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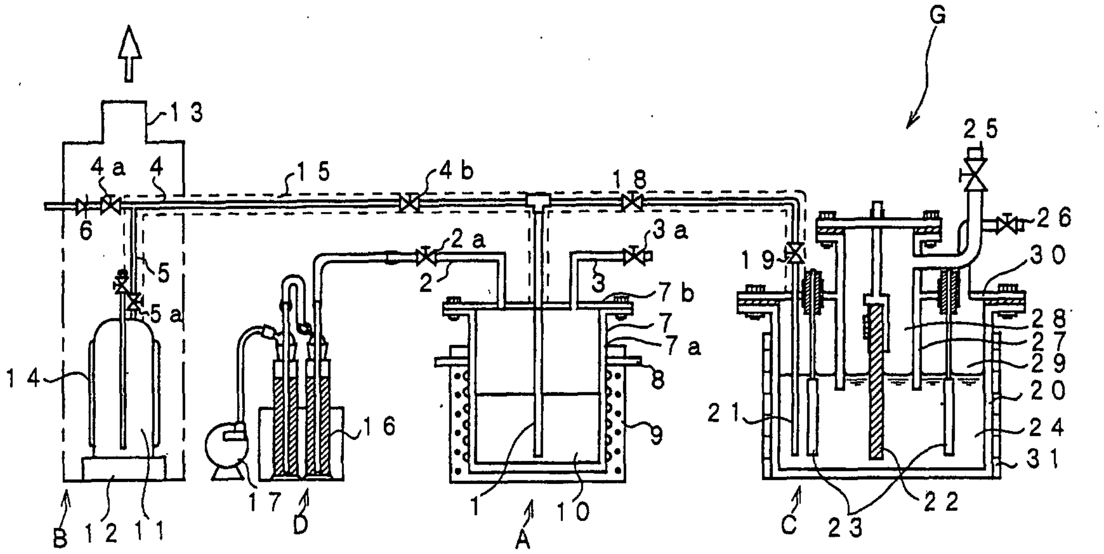
(54) APPARATUS FOR GENERATING F SB 2 /sb GAS AND METHOD FOR GENERATING F SB 2 /SB GAS, AND F SB 2 /SB GAS

(57) An F_2 gas generating apparatus for generating a high purity F_2 gas by subjecting an electrolytic bath made of KF·2HF to electrolysis is characterized by comprising a preparing system for preparing KF·2HF from KF or KF·HF, an HF supplying system for supplying HF into the electrolytic bath and the preparing system, and an F_2 gas generating system for generating the F_2 gas by subjecting KF·2HF prepared by the preparing system to electrolysis.

FIG. 1



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Description

Technical Field

[0001] The present invention relates to an apparatus for generating F_2 gas, a method for generating the F_2 gas, and F_2 gas. Particularly, the present invention relates to an F_2 gas generating apparatus for generating high purity F_2 gas, in which a quantity of an impurity is extremely small, for use in a manufacturing process of semiconductor or the like, method for generating F_2 gas, and F_2 gas.

Background Art

[0002] F_2 gas has been used as a primary gas indispensably, for example, in a field of semiconductor manufacturing. Although the F_2 gas may sometimes be used alone, nitrogen trifluoride gas (hereinafter also referred to as "NF_3 gas") which has been synthesized based on the F_2 gas has been recently used as a cleaning gas or a dry etching gas for semiconductor. Further, neon fluoride gas (hereinafter also referred to as "NeF gas"), argon fluoride gas (hereinafter also referred to as "ArF gas"), krypton fluoride gas (hereinafter also referred to as "KrF gas") and the like are excimer laser oscillation gases used for patterning of a semiconductor integrated circuit. Mixed gas of rare gas and the F_2 gas is in many cases used as a raw material of the excimer laser oscillation gas.

[0003] The F_2 gas is generated by performing electrolysis by using carbon as an anode and nickel as a cathode in an electrolytic cell containing a bath comprising a predetermined quantity of KF·HF. Ordinarily, the KF·HF contained in the electrolytic cell is used in a form of KF·2HF to be prepared by further appropriately supplying HF into a predetermined quantity of an initially loaded HF. In a case in which KF·2HF is insufficient, KF·HF is loaded and, then, HF is once again added thereto to prepare a predetermined quantity of the bath.

[0004] KF, as a component of the bath, is high in hygroscopicity and ordinarily comes to contain moisture at the time of constructing the bath. We have previously made an application (WO 01/77412A1) having a content regarding an apparatus for generating a high purity fluorine gas having a small quantity of impurities.

