolytic bath comprising hydrogen fluoride-containing molten salt and thereby generates, in a first gas phase region on the anode side, product gas whose main component is fluorine gas and at the same time generates, in a second gas phase region on the cathode side, by-product gas whose main component is hydrogen gas, a starting material conduit that feeds starting hydrogen fluoride into the molten salt, a first conduit that withdraws the product gas from the first gas phase region, a second conduit that withdraws the by-product gas from the second gas phase region, a first pressure gauge that continuously measures the pressure in the first gas phase region, a second pressure gauge that continuously measures the pressure in the second gas phase region, a first flow rate control valve disposed in the first conduit, a second flow rate control valve disposed in the second conduit, a first control member that based on the measurement result from the first pressure gauge adjusts the aperture of the first flow rate control valve so as to maintain the pressure of the first gas phase region at a first set value, and a second control member that based on the measurement result from the second pressure gauge adjusts the aperture of the second flow rate control valve so as to maintain the pressure of the second gas phase region at a second set value that is substantially equal to the first set value.

The first and second set values may be 760-820 Torr.

The apparatus may be additionally provided with a first suction means that is disposed in the first conduit downstream from the first flow rate control valve and that can suction the first conduit.

The second conduit may be disposed so as to connect downstream from the second flow rate control valve to a second suction means that can suction the second conduit.

The apparatus may also be provided with a switching valve disposed in the starting material conduit,

a current integrator that integrates the electric current fed between the electrode on the anode side of the electrolytic cell and the electrode on the cathode side of the electrolytic cell, and

a control member that based on the measurement result produced by the current integrator operates the switching valve so as to control the feed of hydrogen fluoride into the molten salt.

The hydrogen fluoride fed through the starting material conduit may be a gas.

The starting material conduit may be disposed so as to feed the hydrogen fluoride gas into the molten salt on the cathode side of the electrolytic cell and in that a conduit that can feed nitrogen gas into the starting material conduit is connected thereto downstream from the aforesaid switching valve and the hydrogen fluoride gas is fed mixed with nitrogen gas into the molten salt.

In a second aspect of the present invention, there is provided an apparatus for the generation of fluorine gas, that is characteristically provided with an electrolytic cell that carries out the electrolysis of hydrogen fluoride in an electrolytic bath comprising hydrogen fluoride-containing molten salt and thereby generates, in a first gas phase region on the anode side, product gas whose main component is fluorine gas and at the same time generates, in a second gas phase region on the cathode side, by-product gas whose main component is hydrogen gas, a starting material conduit that feeds starting hydrogen fluoride into the molten salt, a first conduit that withdraws the product gas from the first gas phase region, a second conduit that withdraws the by-product gas from the second gas phase region, a switching valve disposed in the starting material conduit, a current integrator that integrates the electric current fed between the electrode on the aforesaid anode side of the electrolytic cell and the electrode on the aforesaid cathode side of the electrolytic cell, and a control member that based on the measurement result produced by the current integrator operates the switching valve so as to control the feed of hydrogen fluoride into the molten salt.

The hydrogen fluoride fed through the starting material conduit may be a gas.

The starting material conduit may be disposed so as to feed the hydrogen fluoride gas into the molten salt on the cathode side of the electrolytic cell and in that a conduit that can feed nitrogen gas into the starting material conduit is connected thereto downstream from the aforesaid switching valve and the hydrogen fluoride gas is fed mixed with nitrogen gas into the molten salt.

In addition, the embodiments of this invention explore a variety of executions of this invention, and various embodiments of this invention can be derived by suitable combination of the plural number of disclosed constituent elements. For example, when an embodiment of the invention has been derived in which some constituent elements have been omitted from the overall set of constituent elements presented for the embodiment, these omitted elements can be suitably fulfilled by conventional well-known technologies in the actual working of the derived inventive embodiment.

Embodiments of the Invention

During the course of developing this invention, the inventors investigated the safety and reliability issues associated with the prior art fluorine gas generator described with reference to Figure 3. The inventors acquired the following knowledge as a result of these investigations.

