

IN SITU CHEMICAL GENERATOR AND METHOD

This invention pertains generally to the fabrication of semiconductor devices and, more particularly, to a method and apparatus for generating important chemical species in the deposition, etching, cleaning, and growth of various materials and layers.

- 5 It is in general an object of the invention to provide a new and improved chemical generator and method for generating chemical species at or near the location where they are to be used.

- Another object of the invention is to provide a chemical generator and method of the above character which are particularly suitable for
10 generating chemical species for use in the fabrication of semiconductor devices.

- These and other objects are achieved in accordance with the invention by providing a chemical generator and method for generating a chemical species at a point of use such as the chamber of a reactor in which a
15 workpiece such as a semiconductor wafer is to be processed. The species is generated by creating free radicals, and combining the free radicals to form the chemical species at the point of use.

Figure 1 is a diagrammatic view of one embodiment of an in situ chemical generator incorporating the invention.

Figure 2 is an enlarged cross-sectional view taken along line 2—2 of Figure 1.

As illustrated in Figure 1, the chemical generator includes a free radical source 11 which has one or more chambers in which free radicals are created and delivered for recombination into stable species. In the embodiment illustrated, the source has three chambers which are formed by elongated, concentric tubes 12 - 14. Those chambers include a first annular chamber 16 between the outermost tube 12 and the middle tube 13, a second annular chamber 17 between middle tube 13 and the innermost tube 14, and a third chamber 18 inside the innermost tube. The tubes are fabricated of a material such as ceramic, quartz or metal.

The number of tubes which are required in the generator is dependent upon the chemical species being generated and the reaction by which it is formed, with a separate chamber usually, but not necessarily, being provided for each type of free radical to be used in the process.

Gases or other precursor compounds from which the free radicals are formed are introduced into the chambers from sources 21 - 23 or by other suitable means. Such precursors can be in gaseous, liquid and/or solid form, or a combination thereof.

A plasma is formed within the chambers to create the free radicals, and in the embodiment illustrated, the means for generating the plasma includes an induction coil 26 disposed concentrically about the tubes, a radio frequency (RF) power generator 27 connected to the coil by a matching network 28, and a Tesla coil 29 for striking an arc to ignite the plasma. The plasma can, however, be formed by any other suitable means such as RF electrodes or microwaves.

Downstream of the tubes, the free radicals are recombined to form the desired species. In the embodiment illustrated, recombination takes place in a chamber 31 which is part of a reactor 32 in which a semiconductor wafer 33 is being processed. Recombination can be promoted by any
5 suitable means such as by cooling 36 and/or by the use of a catalyst 37.

Cooling can be effected in a number of ways, including the circulation of a coolant such as an inert gas, liquid nitrogen, liquid helium or cooled water through tubes or other suitable means in heat exchange relationship with the reacting gases. It can also be effected by passing the gases through
10 an expansion nozzle to lower their temperature, or by the use of either a permanent magnet or an electromagnet to converge and then subsequently expand the plasma to lower its temperature.

A catalyst can be placed either in the cooling zone or downstream of it. It can, for example, be in the form of a thin film deposited on the wall of
15 a chamber or tube through which the reacting gases pass, a gauze placed in the stream of gas, or a packed bed. The important thing is that the catalyst be situated in such a way that all of the gas is able to contact its surface and react with it.

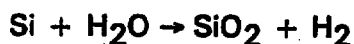
If desired, monitoring equipment such as an optical emission spectrometer
20 can be provided for monitoring parameters such as species profile and steam generation.

In the embodiment illustrated, the chemical generator is part of the reactor, and the species produced is formed in close proximity to the wafer being processed. That is the preferred application of the generator, although it
25 can also be used in stand-alone applications as well. It can be added to existing process reactors as well as being constructed as an integral part of new reactors, or as a stand-alone system.

The generator can be employed in a wide variety of applications for generating different species for use in the fabrication of semiconductor devices, some examples of which are given below.

Oxidation

- 5 Steam for use in a wet oxidation process for producing SiO_2 according to the reaction



- can be generated in accordance with the invention by admitting H_2 and O_2 into one of the plasma generating chambers. When the plasma is struck,
10 the H_2 and O_2 react to form steam in close proximity to the silicon wafer. If desired, oxygen admitted alone or with N_2 and/or Ar can be used to produce ozone (O_3) to lower the temperature for oxidation and/or improve device characteristics.