[0005] However, an F_2 gas to be generated in a manner as described above is such a type of F_2 gas as an initially generated F_2 gas contains oxygen by from 45% to 55% therein. The F_2 gas to be generated and water in an electrolytic bath are reacted with each other in accordance with the formula (1) described below, thereby ordinarily reducing a quantity of oxygen contained in the F_2 gas. Nevertheless, it is difficult to bring the quantity thereof to 3000 ppm or less.

$$2F_2 + H_2O \rightarrow F_2O + 2HF \qquad (1)$$

[0006] The high purity F_2 gas is required as the above-described excimer laser oscillation gas or for performing a surface treatment on a stepper lens (CaF_2 single crystal) of the excimer laser. An oxygen concentration to be contained in the F_2 gas is required to be 1000 ppm or less as the excimer laser oscillation gas in the former case and 500 ppm or less as a gas for such surface processing of the stepper lens (CaF_2 single crystal) of the excimer laser in the latter case.

[0007] An object according to the invention is to provide an F_2 gas generating apparatus which can consistently generates a high purity F_2 gas in which a quantity of oxygen to be contained is extremely small amount, an F_2 gas generating method and the high purity F_2 gas.

Disclosure of the Invention

[0008] To solve the above-described problems, the present invention provides an F_2 gas generating apparatus for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, being characterized by comprising:

a preparing system for preparing KF·2HF from KF or KF·HF;
an HF supplying system for supplying HF into the electrolytic bath and the preparing system; and
an F_2 gas generating system for generating the F_2 gas by subjecting KF·2HF prepared by the preparing system to electrolysis.

[0009] After KF·2HF is prepared from KF or KF·HF in a closed preparing system, the thus-prepared KF·2HF is loaded in an electrolytic cell connected with the preparing system in a closed space. Accordingly, KF·2HF loaded in the electrolytic cell is allowed to be an electrolytic bath without absorbing moisture, namely, having a small oxygen content. By this, a quantity of oxygen to be contained in the F_2 gas to be obtained by subjecting this electrolytic bath to electrolysis is allowed to be small from an initial stage of generation.

[0010] Further, the F_2 gas generating apparatus according to the invention is characterized in that a moisture removing device for removing moisture in the KF or KF·HF is attached to the preparing system.

[0011] At the time of preparing KF·2HF from KF or KF·HF, a quantity of oxygen can surely be reduced.

[0012] Further, the F_2 gas generating apparatus according to the invention is an F_2 gas generating apparatus in which an oxygen concentration in the thus-generated F_2 gas is 2% or less.

[0013] The quantity of oxygen in the F_2 gas is reduced to be 2% or less, preferably 0.2% or less (2000 ppm or less) and more preferably 0.02% or less (200 ppm or less). Accordingly, the F_2 gas can be used as an excimer laser oscillating gas or as a gas for surface treatment of a stepper lens (CaF_2 single crystal) of an excimer laser.

[0014] Further, the F_2 gas generating apparatus according to the invention is an F_2 gas generating apparatus for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, comprising:

> a preparing system for preparing KF·2HF from KF or KF·HF;
> an HF supplying system for supplying HF into the electrolytic bath and the preparing system; and
> an F_2 gas generating system for generating the F_2 gas by subjecting KF·2HF prepared by the preparing system to electrolysis, being characterized by being provided with a moisture controlling device for adjusting moisture in an atmosphere outside each of the preparing system, the HF supplying system, and the F_2 gas generating system or all the systems as a whole.

[0015] Since the moisture controlling device controlling the moisture in the atmosphere outside each of the preparing system, the HF supplying system and the F_2 gas generating systems or all the systems as a whole is provided, contamination of oxygen can surely be controlled.

[0016] Further, the F_2 gas generating apparatus according to the invention is an F_2 gas generating apparatus in which the moisture controlling device is a box which contains each of the systems or all the systems as a whole and is capable of controlling an atmosphere inside the box.

[0017] Since the moisture controlling device is a box capable of controlling the atmosphere, adjustment of atmosphere moisture of each of the systems or all the systems as a whole can easily be performed. Accordingly, contamination of oxygen can surely be controlled.

[0018] Further, an F_2 gas generating method according to the invention is an F_2 gas generating method for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, comprising the steps of:

> heat-deaerating KF or KF·HF for a predetermined period of time in an atmosphere of vacuum or an inert gas in a preparing system, for preparing KF·2HF from the KF or KF·HF, which is attached with a moisture removing device for removing moisture in the KF or KF·HF;
> cooling the KF or KF·HF to room temperature in an atmosphere of vacuum or the inert gas in the preparing system;
> supplying HF changed into a vapor phase from an HF supplying system into the preparing system;
> allowing the KF or KF·HF, and the HF to react with each other in the preparing system to generate KF·2HF;
> supplying the thus-generated KF·2HF into an electrolytic cell in an F_2 gas generating system; and
> subjecting the KF·2HF to electrolysis to generate an F_2 gas having a low oxygen concentration.