In the operation of the apparatus illustrated in Figure 3, the valve 122 is opened at the upper limit for the pressure in the capacitor 116 and the valve 122 is closed at the lower limit for this pressure. This results in the generation of large pressure variations in the fluorine gas conduit 120. The molten salt mist caused by these large pressure variations accumulates at the inlet to the conduit 120, which causes the conduit 120 to become clogged. In addition, due to the frequent opening and closing of the valve 122, the seat of the valve 122 is quite prone to damage by the mechanical action of solidified molten salt particles and the chemical action of the fluorine gas.

With regard to another issue associated with the apparatus illustrated in Figure 3, one notes that the hydrogen gas produced on the cathode side passes through the conduit 121 of the exhaust system and is discharged from the system after dilution at a minimum down to the usual regulatory value. It can be expected here that the pressure in the discharge system will vary as a function of the plant environment. For example, when the exhaust system has a high suction capacity, the pressure on the cathode side will spontaneously become a negative pressure and in association therewith the molten salt level on the cathode side will rise. The

surface level undergoes a major change in this case, which results in molten salt being pulled into the hydrogen gas conduit 121 and hence in clogging of the conduit 121.

Once the molten salt has solidified in the conduits 120 and 121, it becomes necessary to stop the apparatus and carry out maintenance operations, which also causes downtime for the entire system to which the apparatus is connected. Beyond this, the obstruction of either the fluorine gas conduit 120 or the hydrogen gas conduit 121 also results in a disturbance in the pressure balance within the electrolytic cell 112. The occurrence of a major disturbance in the pressure balance within the electrolytic cell 112 can result in contact between fluorine gas and hydrogen gas within the electrolytic cell 112, which creates an explosion risk.

This invention has a structure that is based on the knowledge described above. Embodiments of this invention are explained in the following with reference to the drawings appended herewith. In the explanation that follows, those constituent elements that have approximately the same structure and function are assigned a common reference symbol and their explanation will be repeated only when necessary.

Figure 1 contains a schematic drawing that illustrates a semiconductor processing system that incorporates a fluorine gas generator that is an embodiment of this invention. This semiconductor processing system contains a semiconductor processing apparatus 10 that executes a process, e.g., film formation, etching, or diffusion, on a target substrate, e.g., a semiconductor wafer or LCD substrate.

The semiconductor processing apparatus 10 is provided with a process chamber 12 that holds the target substrate and in which the semiconductor process is implemented. Disposed within the process chamber 12 is a mounting platform 14 (support member) that functions both as a lower electrode and as a platform for mounting the target substrate. An upper electrode 16 is also disposed within the process chamber 12 facing the mounting platform 14. RF (high frequency) power can be applied from an RF power source 15 across the two electrodes 14 and 16 in order to form an RF field in the process chamber 12 for the purpose of converting the

process gas into a plasma. An exhaust system 18 is connected to the lower region of the process chamber 12 for the purpose of evacuating the interior of the chamber and establishing a vacuum therein. A gas supply system 20 is connected to the upper region of the process chamber 12 for the purpose of supplying the process gas.

5 Figure 2 contains a schematic drawing that illustrates a modified example 10x of the semiconductor processing apparatus that can be used in combination with the gas supply system 20 illustrated in Figure 1. This semiconductor processing apparatus 10x is provided with a process chamber 12 that holds the target substrate and in which the semiconductor process is implemented. A mounting platform 14 (support member) is disposed within the
10 process chamber 12 for the purpose of mounting the target substrate. An exhaust system 18 is connected to the lower region of the process chamber 12 for the purpose of evacuating the interior of the chamber and establishing a vacuum therein. A remote plasma chamber 13 is connected to the upper region of the process chamber 12 for the purpose of forming a plasma. The periphery of this remote plasma chamber 13 is wrapped with a coil antenna 17. The
15 application of RF (high frequency) power from the RF power source 15 to the coil antenna 17 results in the formation in the remote plasma chamber 13 of an induction field for the purpose of converting the process gas to a plasma. A gas supply system 20 is connected to the upper region of the remote plasma chamber 13 in order to supply the process gas.

20 The fluorine gas generator comprising the embodiment of this invention can also be used with semiconductor process equipment that does not employ a plasma, for example, to supply cleaning gas to a thermal CVD apparatus.