- It is known that the use of NO in the oxidation of silicon with O_2 can
15 improve the device characteristics of a transistor by improving the interface between silicon and silicon oxide which functions as a barrier to boron. Conventionally, NO is supplied to the reactor chamber from a source such as a cylinder, and since NO is toxic, special precautions must be taken to avoid leaks in the gas lines which connect the source to the reactor. Also,
20 the purity of the NO gas is a significant factor in the final quality of the interface formed between the silicon and the silicon oxide, but it is difficult to produce extremely pure NO.

With the invention, highly pure NO can be produced at the point of use through the reaction

- 25
$$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$$

by admitting N_2 and O_2 to one of the chambers and striking a plasma. When the plasma is struck, the N_2 and O_2 combine to form NO in close proximity to the wafer. Thus, NO can be produced only when it is needed,

and right at the point of use, thereby eliminating the need for expensive and potentially hazardous gas lines.

NO can also be produced by other reactions such as the cracking of a molecule containing only nitrogen and oxygen, such as N₂O. The NO is produced by admitting N₂O to the plasma chamber by itself or with O₂. If desired, a gas such as Ar can be used as a carrier gas in order to facilitate formation of the plasma.

N₂O can be cracked by adding a small amount of O₂ to the N₂O to form NO₂, which then dissociates to NO and O₂. In rapid thermal processing chambers and diffusion furnaces where temperatures are higher than the temperature for complete dissociation of NO₂ to NO and O₂ (620°C), the addition of NO₂ will assist in the oxidation of silicon for gate applications where it has been found that nitrogen assists as a barrier for boron diffusion. At temperature below 650°C, a catalyst can be used to promote the conversion of NO₂ to NO and O₂. If desired, nitric acid can be generated by adding water vapor or additional H₂ and O₂ in the proper proportions.

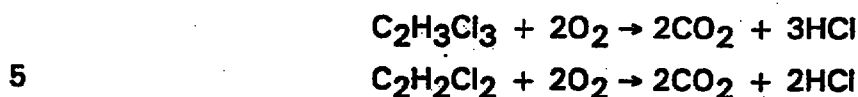
Similarly, NH₃ and O₂ can be combined in the plasma chamber to produce NO and steam at the point of use through the reaction

$$\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}.$$

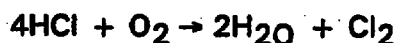
By using these two reagent gases, the efficacy of NO in the wet oxidation process can be mimicked.

It is often desired to include chlorine in an oxidation process because it has been found to enhance oxidation as well as gettering unwanted foreign contaminants. Using any chlorine source such as TCA or DCE, complete combustion can be achieved in the presence of O₂, yielding HCl + H₂O + CO₂. Using chlorine alone with H₂ and O₂ will also yield HCl and H₂O.

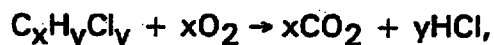
When TCA or DCE is used in oxidation processes, it is completely oxidized at temperatures above 700°C to form HCl and carbon dioxide in reactions such as the following:



The HCl is further oxidized in an equilibrium reaction:



10 Decomposition of various organic chlorides with oxygen at elevated temperatures provides chlorine and oxygen-containing reagents for subsequent reactions in, *e.g.*, silicon processing. Such decomposition is generally of the form



where *x* and *y* are typically 2, 3 or 4.

15 All of the foregoing reactions can be run under either atmospheric or subatmospheric conditions, and the products can be generated with or without a catalyst such as platinum.

20 The invention can also be employed in the cleaning of quartz tubes for furnaces or in the selective etching or stripping of nitride or polysilicon films from a quartz or silicon oxide layer. This is accomplished by admitting a reactant containing fluorine and chlorine such as a freon gas or liquid, *i.e.* $\text{C}_x\text{H}_y\text{F}_z\text{Cl}_q$, where

$$x = 1, 2, \dots$$

$$y = 0, 1, \dots$$

$$z = 0, 1, \dots$$

25 $q = 0, 1, \dots$

and the amount of fluorine is equal to or greater than the amount of chlorine. It is also possible to use a mixture of fluorinated gases (*e.g.*, CHF_3 , CF_4 , etc.) and chlorinated liquids (*e.g.*, CHCl_3 , CCl_4 , etc.) in a ratio which provides effective stripping of the nitride or polysilicon layer.

Dielectric Films

Other dielectric films can be formed from appropriate precursor gases. Polysilicon can be formed using SiH_4 and H_2 , or silane alone. The silane may be introduced downstream of the generator to avoid nucleation and particle formation.

