

Apparatus for the generation and supply of fluorine gas

Field of the Invention

This invention relates to an apparatus that is disposed in the gas supply system of a semiconductor processing system and that generates and supplies fluorine gas. 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 or to clean the interior of process compartments, which are not necessarily limited to semiconductor processes.

Fluorine-type process gases are generally made available to the gas supply system of a semiconductor processing system as an already prepared fluorine compound filled in a cylinder. Gases of this type are seldom produced on-site from their essential precursors, e.g., fluorine. The reasons for this relate not just to problems with the reliability of the gas composition, but also to the extreme danger associated with placing a cylinder filled to high pressures (typically at least 5 kg/cm^2) with a strong oxidizer such as fluorine in the gas supply system of a semiconductor processing system.

United States Patent No. 5,688,384, on the other hand, discloses an apparatus that automatically controls the on/off switching of fluorine gas generation in response to demand. As its fluorine gas generation module this apparatus uses an electrolytic cell

that generates fluorine gas by the electrolysis of hydrogen fluoride. Since such electrolytic-type apparatuses can as necessary produce fluorine gas at near atmospheric pressure, they can avoid the safety problems associated with the installation of fluorine cylinders.

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Problems to Be Solved by the Invention

When a fluorine gas-generating and -supply apparatus as described above is placed in the gas supply system of a semiconductor processing system, it is also necessary to provide a back-up means in order to prevent perturbations in the operation of the main processing apparatus even when abnormalities occur in the fluorine gas-generating and -supply apparatus. In a typical strategy, two fluorine gas-generating and -supply apparatuses are installed in a gas supply system and are operated in rotation as the online apparatus and back-up apparatus. This back-up strategy, however, causes high initial costs and high operating costs for the gas supply system. Moreover, while fluorine cylinders can also be used as a back-up means, safety problems are incurred by the disposition of high-pressure fluorine cylinders in the gas supply system of a semiconductor processing system.

This invention was developed in view of the problems identified above for the prior art. The object of this invention is to provide a fluorine gas-generating and -supply apparatus that is disposed in the gas supply system of a semiconductor processing system and that in the event of abnormalities in the apparatus enables back up by a safe and inexpensive structure.

A particular object of this invention is to provide an apparatus that can generate and supply fluorine gas both on-site and on-demand. As used herein, on-site means that the mechanism for generating and supplying the fluorine gas 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.

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Means Solving the Problems

The first aspect of this invention is an apparatus that generates and supplies fluorine gas and is disposed in the gas supply system of a semiconductor processing system, said apparatus being characteristically provided with an electrolytic cell that generates fluorine gas by the electrolysis of hydrogen fluoride in
5 an electrolytic bath comprising hydrogen fluoride-containing molten salt,
a cylinder that stores a substitute gas selected from the group consisting of nitrogen fluoride, sulfur fluoride, and chlorine fluoride,
a gas switching section that is connected to the electrolytic cell and cylinder and that selectively supplies a gas utilization section with fluorine gas from the electrolytic
10 cell or substitute gas from the cylinder,
an electrolytic cell detector that detects the state of the electrolytic cell, and
a controller that, upon detection of an abnormal state at the electrolytic cell by the electrolytic cell detector, exercises control on the gas switching section so as to feed the substitute gas from the cylinder to the gas utilization section.

15 The second aspect of this invention is an apparatus in accordance with the first aspect with the additional characteristic feature that the electrolytic cell detector detects a state that is representative of the composition of the electrolytic bath.

The third aspect of this invention is an apparatus in accordance with the second aspect with the additional characteristic feature that the electrolytic cell detector detects
20 a state selected from the electrical current characteristics, liquid level, and temperature of the electrolytic bath.

The fourth aspect of this invention is an apparatus in accordance with any of the first to third aspects, characterized in that the apparatus is additionally provided with a path detector that can detect an abnormal state in the gas supply path that supplies
25 fluorine gas from the electrolytic cell to the gas utilization section and in that the controller, upon detection of an abnormal state at the electrolytic cell by the electrolytic cell detector or upon detection of an abnormal state in the gas supply path by the path detector, exercises control on the gas switching section so as to feed the substitute gas from the cylinder to the gas utilization section.