[0019] By providing such arrangement, it becomes possible to allow the quantity of oxygen in the F_2 gas generated to be small amount. As a result, the F_2 gas is allowed to be used as the excimer laser oscillating gas or as a gas for surface processing of the stepper lens (CaF_2 single crystal) of the excimer laser.

[0020] Further, the F_2 gas generating method according to the invention is an F_2 gas generating method in which, in the preparing system, the KF or KF·HF is heated at from 200°C to 300°C to remove adsorbed water or crystallization water of the KF or KF·HF therefrom.

[0021] Accordingly, the moisture in KF or KF·HF can surely be removed. To this end, it becomes possible to remove oxygen in the moisture whereupon the oxygen concentration in the F_2 gas to be generated can surely be reduced from an initial stage of F_2 gas generation.

[0022] Further, an F_2 gas according to the invention is an F_2 gas generated by a method comprising the steps of:

> heat-deaerating KF or KF·HF for a predetermined period of time in an atmosphere of vacuum or an inert gas in a preparing system, for preparing KF·2HF from KF or KF·HF, which is attached with a moisture removing device for removing moisture in the KF or KF·HF;
> cooling the KF or KF·HF to room temperature in an atmosphere of vacuum or the inert gas in the preparing system;
> supplying HF changed into a vapor phase from an HF supplying system into the preparing system;
> allowing the KF or KF·HF, and the HF to react with each other in the preparing system to generate KF·2HF;
> supplying the thus-generated KF·2HF into an electrolytic cell in an F_2 gas generating system; and
> subjecting the KF·2HF to electrolysis. Therefore, since the F_2 gas is a high purity F_2 gas which is extremely low in the oxygen concentration, it can be used as various types of primary gases for a semiconductor manufacture.

[0023] Further, the F_2 gas according to the invention is an F_2 gas in which an oxygen concentration is 2% or less.

[0024] The oxygen concentration is reduced to be preferably 0.2% or less (2000 ppm or less) and more preferably 0.02% or less (200 ppm or less). To this end, The F_2 gas can be used as the excimer laser oscillating gas or as the gas for the surface processing of the stepper lens (CaF_2 single crystal) of the excimer laser.

Brief Description of the Drawings

[0025]

> FIG. 1 is a schematic view of a fluorine gas generating apparatus according to the present invention.
> FIG. 2 is a chart showing a relationship among quantities of electricity in cases of Example 1, Comparative Examples 1 and 3, and a quantity of O_2 in F_2 gas.

Best Mode for Carrying Out the Invention

[0026] Hereinafter, an example of embodiments according to the present invention will be described with reference to FIG. 1.

[0027] An F_2 gas generating apparatus G according to the present embodiment, which generates a high purity F_2 gas by subjecting an electrolytic bath 24 comprising KF·2HF to electrolysis, comprises a preparing system A which prepares KF·2HF from KF or KF·HF, an HF supplying system B which supplies HF to the electrolytic bath 24 and the preparing system A, and an F_2 gas generating system C which generates an F_2 gas by subjecting KF·2HF which has been prepared by the preparing system A to electrolysis.

[0028] In FIG. 1, the preparing system A which prepares KF·2HF from KF or KF·HF comprises a KF·2HF preparing device 7 comprising a vessel 7a made of Ni which contains KF 10, and an upper cover 7b which hermetically seals the vessel 7a, a heater 9 which covers the vessel 7a of the KF·2HF preparing device 7 and heats KF 10 inside the vessel 7a, a cooling water pipe 8 for use in cooling, a vacuum piping 2, provided in the upper cover 7b, which is connected with a vacuum-exhausting system D, an inert gas purging piping 3, and an HF supplying and a KF·2HF sending-out piping 1 which is inserted in KF 10 and connected to both the HF supplying system B and the F_2 gas generating system C.

[0029] In the HF supplying system B which supplies HF to the preparing system A, an HF cylinder 11 placed on a load cell 12 is arranged in a box 13, which is connected to an acrylic scrubber (not shown). A surface of the HF cylinder 11 is covered by a heater 14 to maintain an interior of the HF cylinder 11 at a predetermined temperature. Further, a quantity of gas inside the HF cylinder 11 is measured by a load cell 12 to measure a quantity of an HF gas to be supplied to both the preparing system A and the F_2 gas generating system C. The HF cylinder 11 is connected with the preparing system A via the HF sending-out piping 5.