25 With reference again to Figure 1, a flow management section 22 is disposed in the gas supply system 20; this flow management section 22 can feed any designated gas, for example, process gas for carrying out a semiconductor process or process gas for cleaning the interior of the process chamber 12, into the process chamber 12 at a specified flow rate and is also capable of selective switching. A gas storage section 24 is connected to the flow management

section 22. This gas storage section 24 contains a plurality of gas sources and stores various active and/or inert gases. Also connected to the flow management section 22 is a gas production section 26 that produces fluorine gas-type process gas by a reaction process.

A fluorine gas generator 30 comprising an embodiment of this invention is detachably
5 connected to the flow management section 22 and the gas production section 26. More specifically, this generator 30 either directly supplies fluorine gas to the flow management section 22 or is used to supply starting fluorine gas to the gas production section 26 (switching valve not shown). The gas production section 26 can produce, for example, an interhalogen fluorine compound gas by reacting the starting fluorine gas with another halogen gas such as
10 chlorine.

The generator 30 contains an airtight electrolytic cell 32 that holds an electrolytic bath comprising hydrogen fluoride-containing molten salt. This molten salt comprises a mixture (KF/2HF) of potassium fluoride (KF) and hydrogen fluoride (HF) or a mixture of hydrogen fluoride and Frey's salt. The electrolytic cell 32 is divided into an anode compartment 34 and
15 a cathode compartment 36 by a partition sheet 35 that extends from the top into the molten salt. A carbon electrode (anode) 42 is immersed in the molten salt in the anode compartment 34 while a nickel electrode (cathode) 44 is immersed in the molten salt in the cathode compartment 36. Attached to the electrolytic cell 32 are a current source 38 that can supply current between the anode 42 and cathode 44 and a current integrator 40 that integrates the
20 supplied current.

During the electrolytic process the electrolytic cell 32 is heated to and held at 80-90°C by the attached heater 33. Electrolysis of the hydrogen fluoride in the electrolytic bath results in the production in the gas phase region of the anode compartment 34 of product gas whose main component is fluorine gas (F₂) and in the production in the gas phase region of the
25 cathode compartment 36 of by-product gas whose main component is hydrogen gas. Hydrogen fluoride gas is admixed (for example, at 5%) in both the product gas and by-product

gas in accordance with the vapor pressure contribution of the hydrogen fluoride gas in the starting molten salt. A first pressure gauge 46 is disposed on the anode compartment 34 and a second pressure gauge 48 is disposed on the cathode compartment 36 in order to continuously measure the pressure of the respective gas phase regions.

5 A first conduit 52 is connected to the anode compartment 34 in order to withdraw product gas and transport same to the flow management section 22 and gas production section 26 of the gas supply system 20. Disposed in this first conduit 52, in the given sequence from the upstream side, are a first flow rate control valve 54, an adsorption cartridge 56, a minibuffer tank 58, a compressor (suction means) 62, and a main buffer tank 64. The product gas
10 produced in the anode compartment 34 is forcibly withdrawn from the anode compartment 34 by suction of the first conduit 52 by the compressor 62 and is stored in the main buffer tank 64. Reference number 66 in Figure 1 denotes a line filter.

As noted above, hydrogen fluoride will be admixed at several percent (for example, 5%) in the product gas. This hydrogen fluoride is removed when the product gas passes through
15 the adsorption cartridge 56. This cartridge 56 should therefore hold adsorbent capable of adsorptively capturing hydrogen fluoride. Based on handling and pressure loss considerations, the adsorbent should be composed of a large number of pellets filled in the cartridge 56. The adsorbent may be composed, for example, of adsorbent whose adsorption capacity varies as a function of temperature, such as sodium fluoride (NaF). A temperature-regulating jacket
20 (heater) 57 is disposed over the circumference of the cartridge 56 in order to regulate the temperature of the cartridge 56.

The pressure within the main buffer tank 64 is continuously measured by a pressure gauge 65 disposed on the tank 64. This measurement result is transmitted to the control member 39 connected to the current source 38. The control member 39 controls the feed of
25 current to the electrolytic cell 32 based on the transmitted measurement result by switching the current source 38 on and off. Thus, when the pressure within the tank 64 has declined to a

certain pressure, the current source 38 is switched on and fluorine gas production is begun. When the pressure within the tank 64 has increased to a certain pressure, the current source 38 is switched off and fluorine gas production is halted. This enables electrolysis to be stopped without setting up differences in the molten salt surface levels within the electrolytic cell 32 between the anode compartment 34 and cathode compartment 36. The pressure within the tank 64 is set, for example, to atmospheric pressure to atmospheric pressure + 0.18 MPa.