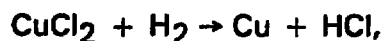
Silicon nitride can be formed by using NH_3 or N_2 with silane (SiH_4) or one of the higher silanes, *e.g.* Si_2H_6 . The silane can be introduced downstream of the generator to avoid nucleation and particle formation.

In addition to gases, the chemical generator is also capable of using liquids and solids as starting materials, so that precursors such as TEOS can be used in the formation of conformal coatings. Ozone and TEOS have been found to be an effective mixture for the deposition of uniform layers.

Metal and Metal Oxide Films

Metal and metal oxide films can be deposited via various precursors in accordance with the invention. For example, Ta_2O_5 films which are used extensively in memory devices can be formed by generating a precursor such as TaCl_5 via reduction of TaCl_5 , followed by oxidation of the TaCl_5 to form Ta_2O_5 . In a more general sense, the precursor from which the Ta_2O_5 is generated can be expressed as TaX_m , where X is a halogen species, and m is the stoichiometric number.

Copper can be deposited as a film or an oxide through the reaction



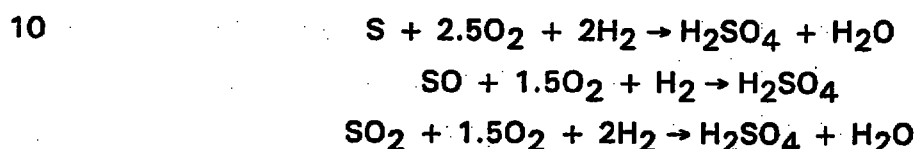
and other metals can be formed in the same way. Instead of a gaseous precursor, a solid precursor such as Cu or another metal can also be used.

Wafer and Chamber Cleaning

With the invention, organic residue from previous process steps can be effectively removed by using O_2 to form ozone which is quite effective in

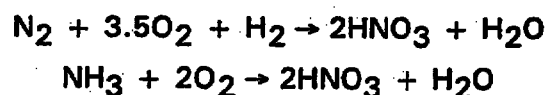
the removal of organic contaminants. In addition, reacting H₂ with an excess of O₂ will produce steam and O₂ as well as other oxygen radicals, all of which are effective in eliminating organic residue. The temperature in the chamber should be below about 700°C if a wafer is present, in order to prevent oxide formation during the cleaning process.

Sulfuric acid, nitric acid and hydrofluoric acid for use in general wafer cleaning are also effectively produced with the invention. Sulfuric acid (H₂SO₄) is generated by reacting either S, SO or SO₂ with H₂ and O₂ in accordance with reaction such as the following:



then quickly quenching the free radicals thus formed with or without a catalyst.

Nitric acid (HNO₃) is generated by reacting NH₃ with H₂ and O₂, or by a reaction such as the following:



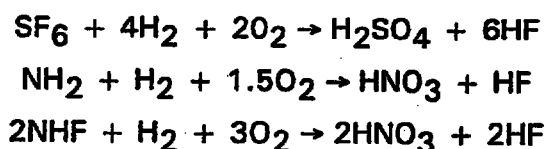
Hydrofluoric acid is generated by co-reacting H₂ and O₂ with a compound containing fluorine such as NF₃ or C_xH_yF_z, where