[0030] The F_2 gas generating system C comprises, as primary members, an electrolytic bath 24 comprising a KF·2HF mixed molten salt, an electrolytic cell 20 which contains the electrolytic bath 24, both an anode 22 and a cathode 23 which electrolyze the electrolytic bath 24.

[0031] The electrolytic cell 20 is integrally formed of a metal, such as Ni, MONEL®, pure iron, and stainless steel. The electrolytic cell 20 is separated into an anode chamber 28 and a cathode chamber 29 by a partition wall 27 comprising Ni or MONEL®. The anode 22 comprising a low polarized carbon, and the cathode 23 comprising Ni, or Fe are disposed in the anode chamber 28 and the cathode chamber 29, respectively. A discharge port 25 for the F_2 gas to be generated from the anode chamber 28 and the cathode chamber 29 and a discharge port 26 for an H_2 gas to be generated from the cathode chamber 7 are disposed in the upper cover 30 of the electrolytic cell 20. Further, the electrolytic cell 20 is provided with a heater 31 for heating an interior of the electrolytic cell 20 whereupon a heat insulating material (not shown) is provided around the heater 12. The heater 12 is not limited to any particular form but any forms, including a ribbon-type heater, a nichrome wire and the like are permissible. Preferably, the heater 12 is allowed to be in form such that it covers a whole circumference of the electrolytic cell 2.

[0032] The vacuum-exhausting system D is constructed by molecular sieves 16 and a vacuum pump 17 and sucks moisture which is desorbed from KF 10 when KF 10 contained in the preparing system A is heated by a heater 9.

[0033] Next, an operation of the F_2 gas generating apparatus G will be explained.

[0034] After the preparing system A is subjected to thermal processing at from 250°C to 300°C by the heater 9, a predetermined quantity of KF 10 is loaded in the vessel 7a. The preparing system A thus loaded with KF is once again heated at from 250°C to 300°C either in vacuum or while being purged with an ultra-high purity inert gas and left to stand for from 24 hours to 48 hours to allow KF 10 therein to be dried. On this occasion, an interior of the vessel 7b is exhausted by the vacuum-exhausting system D in a state in which a vacuum piping valve 2a is opened and a valve 3a and a valve 4b are closed. By subjecting KF 10 to such heating processing for from 24 hours to 48 hours at from 250°C to 300°C while being purged by the ultra-high purity inert gas in a manner as described above, adsorbed water and crystallization water in KF 10 can be desorbed therefrom.

[0035] When thermogravimetry (hereinafter also referred to as "TG" in short) and differential thermal analysis (hereinafter also referred to as "DTA" in short) were performed, endothermic peaks were observed at 43.4°C, 64.4°C, 90.8°C and 151.6°C. The endothermic peaks at 43.4°C, 64.4°C, and 90.8°C thereamong are attributable to desorption of adsorbed water while the endothermic peak at 151.6°C is attributable to desorption of crystallization water. It is considered that the adsorbed water of KF as a starting material can easily be decomposed by a reaction represented by the formula (1). On the other hand, since not only the crystallization water corresponding to the endothermic peak which appears at 151.6°C of the DTA is strong in an interaction with KF, but also HF contained in the electrolytic bath as a major component forms a network by hydrogen bonds, it is considered that, when the crystallization water becomes extremely small in quantity, it becomes hardly diffused, thereby allowing it difficult to be removed. Therefore, as described above, by subjecting KF to thermal processing such that it is once again heated at from 250°C to 300°C while being purged by the ultra-high purity inert gas for from 24 hours to 48 hours and preferably for from 10 hours to 30 hours, the crystallization water became capable of being desorbed.

[0036] Thereafter, the resultant KF is cooled to room temperature, the valve 2a is closed, and the valve 4b and the valve 3a are opened. On this occasion, an ultra-purity inert gas piping 4 is previously heated by a line heater 15 to be at from 30°C to 35°C. Then, the HF gas cylinder 11 is heated by a heater 14 to gasify HF and, when a valve 5 is opened, HF is gradually introduced into KF 10 in the preparing system A. At such introduction, KF 10 and HF are vigorously reacted with each other to generate heat whereupon water is allowed to flow in a pipe 8 for cooling water in order to cool the KF·2HF adjusting device 7 and prevent the temperature thereof from being 100°C or more. This is performed because, when the temperature exceeds 100°C and reaches 200°C, a vigorous bumping of HF is generated to exhibit a state like an explosion.