The fifth aspect of this invention is an apparatus that generates and supplies fluorine gas and is disposed in the gas supply system of a semiconductor processing system, said apparatus being characteristically provided with an electrolytic cell that generates fluorine gas by the electrolysis of hydrogen fluoride in
5 an electrolytic bath comprising hydrogen fluoride-containing molten salt,
a cylinder that stores a substitute gas selected from the group consisting of nitrogen fluoride, sulfur fluoride, and chlorine fluoride,
a gas switching section that is connected to the electrolytic cell and cylinder and that selectively supplies a gas utilization section with fluorine gas from the electrolytic
10 cell or substitute gas from the cylinder,
a path detector that can detect an abnormal state in the gas supply path that supplies fluorine gas from the electrolytic cell to the gas utilization section, and
a controller that, upon detection of an abnormal state in the gas supply path by the path
15 detector, exercises control on the gas switching section so as to feed the substitute gas from the cylinder to the gas utilization section.

The sixth aspect of this invention is an apparatus in accordance with the fourth or fifth aspect, characterized in that the gas supply path is provided with a buffer section that controls the pressure and flow rate of the fluorine gas that is supplied from the electrolytic cell to the gas switching section and in that the path detector is provided
20 with a buffer detector that detects the state of the buffer section.

The seventh aspect of this invention is an apparatus in accordance with the sixth aspect, characterized in that the buffer section is provided with a compressor that pressurizes the fluorine gas from the electrolytic cell and in that the buffer detector detects the operational status of the compressor.

25 The eighth aspect of this invention is an apparatus in accordance with the sixth aspect, characterized in that the buffer section is provided with a buffer tank that temporarily stores fluorine gas from the electrolytic cell and in that the buffer detector detects the pressure within the buffer tank.

30 The ninth aspect of this invention is an apparatus in accordance with the sixth aspect, characterized in that the buffer section is provided with a flow controller that supplies fluorine gas from the electrolytic cell to the gas switching section at a specified

flow rate and in that the buffer detector detects the fluorine gas flow rate at said flow controller.

The tenth aspect of this invention is an apparatus in accordance with any of the first through ninth aspects, characterized in that the substitute gas comprises chlorine fluoride.

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

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 an embodiment of the inventive apparatus for the generation and supply of fluorine gas. This semiconductor processing system contains a semiconductor processing apparatus **10** that executes a process, such as film formation, etching, or diffusion, on a target substrate such as 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.

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 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 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.

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 gas 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 generates fluorine gas-type process gas by a reaction process.

An inventive apparatus **30** for the generation and supply of fluorine gas is connected in the embodiment under consideration to the flow management section **22** and the gas production section **26**. More specifically, this generation and supply apparatus **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 chlorine.

The generation and supply apparatus **30** contains an electrolytic cell **34** that generates fluorine gas (F_2) by the electrolysis of hydrogen fluoride in 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 Fremy's salt. The electrolytic cell **34** is connected to a hydrogen fluoride source **32** that supplies hydrogen fluoride, the starting material that undergoes depletion. A detector **36** is disposed within the electrolytic cell **34** for the purpose of detecting, as a state representative of changes in the composition of the electrolytic bath, the electrical current characteristics, liquid level, temperature, etc., of the electrolytic bath. The detection results generated by the detector **36** are fed to a controller **40**. The electrolytic cell **34** is replenished with hydrogen fluoride — the consumable starting material — from the hydrogen fluoride source **32** based on the detection result yielded by the detector **36** and under control by the controller **40** using a quantitative threshold value as the criterion.

The fluorine gas generated by the electrolytic cell **34** is fed to a gas switching section **56** across a buffer section **42**; the purpose of the buffer section **42** is to control the pressure and flow rate of the fluorine gas present in the supply conduit **38**. This buffer section **42** is provided with a compressor **44** in order to pressurize the fluorine gas generated at substantially atmospheric pressure at the electrolytic cell **34**, a buffer tank **46** that temporarily holds the fluorine gas, and a flow controller **48** that feeds fluorine gas from the buffer tank **46** to the gas switching section **56** at a specified flow rate. An operations detector **50** is disposed at the compressor **44** in order to detect the

operational status of the compressor **44**. A pressure detector **52** is disposed at the buffer tank **46** in order to detect the pressure within the buffer tank **46**. A flow rate detector **54** is disposed at the flow controller **48** in order to detect the flow rate of the fluorine gas in the flow controller **48**. The detection results generated by these
5 detectors **50**, **52**, and **54** are fed to the controller **40**.