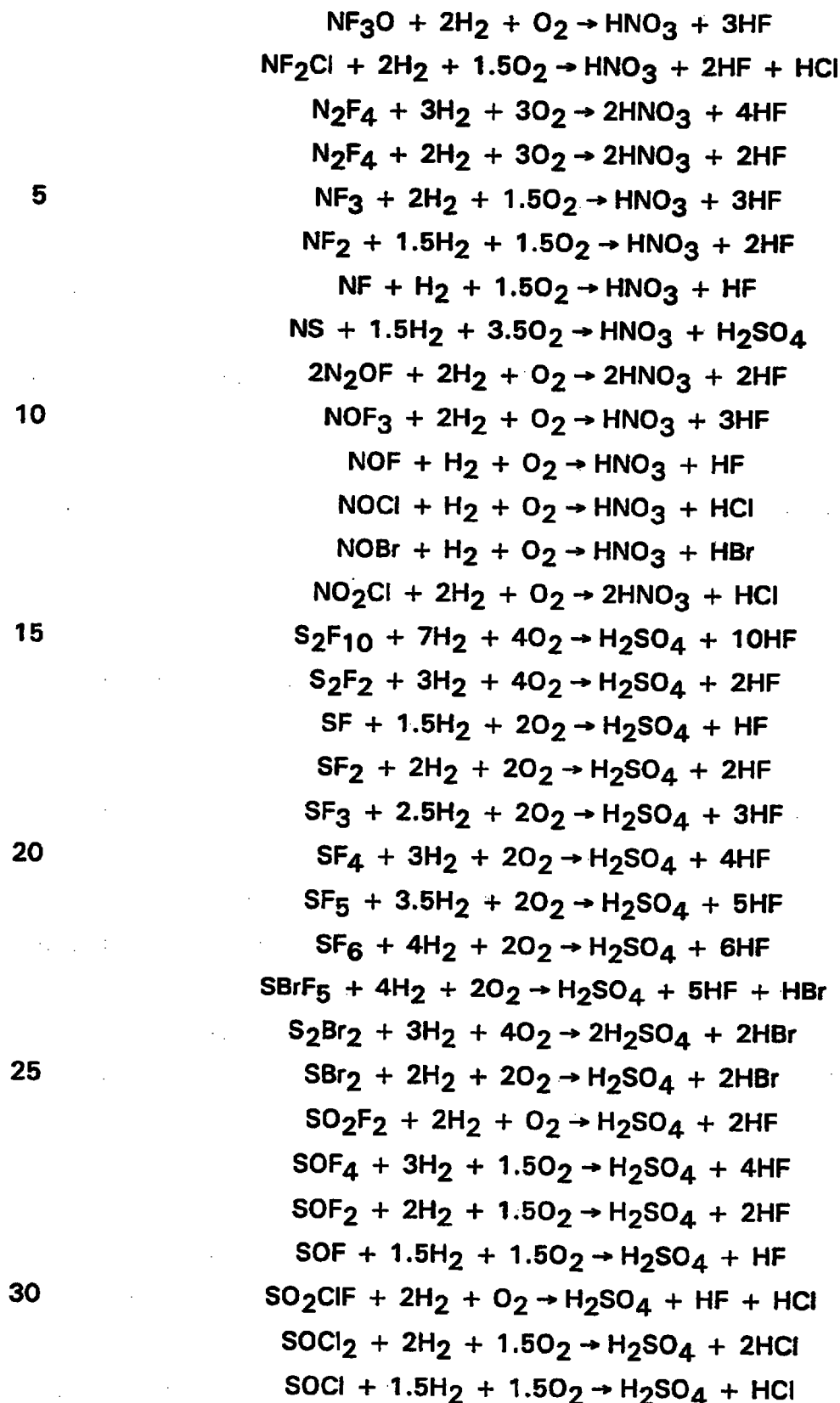
$$x = 1, 2, \dots$$

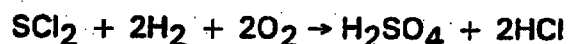
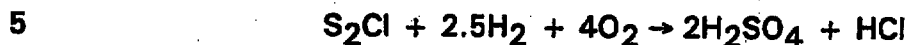
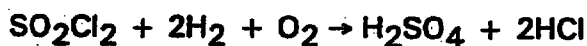
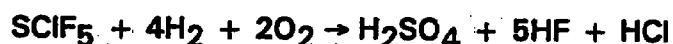
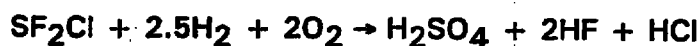
$$y = 0, 1, \dots$$

$$z = 1, 2, \dots$$

Mixed acids can be generated from a single precursor by reactions such as the following:







These are but a few examples of the many reactions by which mixed acids can be generated in accordance with the invention. Including more H_2 and O_2 in the reactions will allow steam to be generated in addition to the mixtures of acids.

In order to devolitize the various resultant products of the reaction of HCl , HF , H_2SO_4 or HNO_3 , either H_2O or H_2 and O_2 can be co-injected to form steam so that the solvating action of water will disperse in solution in the products. The temperature of the water must be cool enough so that a thin film of water will condense on the wafer surface. Raising the temperature of the water will evaporate the water solution, and spinning the wafer will further assist in the removal process.

Native Oxide Removal

The native oxide which is ever present when a silicon wafer is exposed to the atmosphere can be selectively eliminated by a combination of HF and steam formed by adding a fluorine source such as NF_3 or CF_4 to the reagent gases H_2 and O_2 . In order for the native oxide elimination to be most effective, the reaction chamber should be maintained at a pressure below one atmosphere.