[0037] In a manner as described above, HF is introduced into the preparing system A and, when a molar ratio of HF against KF 10 becomes higher than that of KF·HF, a supply speed of HF can be elevated. Then, after it is confirmed by a load cell 12 in the HF supplying system B that a predetermined quantity of HF was supplied into the preparing system A, a valve 5a is closed and, at the same time, the valve 4a is opened to allow the high purity inert gas to be introduced through a piping 1 and exhausted through the inert gas purging piping 3. This is performed to prevent possible flow-back into the piping 1 and solidification therein of KF·2HF which has been prepared from KF 10 to be caused by allowing HF in the piping 1 to be rapidly absorbed in KF·2HF 10.

[0038] Then, after an interior of the preparing system A is purged by the inert gas for an appropriate duration of time, the valve 4b is closed. Subsequently, the inert gas is supplied through the inert gas purging piping 3. At the same time, a valve 18 and valve 19 are opened. The preparing system A sends out KF·2HF thus prepared therein into the electrolytic cell 20 in the F_2 gas generating system C through the piping 1 by a gas pressure of the inert gas to be introduced through the inert gas purging piping 3. On this occasion, the electrolytic cell 20 has previously been subjected to thermal processing at from 250°C to 300°C to allow the adsorbed water and the like to be desorbed.

[0039] In such a manner as described above, the F_2 gas generating apparatus according to the invention can supply high purity KF·2HF which is small amount in a moisture adsorption quantity into the electrolytic cell in the F_2 gas generating apparatus without allowing high purity KF·2HF to contact with air to construct a high purity electrolytic bath, that is, KF·2HF bath inside the electrolytic cell. In such a manner as described above, an oxygen concentration in the electrolytic bath is extremely reduced.

[0040] Further, the preparing system A, the HF supplying system B, and the F_2 gas generating system C can be contained in boxes respectively in which atmospheres thereof can be controlled. In this manner, moistures in the atmospheres outside respective systems can be adjusted, and thereby oxygen to be incorporated in respective systems can be controlled. Alternatively, all of the systems, that is, the F_2 gas generating apparatus G, can be contained in one box. Furthermore, by placing all of the systems in a clean room, same effect as that to be obtained by placing the system in the box in which the atmosphere can be controlled can be obtained. As mentioned above, by controlling such contamination of oxygen, it becomes possible to more surely reduce the oxygen concentration in the F_2 gas to be generated.

[0041] Still further, the F_2 gas generating apparatus and the F_2 gas generating method according to the invention are not limited to the aforementioned embodiments.

(EXAMPLES)

[0042] Hereinafter, the F_2 gas generating apparatus according to the invention will specifically be explained with reference to Examples.

(Example 1)

[0043] In an F_2 gas generating apparatus G as shown in FIG. 1, after a preparing system A was previously subjected to thermal processing at from 250°C to 300°C by a heater 9, KF 10 was loaded in a vessel 7a. Then, the preparing system A was once again subjected to thermal processing at from 250°C to 300°C, while being purged by a high purity N_2 gas having a purity of 99.9999%, and left to stand for from 24 hours to 48 hours to allow KF 10 to be dried. Thereafter, the system A is cooled to room temperature and, then, HF was introduced into KF 10 in the preparing system A. On this occasion, water was allowed to flow in a cooling water pipe 8 for cooling a KF·2HF adjusting device 7 to be 100°C or less. Next, after it was confirmed by a load cell 12 in an HF supplying system B that a predetermined quantity of HF was supplied in the preparing system A, an interior of the preparing system A was purged by a high purity N_2 gas for an appropriate duration of time and, then, a high purity N_2 gas was supplied therein and, thereafter, such KF·2HF prepared was sent out into an electrolytic cell 20 in a F_2 gas generating system C through piping 1 to construct an electrolytic bath having a bath volume of 7 1. Subsequently, in the F_2 gas generating system C, a constant current electrolysis was performed at an applied current density of 10 A/dm^2 while using a carbon electrode and a Ni electrode as an anode and a cathode, respectively. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 650 ppm.

(Example 2)

[0044] A constant current electrolysis was performed at an applied current density of 15 A/dm^2 using KF·2HF similar to that in Example 1 as an electrolytic bath while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 450 ppm.

(Example 3)

[0045] A constant current electrolysis was performed at an applied current density of 2 A/dm^2 using KF·2HF similar to that in Example 1 as an electrolytic bath, while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 950 ppm.