A back-up section **60** is provided against the contingency of the appearance of abnormalities in the electrolytic cell **34** (fluorine gas generator), supply conduit that runs from the electrolytic cell **34** to the gas utilization section, or fluorine gas supply path (including the buffer section **42**). This back-up section **60** is provided with a cylinder **62**
10 (or cylinder group) that holds the substitute gas used as a fluorine gas substitute. The substitute gas exiting the valve **64** of the cylinder **62** is supplied, adjusted to a specified flow rate by the flow controller **66**, to the gas switching section **56**.

The substitute gas is selected from the group consisting of nitrogen fluoride, sulfur fluoride, and chlorine fluoride. Among these, the use of nitrogen fluoride as the
15 substitute gas is particularly desirable due to its low reactivity at room temperature and because it is a relatively safe gas. When nitrogen fluoride (NF_3) is used as the substitute gas, it will be desirable to configure the flow controller to automatically bring the nitrogen fluoride flow rate to approximately two-thirds the fluorine flow rate when a switch is made from fluorine gas to nitrogen fluoride. This configuration can maintain a
20 constant processing capacity at the location where the substitute gas is used. The preferred substitute gas will also vary as a function of the type of process and the nature of the semiconductor processing apparatus. For example, nitrogen fluoride (NF_3) is preferably used as the substitute gas in the case of plasma cleaning while chlorine fluoride is preferably used as the substitute gas in the case of thermal cleaning.

25 The controller **40** controls the gas switching section **56** in such a manner that substitute gas is supplied to the gas utilization section (the main process facility) from the cylinder **62** when an abnormal state is detected in the electrolytic cell **34** and/or in the buffer section **42**. Accompanying this gas switching at the gas switching section **56**, the controller **40** also adjusts the status of the valve **64** on the cylinder **62** and adjusts

the ON/OFF status of the operation of the buffer section **42** (for example, the operation of the compressor **44**).

An abnormal state in the electrolytic cell **34** is sensed by the electrolytic cell detector **36**. In specific terms, the detector **36** detects, for example, the electric current characteristics, liquid level, or temperature of the electrolytic bath as a state representative of changes in the composition of the electrolytic bath and transmits the result to the controller **40**. The controller **40** then compares the detected value with a preliminarily set threshold value and determines whether the electrolytic bath **34** resides in a normal state or has entered into an abnormal state.

Likewise, an abnormal state at the buffer section **42** is detected by means of three detectors making up the buffer detector, i.e., the operations detector **50**, the pressure detector **52**, and the flow rate detector **54**. In specific terms, these detectors **50**, **52**, and **54** detect, respectively, the operational status of the compressor **44**, the pressure within the buffer tank **46**, and the fluorine gas flow rate at the flow controller **48**, and transmit their results to the controller **40**. The controller then compares these detected values with preliminarily set threshold values and determines whether the buffer section **42** resides in a normal state or has entered into an abnormal state.

Thus, the detectors **36**, **50**, **52**, and **54** are respectively disposed in each of the main constituent members on the fluorine gas generation and supply side, which enables the location and type of an abnormal state on the generation and supply side to be recognized by the controller **40**. This enables the controller **40** to carry out, in correspondence to the location and type of an abnormal condition, a variety of information processing in connection with control of the gas switching section **56**, including, for example, the decision on the timing of gas switching, the execution prior to gas switching of a program that checks the status of each main constituent member, transmission of an alarm signal that alerts the operator of the location, etc., of the abnormal state, and a manual operation indication.