A second conduit 72 is connected to the cathode compartment 36 in order to withdraw the by-product gas. This second conduit 72 is detachably connected to a conduit of the exhaust system (suction means) 78 of, for example, a semiconductor fabrication plant. A second flow rate control valve 74 and a detoxifier 76 are disposed in this second conduit 72. The by-product gas produced in the cathode compartment 36 is forcibly suctioned from the cathode compartment 36 by the suction in the second conduit 72 due to the exhaust system 78 and is moved through the detoxifier 76 and transported into the exhaust system 78.

As noted above, the pressure balance between the anode compartment 34 and cathode compartment 36 can for various reasons become disturbed during the electrolytic process, with the result that changes in the surface level within the electrolytic cell 32 are prone to occur. The surface level in the electrolytic cell 32 is also generally prone to change immediately after a gas-switching operation, such as a nitrogen purge of the interior of the electrolytic cell 32 or the nitrogen purge process after the end of feed of starting hydrogen fluoride gas. These surface level variations can have adverse effects on the safety and reliability of the fluorine gas generator.

In the case of the fluorine gas generator illustrated in Figure 1, however, the pressure of the gas phase region in the anode compartment 34 is continuously measured by a first pressure gauge 46 and the pressure of the gas phase region in the cathode compartment 36 is continuously measured by a second pressure gauge 48. These measurement results are transmitted to first and second control members 55 and 75 connected, respectively, to first and

second flow rate control valves 54 and 74. Based on the transmitted measurement results, the first and second control members 55 and 75 adjust the apertures of the first and second flow rate control valves 54 and 74 so as to maintain the pressure in the gas phase region of the anode compartment 34 and the pressure in the gas phase region of the cathode compartment 36, respectively, at first and second set values that are substantially equal to each other.

Since the pressures in the anode compartment 34 and cathode compartment 36 are each continuously and independently measured and controlled, a uniform state is maintained for the surface level of the molten salt in the anode compartment 34 and cathode compartment 36. In other words, this structure protects the electrolytic cell 32 from the adverse effects of variations in the conditions of fluorine production, in the conditions within the first and second conduits 52 and 72, in the operating conditions of the exhaust system 78 of the semiconductor fabrication plant and the compressor 62, and in other circumstances. This makes it possible to prevent damage to the expensive electrodes, for example, the anode effect, and to carry out the process safely and without abrupt stoppages in electrolysis. In addition, frequent maintenance is no longer necessary since clogging due to the solidification of molten salt at the inlets to the first and second conduits 52 and 72 does not occur.

The first set value for the gas phase region in the anode compartment 34 and the second set value for the gas phase region in the cathode compartment 36 are preferably atmospheric pressure to 820 Torr and more preferably atmospheric pressure to 770 Torr. In order to stabilize the pressure in the anode compartment 34 and cathode compartment 36, the aperture of the first and second flow rate control valves 54 and 74 must be continuously adjustable in a highly responsive manner. This consideration makes it preferable to use a piezovalue for the first and second flow rate control valves 54 and 74.

Returning again to Figure 1, a starting material conduit 82 is disposed in the cathode compartment 36 of the electrolytic cell 32 in order to feed hydrogen fluoride gas (consumable starting material) into the molten salt; this starting material conduit 82 is disposed immersed in

the molten salt. A hydrogen fluoride source 84 and a nitrogen source 94 are detachably connected through conduits 83 and 93 to the starting material conduit 82.

A switching valve 96 is disposed in the conduit 93 for the nitrogen source 94 in order to switch the conduit 93 between open and closed states. The switching valve 96 is always open during operation of the fluorine gas generator 30 and nitrogen gas is always fed into the molten salt of the electrolytic cell 32 during operation of the fluorine gas generator 30. The nitrogen gas flow rate is set at 0.2 to 50 L/min and preferably 2 to 10 L/min for a hydrogen fluoride gas flow rate of 1 to 50 L/min. The nitrogen gas is almost completely insoluble in the molten salt and passes through the molten salt on the cathode side and is discharged.