(Example 4)

[0046] A constant current electrolysis was performed at an applied current density of 20 A/dm^2 using KF·2HF similar to that in Example 1 as an electrolytic bath, while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C which was contained in a box (not shown), namely, a moisture controlling device, to control moisture inside the box to be 40%. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 70 ppm.

(Comparative Example 1)

[0047] A constant current electrolysis was performed at an applied current density of 10 A/dm^2 using KF·2HF prepared in a conventional method as an electrolytic bath, while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 30000 ppm.

(Comparative Example 2)

[0048] A constant current electrolysis was performed at an applied current density of 15 A/dm^2 using KF·2HF prepared in a conventional method as an electrolytic bath, while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 25000 ppm.

(Comparative Example 3)

[0049] A constant current electrolysis was performed at an applied current density of 1 A/dm^2 using KF·2HF similar to that in Example 1 as an electrolytic bath, while using a carbon electrode as an anode and a Ni electrode as a cathode in an F_2 gas generating system C. Then, when a quantity of electricity reached about 100 Ahr, a quantity of O_2 in such F_2 gas generated was measured by gas chromatography, thereby finding it to be about 21000 ppm.

[0050] In FIG. 2, shown is a relationship among quantities of electricity in cases of Example 1, Comparative Examples 1 and 3, and a quantity of O_2 in the F_2 gas.

[0051] As shown in FIG. 2, it is found that, in Example 1 in which KF·2HF which was prepared after moisture was desorbed from KF by drying it was used as an electrolytic bath, a quantity of O_2 in the F_2 gas was small from an initial stage of F_2 gas generation.

Industrial Applicability

[0052] The present invention is constituted as described above whereupon, by using KF·2HF after KF is dried allowing adsorbed water or crystallization water to be desorbed therefrom, it becomes possible to stably generate an F_2 gas in which an oxygen concentration to be contained is extremely low from an initial stage of the F_2 gas generation.

Claims

1. An F_2 gas generating apparatus for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, being **characterized by** comprising:

   a preparing system for preparing KF·2HF from KF or KF·HF;
   an HF supplying system for supplying HF into the electrolytic bath and the preparing system; and
   an F_2 gas generating system for generating the F_2 gas by subjecting KF·2HF prepared by the preparing system to electrolysis.

2. The F_2 gas generating apparatus as set forth in Claim 1, being **characterized in that** a moisture removing device for removing moisture in said KF or KF·HF is attached to the preparing system.

3. The F_2 gas generating apparatus as set forth in Claim 1, wherein an oxygen concentration in the thus-generated F_2 gas is 2% or less.

4. An F_2 generating apparatus for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, comprising:

a preparing system for preparing KF·2HF from KF or KF·HF;
an HF supplying system for supplying HF into the electrolytic bath and the preparing system; and
an F_2 gas generating system for generating the F_2 gas by subjecting KF·2HF prepared by the preparing system to electrolysis, being **characterized by** being provided with a moisture controlling device for adjusting moisture in an atmosphere outside each of the preparing system, the HF supplying system, and the F_2 gas generating system or all the systems as a whole.

5. The F_2 gas generating apparatus as set forth in Claim 4, wherein the moisture controlling device is a box which contains each of the systems or all the systems as a whole and is capable of controlling an atmosphere inside the box.

6. An F_2 gas generating method for generating an F_2 gas by subjecting an electrolytic bath comprising KF·2HF to electrolysis, comprising the steps of:

heat-deaerating KF or KF·HF for a predetermined period of time in an atmosphere of vacuum or an inert gas in a preparing system, for preparing KF·2HF from said KF or KF·HF, which is attached with a moisture removing device for removing moisture in said KF or KF·HF;
cooling said KF or KF·HF to room temperature in an atmosphere of vacuum or the inert gas in the preparing system;
supplying HF changed into a vapor phase from an HF supplying system into said preparing system;
allowing said KF or KF·HF, and said HF to react with each other in the preparing system to generate KF·2HF;
supplying the thus-generated KF·2HF into an electrolytic cell in an F_2 gas generating system; and
Subjecting said KF·2HF to electrolysis to generate an F_2 gas having a low oxygen concentration.