The generation and supply apparatus **30** shown in Figure 1 uses a cylinder of the substitute gas as its back-up section rather than providing an additional iteration of the fluorine gas generation and supply structure that runs from the electrolytic cell **34** up to and including the buffer section **42**. This results in lower initial costs and lower

operating costs for the gas supply system. The substitute gas selected from the group consisting of nitrogen fluoride, sulfur fluoride, and chlorine fluoride, while supplied filled in a cylinder, does not produce the problems associated with high-pressure fluorine cylinders and is therefore preferred from a safety standpoint.

Figure 3 contains a schematic diagram of a fluorine gas generation and supply apparatus that is another embodiment of this invention. In this embodiment the controller **40** controls the gas switching section **56** with reference only to the detectors that detect an abnormal state in the gas supply path that supplies fluorine gas from the electrolytic cell **34** to the gas utilization section, and specifically only to the detection results for the state of the buffer section **42** generated by the detectors **50**, **52**, and **54**. The detection results for the liquid level of the electrolytic bath generated by the detector **36** are not transmitted to the controller **40**, but rather are used by a controller **70** for replenishment of the electrolytic cell **34** with hydrogen fluoride from the hydrogen fluoride source **32**.

An abnormal state at the electrolytic cell **34** will generally also cause an abnormality or perturbation in the status of the generated fluorine gas. As a consequence, the basic information necessary for controlling the gas switching section **56** can be obtained by sensing an abnormal state in the gas supply path that supplies fluorine gas from the electrolytic cell **34** to the gas utilization section, for example, an abnormal state for the fluorine gas in the downstream buffer section **42**. However, in this case it will be desirable to have enabled a separate sensing of any abnormal state at the electrolytic cell **34** unrelated to control of the gas switching section **56**.

Figure 4 contains a schematic diagram of a fluorine gas generation and supply apparatus that is another embodiment of this invention. This embodiment lacks detectors for detecting abnormal conditions at the compressor **44**, buffer tank **46**, and flow controller **48** in the buffer section **42**. A detector **72** that detects the pressure and flow rate in the gas supply conduit is provided instead to function as a detector of abnormal conditions in the gas supply path that feeds fluorine gas from the electrolytic cell **34** to the gas utilization section. The controller **40** exercises control on the gas switching section **56** with reference not only to the detection result for the status of the electrolytic cell **34** afforded by the detector **36**, but also to the detection results afforded

by the detector **72** for the pressure and flow rate in the fluorine gas supply conduit. As illustrated by the dash-and-dot line in Figure 4, the detector **72** can also be provided downstream from the gas switching section **56**.

An abnormal state in the buffer section **42** will generally also cause an abnormal state or condition in the pressure and flow rate in the fluorine gas supply conduit. As a consequence, the basic information necessary for controlling the gas switching section **56** can be obtained by sensing an abnormal state in the pressure and flow rate within the fluorine gas supply conduit downstream from the buffer section **42**.

The gas switching section **56** may also be disposed between the electrolytic cell **34** and the buffer section **42** in each of the embodiments discussed above. In such a case the controller **40** will exercise control on the gas switching section **56** with reference only to the detection result afforded by the detector **36** for the state of the electrolytic cell **34**. Moreover, while the fluorine gas is fed either to the flow management section **22** or to the gas production section **26** in the embodiments discussed above, this gas can be supplied directly to the process chamber **12** separately from other process gases. The gas production section **26** can also be configured to produce other fluorine-type process gases instead of interhalogen fluorine compound gases. A cylinder of fluorine gas can be used in each of the embodiments elaborated hereinabove in place of the cylinder of substitute gas insofar as the corresponding safety issues can be resolved.

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 such modifications and alterations also fall within the scope of this invention.

Advantageous Effects of the Invention

As has been described in detail hereinabove, this invention provides a fluorine gas-generation and -supply apparatus that is disposed in the gas supply system of a semiconductor processing system and that in the event of abnormalities in the apparatus enables back up by a safe and inexpensive structure.

Brief Description of the Drawings

Figure 1 contains a schematic drawing that illustrates a semiconductor processing system that incorporates an apparatus for the generation and supply of fluorine gas that is an embodiment of this invention.

5 Figure 2 contains a schematic drawing that illustrates an exemplary modification of the semiconductor processing apparatus that is used in combination with the gas supply system shown in Figure 1.

Figure 3 contains a schematic drawing that illustrates an apparatus for the generation and supply of fluorine gas that is another embodiment of this invention.