A switching valve 86 is disposed in the conduit 83 for the hydrogen fluoride source 84 in order to switch the conduit 83 between open and closed states. This switching valve 86 is opened and closed under control by the control member 87 attached thereto. The current fed during the electrolysis process between the anode 42 and the cathode 44 is integrated by the current integrator 40 and this value is transmitted to the control member 87. Based on the measurement value transmitted thereto, the control member 87 operates the switching valve 86 so as to regulate the feed of hydrogen fluoride gas (mixture of hydrogen fluoride gas in nitrogen) into the molten salt. The set value for the control member 87 is established, for example, so as to maintain the hydrogen fluoride concentration in the molten salt in the range from 39 to 41%.

The feed of hydrogen fluoride (HF) gas to the electrolytic cell 32 is controlled, based on the following theory, by integration of the supplied current. Thus, according to Faraday's law the amount of fluorine (F_2) produced by electrolysis is directly proportional to the amount of electricity. This law applies regardless of the electrolysis conditions (temperature, concentration, type of electrode). Fluorine gas production by the electrolytic cell 32 in the embodiment under consideration can be approximately determined, based on the current efficiency relationship, using equation (1).

$$Z = 6.8X \quad (1)$$

wherein

Z = fluorine production flow rate (cc/min)

X = amount of electricity (in this case the electrolysis current value (A))

5 The initial hydrogen fluoride concentration in the molten salt is set, for example, to 41%. The supply of starting hydrogen fluoride gas is then timed to occur after the hydrogen fluoride concentration in the molten salt has fallen from its initial 41% concentration and prior to reaching a lower concentration limit, for example, 39%. The increase in the melting point of the molten salt when the hydrogen fluoride concentration falls below the lower concentration limit can in the worst case result in solidification of the molten salt and make it impossible to carry out electrolysis. When the hydrogen fluoride concentration exceeds the initial concentration the resulting high vapor pressure of the hydrogen fluoride in the molten salt will also raise the concentration of hydrogen fluoride mixed in the fluorine. This creates a high load at the adsorption cartridge 56 on the adsorbent (for example, sodium fluoride (NaF)) that adsorptively captures the hydrogen fluoride. It is therefore necessary to maintain the hydrogen fluoride concentration in the aforementioned range, for example, in the range of 39 to 41%. Equation (2) shows the relationship between fluorine gas production and hydrogen fluoride gas consumption. Here, 2 moles hydrogen fluoride are required for the production of 1 mole fluorine.

$$20 \quad (2Z + 0.05Z + 0.05Z) t / 1000 = T \quad (2)$$

wherein

2Z = hydrogen fluoride flow rate (cc/min) required to produce 1 mole fluorine

first 0.05Z term = hydrogen fluoride flow rate (cc/min) entrained in 1 mole fluorine

second 0.05Z term = hydrogen fluoride flow rate (cc/min) entrained in 1 mole hydrogen

25 t = production time (min)

T = hydrogen fluoride consumption (L)

Equation (3) is obtained by substituting, based on equation (1), $6.8X$ for Z in equation (2).

$$0.01428X \times t = T \quad (3)$$

wherein

5 X = amount of electricity (A)

t = production time (min)

T = hydrogen fluoride consumption (L)

The amount of consumable hydrogen fluoride depends on the amount of molten salt introduced into the electrolytic cell 32. Given that the hydrogen fluoride concentration in the molten salt prior to the start of electrolysis is 41%, the amount of hydrogen fluoride in the electrolytic cell 32 is then $0.41C$ where C is the amount of molten salt. The relationship between the hydrogen fluoride concentration in the molten salt and hydrogen fluoride consumption is given by equation (4) when the electrolytic cell 32 is used in the 39-41% hydrogen fluoride concentration range. The maximum amount of consumable hydrogen fluoride is then given by equation (5).

$$(0.41C - HFc)/(C - HFc) = 0.39 \quad (4)$$

$$HFc = 0.033C \quad (5)$$

wherein in equations (4) and (5)

C = weight of the molten salt

20 HFc = hydrogen fluoride consumption

Equation (6) and then equation (7) are obtained by substituting T in equation (3) for HFc in equation (5).

$$0.01428X \times t = 0.033C \quad (6)$$

$$25 \quad X \times t = 2.3C \quad (7)$$

wherein in equations (6) and (7)

X = amount of electricity (A)

t = production time (min)

C = weight of the molten salt

Thus, the relationship between the amount of electricity X and the fluorine production time t for the hydrogen fluoride concentration range used of 39-41% can be determined if the weight C of the molten salt (KF/2HF) preliminarily introduced into the electrolytic cell 32 is known. In the present case, the timing (lower limit of the range used) of hydrogen fluoride gas feed can be specified by the value afforded by integration of the amount of electricity along the time axis, and as a consequence the amount of electricity X need not be fixed.