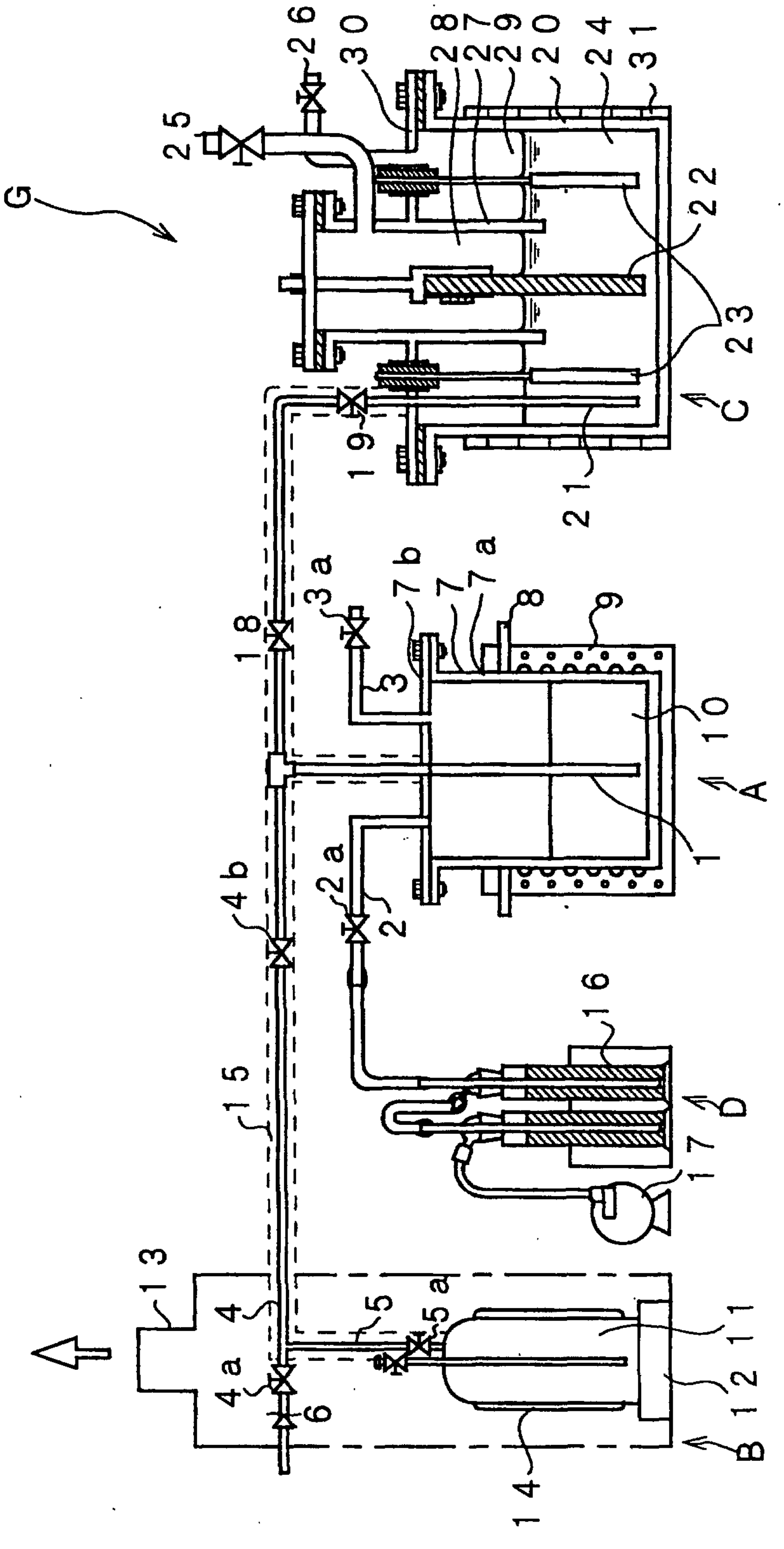
7. The F_2 gas generating method as set forth in Claim 6, wherein, in the preparing system, said KF or KF·HF is heated at from 200°C to 300°C to remove adsorbed water or crystallization water of said KF or KF·HF therefrom.

8. An F_2 gas generated by a method comprising the steps of:

heat-deaerating KF or KF-HF for a predetermined period of time in an atmosphere of vacuum or an inert gas in a preparing system, for preparing KF·2HF from KF or KF·HF, which is attached with a moisture removing device for removing moisture in said KF or KF·HF;
cooling said KF or KF·HF to room temperature in an atmosphere of vacuum or the inert gas in the preparing system;
supplying HF changed into a vapor phase from an HF supplying system into said preparing system;
allowing said KF or KF·HF, and said HF to react with each other in the preparing system to generate KF·2HF;
supplying the thus-generated KF·2HF into an electrolytic cell in an F_2 gas generating system; and
Subjecting said KF·2HF to electrolysis.