10 Figure 4 contains a schematic drawing that illustrates an apparatus for the generation and supply of fluorine gas that is yet another embodiment of this invention.

Claims

1. Apparatus that generates and supplies fluorine gas and is disposed in the gas supply system of a semiconductor processing system, said apparatus being
5 characteristically provided with
an electrolytic cell that generates fluorine gas by the electrolysis of hydrogen fluoride in
an electrolytic bath comprising hydrogen fluoride-containing molten salt,
a cylinder that stores a substitute gas selected from the group consisting of nitrogen
fluoride, sulfur fluoride, and chlorine fluoride,
10 a gas switching section that is connected to the electrolytic cell and cylinder and that
selectively supplies a gas utilization section with fluorine gas from the electrolytic
cell or substitute gas from the cylinder,
an electrolytic cell detector that detects the state of the electrolytic cell, and
a controller that, upon detection of an abnormal state at the electrolytic cell by the
15 electrolytic cell detector, exercises control on the gas switching section so as to
feed the substitute gas from the cylinder to the gas utilization section.
2. The apparatus of claim 1 for the generation and supply of fluorine gas,
characterized in that the electrolytic cell detector detects a state that is representative of
20 the composition of the electrolytic bath.
3. The apparatus of claim 2 for the generation and supply of fluorine gas,
characterized in that the electrolytic cell detector detects a state selected from the
electrical current characteristics, liquid level, and temperature of the electrolytic bath.
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4. Apparatus according to any of claims 1 to 3 for the generation and supply of
fluorine gas, characterized in that the apparatus is additionally provided with a path
detector that can detect an abnormal state in the gas supply path that supplies fluorine
gas from the electrolytic cell to the gas utilization section and in that the controller, upon
30 detection of an abnormal state at the electrolytic cell by the electrolytic cell detector or
upon detection of an abnormal state in the gas supply path by the path detector,

exercises control on the gas switching section so as to feed the substitute gas from the cylinder to the gas utilization section.

5 5. Apparatus that generates and supplies fluorine gas and is disposed in the gas supply system of a semiconductor processing system, said apparatus being characteristically provided with

an electrolytic cell that generates fluorine gas by the electrolysis of hydrogen fluoride in an electrolytic bath comprising hydrogen fluoride-containing molten salt,

10 a cylinder that stores a substitute gas selected from the group consisting of nitrogen fluoride, sulfur fluoride, and chlorine fluoride,

a gas switching section that is connected to the electrolytic cell and cylinder and that selectively supplies a gas utilization section with fluorine gas from the electrolytic cell or substitute gas from the cylinder,

15 a path detector that can detect an abnormal state in the gas supply path that supplies fluorine gas from the electrolytic cell to the gas utilization section, and

a controller that, upon detection of an abnormal state in the gas supply path by the path detector, exercises control on the gas switching section so as to feed the substitute gas from the cylinder to the gas utilization section.

20 6. The apparatus according to claim 4 or 5 for the generation and supply of fluorine gas, characterized in that the gas supply path is provided with a buffer section that controls the pressure and flow rate of the fluorine gas that is supplied from the electrolytic cell to the gas switching section and in that the path detector is provided with a buffer detector that detects the state of the buffer section.

25 7. The apparatus according to claim 6 for the generation and supply of fluorine gas, characterized in that the buffer section is provided with a compressor that pressurizes the fluorine gas from the electrolytic cell and in that the buffer detector detects the operational status of the compressor.

8. The apparatus according to claim 6 for the generation and supply of fluorine gas, characterized in that the buffer section is provided with a buffer tank that temporarily stores fluorine gas from the electrolytic cell and in that the buffer detector detects the pressure within the buffer tank.

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9. The apparatus according to claim 6 for the generation and supply of fluorine gas, characterized in that the buffer section is provided with a flow controller that supplies fluorine gas from the electrolytic cell to the gas switching section at a specified flow rate and in that the buffer detector detects the fluorine gas flow rate at said flow controller.

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10. Apparatus according to any of claims 1 through 9 for the generation and supply of fluorine gas, characterized in that the substitute gas comprises chlorine fluoride.