The advantages of the hereinabove-described embodiment of this invention will now be considered.

Japanese Laid Open Patent Application (PCT) Number Hei 9-505853 (referred to below as the 853 publication) discloses a fluorine cell that contains a control sensor means that detects the electrolyte level in the electrolytic cell and a current supply means that responds to a signal from the control sensor means and starts or stops the supply of current in response to this signal. In this case, fluorine production continues until the decline in the surface level reaches a preset position at which a signal is issued. Since in response to this signal the electrolysis controlling apparatus stops the supply of current to the cell, electrolysis is stopped and the fall in the surface level of the electrolyte is also stopped.

In sum, the technology disclosed in this publication deliberately employs changes in the surface level to effect ON/OFF control of the current and does not contemplate suppression of this variation. However, surface level variations must be minimized in the electrolysis in order to continuously produce fluorine gas while maintaining a steady state.

The 853 publication also makes it clear that the anode compartment in the electrolytic cell is to function as a fluorine reservoir. However, due to the difficulty of matching fluorine production to demand, the fluorine generators used for semiconductor processing at a practical

level require a compressor and a capacitor of a certain size. The technology disclosed in the publication under consideration cannot accommodate such changes in the external environment.

Thus, commercial fluorine-generating systems that correspond to the 853 publication are provided with a bellows-type compressor and a capacitor with a capacity of several liters. Such a system intermittently stores fluorine in its buffer tank through the action of an ON/OFF switching valve. The use of this method enables the uninterrupted generation of fluorine without stoppages in fluorine production. However, while gas can be steadily produced in this case, practical experience has nevertheless shown that the following problems occur during long-term production in the case under consideration.

The fine molten salt mist entrained by the fluorine infiltrates into the conduit or into the capacitor present between the compressor and electrolytic cell. Since this mist has a melting point around 80°C, it will be present as a solid in the conduit. As this mist accumulates, it will cause such problems as (1) clogging of the conduit and (2) damage to the valve seat of the ON/OFF valve.

The former problem results in an immediate stoppage of electrolysis and requires an operation to remove the salt obstructing the conduit. Since reactive fluorine gas will also be present in the conduit, this removal operation is hazardous and requires great care. The latter problem again requires that electrolysis be halted due to leakage at the valve. In addition, the frequent repetition of the ON/OFF operation causes the valve to wear out prematurely.

In addition, since the control method under consideration does not avoid a certain degree of variation in the surface level in the anode compartment, the area of contact between the liquid and the electrode surface also constantly undergoes variation. The resulting variations in current efficiency during electrolysis make it quite difficult to maintain the quantity of fluorine production stable. Another problem that arises here is that the anode effect may make it necessary (3) to exchange the electrode (carbon is typically used for the anode).

Nor can changes in the surrounding environment (connection to a compressor in the case under consideration) be accommodated when as in the 853 publication control of the amount of fluorine production is exercised by switching a power source on and off in response to the control sensor. And the use of a compressor at the electrolytic cell is in the final analysis required in the case of service in semiconductor processing. On the other hand, it is essential that fluorine generation not be subject to influences from the downstream side after the electrolytic cell. Viewed from this perspective the control method in the 853 publication is not adaptable to and hence is impractical for semiconductor processing service.

An important feature of the above-described embodiment of this invention is that it is not influenced by changes in the post-cell environment and can continuously and stably generate fluorine. This fluorine-supplying apparatus is consciously designed for semiconductor processing service, i.e., it is essentially premised on the use of a suction apparatus such as a compressor.