9. The F_2 gas as set forth in Claim 8, wherein an oxygen concentration is 2% or less.

FIG. 1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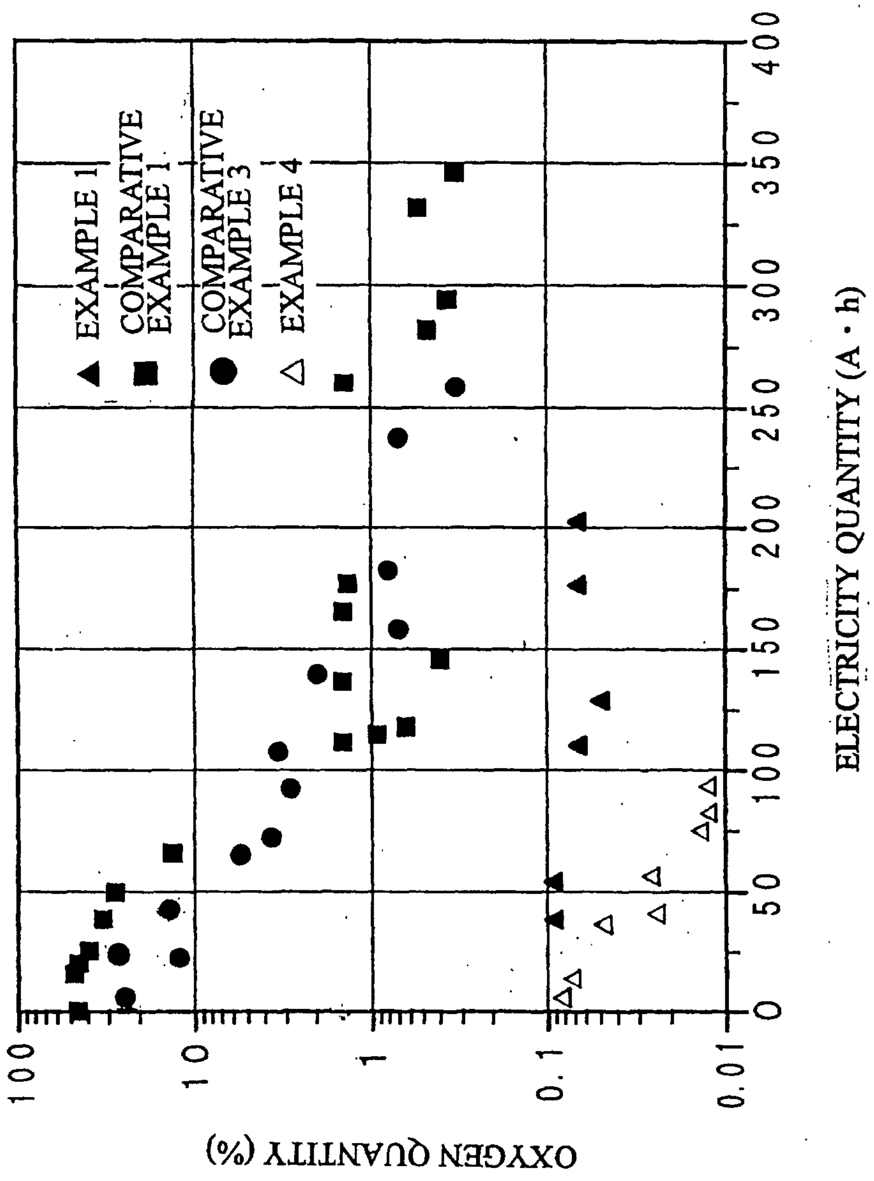
12
4a
6
14
B

FIG. 2


▲ EXAMPLE 1
■ COMPARATIVE EXAMPLE 1
● COMPARATIVE EXAMPLE 3
△ EXAMPLE 4
OXYGEN QUANTITY (%)
100
10
1
0.1
0.01
ELECTRICITY QUANTITY (A · h)
0
50
100
150
200
250
300
350
400

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/12868

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C25B1/24, 15/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C25B1/00-15/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2003
Kokai Jitsuyo Shinan Koho	1971-2003	Jitsuyo Shinan Toroku Koho	1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/77412 A1 (TOYO TANSO CO., LTD.), 18 October, 2001 (18.10.01), (Family: none)	1-9
A	JP 2000-313981 A (TOYO TANSO CO., LTD.), 14 November, 2000 (14.11.00), (Family: none)	1-9
A	JP 58-67877 A (Asahi Glass Co., Ltd.), 22 April, 1983 (22.04.83), (Family: none)	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 04 March, 2003 (04.03.03)	Date of mailing of the international search report 18 March, 2003 (18.03.03)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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