The pressure gauge connected to the buffer tank downstream from the compressor is linked to the current source. When the pressure drops to a certain value, the power source is switched on and fluorine is generated. The power source is switched off when the pressure has increased up to a certain point. The use of this method makes it possible to stop electrolysis without the elaboration of different surface levels as in the 853 publication.

The 853 publication teaches that for safety reasons it is preferable that operations always be carried out with the pressure at the cathode side outlet at atmospheric pressure (or at a pressure slightly above atmospheric pressure). However, it is almost impossible to maintain this in an actual semiconductor plant due to the large pressure variations occurring therein in the cathode side conduit. Moreover, the 853 publication focuses only on pressure changes in the anode compartment and bases this on the premise that the pressure in the cathode compartment is always atmospheric pressure.

Pressure maintenance by independent flow rate controls in the above-described embodiment of this invention enables the pressure in the two electrode compartments of the electrolytic cell to be maintained constant at all times. However, in practice the surface level cannot be determined from the pressure, and for this reason in order to enhance safety one surface level sensor is inserted in a preferred modality on the anode or cathode side and preferably on the cathode side.

The starting anhydrous hydrogen fluoride (AHF) is ordinarily a gas and is fed by bubbling into the molten salt (preferably on the cathode side) of the electrolytic cell. AHF exhibits a very fast rate of absorption into the molten salt, and as a result the cathode compartment can instantaneously assume a negative pressure when the AHF is supplied at a slow flow rate. When this occurs, the molten salt ascends within the AHF feed conduit and in the worst case will end up solidifying and making it impossible to continue the feed. The AHF feed flow rate is therefore preferably rapid, but there are limitations on the AHF flow rate that can be used in practice.

Therefore, in the above-described embodiment of this invention, the AHF is mixed into nitrogen gas during the AHF feed interval with the goal of raising the overall flow rate during AHF feed. Since nitrogen gas is almost completely insoluble in the molten salt, it passes through the molten salt on the cathode side and is discharged. This flow of nitrogen gas into the cathode compartment is maintained at all times regardless of whether electrolysis is actually underway. This results in dilution of the hydrogen generated on the cathode side during electrolysis and makes it possible to maintain conditions outside the explosive limit even when fluorine gas is introduced to the cathode side due to a sudden and unexpected change in surface levels. The nitrogen flow rate is regulated optimally on the basis of the size of the electrolytic cell.

The fluorine gas generator 30 is detachably incorporated in the semiconductor processing system in the embodiment described above, but the generator may also be

permanently installed in this system. In addition, components disposed within the semiconductor fabrication plant itself can be used for several of the components assigned to the fluorine gas generator 30, e.g., the compressor 62, main buffer tank 64, detoxifier 76, and so forth. The fluorine gas may be alternately fed to the flow management section 22 or gas production section 26 or may be directly fed to the process chamber 12 separately from the other process gases. The gas production section 26 can also be configured to produce other fluorine-system process gases rather than interhalogen fluorine compounds.

While various modifications and alterations within the technical sphere of the concept of this invention can be devised by the individual skilled in the art, it should be understood that these modifications and alterations also fall within the scope of this invention.

As has been described above, this invention provides a fluorine gas generator that is capable of very safe and highly reliable operation even during long-term operations.

Brief Description of the Drawings

Figure 1 contains a schematic drawing that illustrates a semiconductor processing system that incorporates a fluorine gas generator that is an embodiment of this invention.

Figure 2 contains a schematic drawing that illustrates a modified example of the semiconductor processing system used in combination with the gas feed system illustrated in Figure 1.

Figure 3 contains a schematic drawing that illustrates a prior art fluorine gas generator.

Reference symbols

10, 10x		semiconductor processing apparatus
12		process chamber
18		exhaust system
20		gas supply system
22		flow management section
24		gas storage section
26		gas production section

	30		gas generator
	32		electrolytic cell
	34		anode compartment
	36		cathode compartment
5	38		current source
	40		current integrator
	42		anode
	44		cathode
	46, 48		pressure gauge
10	52, 72		conduit
	54, 74		flow rate control valve
	55, 75		control member
	56		adsorption cartridge
	58		capacitor
15	62		compressor
	64		buffer tank
	76		detoxifier
	78		exhaust system
	82		starting material conduit
20	84		hydrogen fluoride source
	86		switching valve
	87		control member
	94		nitrogen source
25	96		switching valve

Claims

1. Apparatus for the generation of fluorine gas, that is characteristically provided with an electrolytic cell that carries out the electrolysis of hydrogen fluoride in an electrolytic bath comprising hydrogen fluoride-containing molten salt and thereby generates, in a first gas phase region on the anode side, product gas whose main component is fluorine gas and at the same time generates, in a second gas phase region on the cathode side, by-product gas whose main component is hydrogen gas,
- a starting material conduit that feeds starting hydrogen fluoride into the molten salt,
- a first conduit that withdraws the product gas from the first gas phase region,
- a second conduit that withdraws the by-product gas from the second gas phase region,
- a first pressure gauge that continuously measures the pressure in the first gas phase region,
- a second pressure gauge that continuously measures the pressure in the second gas phase region,
- a first flow rate control valve disposed in the first conduit,
- a second flow rate control valve disposed in the second conduit,
- a first control member that based on the measurement result from the first pressure gauge adjusts the aperture of the first flow rate control valve so as to maintain the pressure of the first gas phase region at a first set value, and
- a second control member that based on the measurement result from the second pressure gauge adjusts the aperture of the second flow rate control valve so as to maintain the pressure of the second gas phase region at a second set value that is substantially equal to the first set value.
2. The apparatus of claim 1 for generating fluorine gas, characterized in that the first and second set values are 760-820 Torr.

3. The apparatus of claim 1 or 2 for generating fluorine gas, that is characteristically also provided with a first suction means that is disposed in the first conduit downstream from the first flow rate control valve and that can suction the first conduit.

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4. The apparatus of claim 3 for generating fluorine gas, characterized in that the second conduit is disposed so as to connect downstream from the second flow rate control valve to a second suction means that can suction the second conduit.

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5. Apparatus according to any of claims 1 to 4 for generating fluorine gas, that is characteristically also provided with

a switching valve disposed in the starting material conduit,

a current integrator that integrates the electric current fed between the electrode on the aforesaid anode side of the electrolytic cell and the electrode on the aforesaid cathode

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side of the electrolytic cell, and

a control member that based on the measurement result produced by the current integrator operates the switching valve so as to control the feed of hydrogen fluoride into the molten salt.

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6. The apparatus of claim 5 for generating fluorine gas, characterized in that the hydrogen fluoride fed through the starting material conduit is a gas.

7. The apparatus of claim 6 for generating fluorine gas, characterized in that the starting material conduit is disposed so as to feed the hydrogen fluoride gas into the molten salt on the cathode side of the electrolytic cell and in that a conduit that can feed nitrogen gas into the

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starting material conduit is connected thereto downstream from the aforesaid switching valve and the hydrogen fluoride gas is fed mixed with nitrogen gas into the molten salt.

8. Apparatus for the generation of fluorine gas, that is characteristically provided with
5 an electrolytic cell that carries out the electrolysis of hydrogen fluoride in an electrolytic bath comprising hydrogen fluoride-containing molten salt and thereby generates, in a first gas phase region on the anode side, product gas whose main component is fluorine gas and at the same time generates, in a second gas phase region on the cathode side, by-product gas whose main component is hydrogen gas,
10 a starting material conduit that feeds starting hydrogen fluoride into the molten salt,
a first conduit that withdraws the product gas from the first gas phase region,
a second conduit that withdraws the by-product gas from the second gas phase region,
a switching valve disposed in the starting material conduit,
a current integrator that integrates the electric current fed between the electrode on the
15 aforesaid anode side of the electrolytic cell and the electrode on the aforesaid cathode side of the electrolytic cell, and
a control member that based on the measurement result produced by the current integrator operates the switching valve so as to control the feed of hydrogen fluoride into the molten salt.

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9. The apparatus of claim 8 for generating fluorine gas, characterized in that the hydrogen fluoride fed through the starting material conduit is a gas.

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Claim 10. The apparatus of claim 9 for generating fluorine gas, characterized in that the starting material conduit is disposed so as to feed the hydrogen fluoride gas into the molten salt on the cathode side of the electrolytic cell and in that a conduit that can feed nitrogen gas into the

starting material conduit is connected thereto downstream from the switching valve and the hydrogen fluoride gas is fed mixed with nitrogen gas into the molten salt.