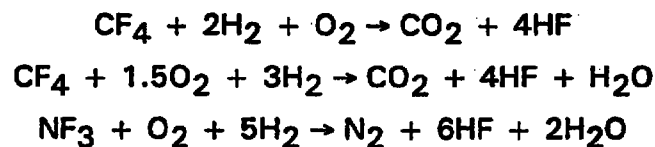
Photoresist Stripping

H_2 and O_2 can also be reacted to form steam for use in the stripping of photoresist which is commonly used in patterning of silicon wafers in the manufacture of integrated circuits. In addition, other components such as HF , H_2SO_4 and HNO_3 which are also generated with the invention can be

used in varying combinations with the steam to effectively remove photoresist from the wafer surface. Hard implanted photoresist as well as residues in vias can also be removed with steam in combination with these acids.

- 5 SO_3 for use in the stripping of organic photoresist can be generated by adding O_2 to SO_2 . Similarly, as discussed above, N_2O can be converted to NO_2 , a strong oxidizing agent which can also be used in the stripping of photoresist.

- 10 Hydrofluoric acid for use in the stripping of photoresist can be generated *in situ* in accordance with any of the following reactions:



- 15 It is apparent from the foregoing that a new and improved chemical generator and method have been provided. While only certain presently preferred embodiments have been described in detail, as will be apparent to those familiar with the art, certain changes and modifications can be made without departing from the scope of the invention as defined by the following claims.

**CLAIMS**

1. In apparatus for generating a chemical species for use in processing a semiconductor wafer in a reaction chamber: a source of free radicals, and means for combining free radicals from the source to form the chemical species in the chamber in close proximity to the wafer.
2. The apparatus of Claim 1 wherein the source of free radicals includes means for forming an ionized plasma of precursor materials to create the free radicals.
3. The apparatus of Claim 1 wherein the source of free radicals includes a plurality of elongated, concentric tubes which define chambers in which the free radicals are formed.
4. The apparatus of Claim 3 wherein the tubes include a first tube in which a first chamber is formed, a second tube surrounding the first tube, with a second chamber being formed between the first and second tubes, and a third tube surrounding the second tube, with a third chamber being
5 formed between the second and third tubes.
5. The apparatus of Claim 3 wherein the source of free radicals further includes an induction coil disposed concentrically about the tubes, and means for applying RF power to the coil.
6. The apparatus of Claim 1 wherein the means for combining the free radicals includes means for cooling the free radicals to promote formation of the chemical species.
7. The apparatus of Claim 1 wherein the means for combining the free radicals includes a catalyst which promotes formation of the chemical species.



8. In apparatus for generating a chemical species at a point of use where a workpiece is to be processed with the species: a source of free radicals, and means for combining free radicals from the source to form the chemical species at the point of use.

9. The apparatus of Claim 8 wherein the source of free radicals includes means for forming an ionized plasma of precursor materials to create the free radicals.

10. The apparatus of Claim 8 wherein the source of free radicals includes a plurality of elongated, concentric tubes which define chambers in which the free radicals are formed.

11. The apparatus of Claim 10 wherein the tubes include a first tube in which a first chamber is formed, a second tube surrounding the first tube, with a second chamber being formed between the first and second tubes, and a third tube surrounding the second tube, with a third chamber being
5 formed between the second and third tubes.

12. The apparatus of Claim 10 wherein the source of free radicals further includes an induction coil disposed concentrically about the tubes, and means for applying RF power to the coil.

13. The apparatus of Claim 8 wherein the means for combining the free radicals includes means for cooling the free radicals to promote formation of the chemical species.

14. The apparatus of Claim 8 wherein the means for combining the free radicals includes a catalyst which promotes formation of the chemical species.



15. In a method of generating a chemical species for use in processing a semiconductor wafer in a reaction chamber, the steps of: creating free radicals, and combining the free radicals to form the chemical species in the chamber in close proximity to the wafer.

16. The method of Claim 15 the free radicals are created by forming an ionized plasma of precursor materials.

17. The method of Claim 16 wherein the plasma is formed in a plurality of elongated, concentric tubes which define chambers in which the free radicals are formed.

18. The method of Claim 17 wherein the plasma is formed in a field created by applying RF power to an induction coil disposed concentrically about the tubes.

19. The method of Claim 15 wherein the step of combining the free radicals includes the step of cooling the free radicals to promote formation of the chemical species.

20. The method of Claim 15 wherein the step of combining the free radicals includes use of a catalyst which promotes formation of the chemical species.

21. In a method of generating a chemical species at a point of use where a workpiece is to be processed with the species, the steps of: creating free radicals, and combining the free radicals to form the chemical species at the point of use.

22. The method of Claim 21 the free radicals are created by forming an ionized plasma of precursor materials.



23. The method of Claim 22 wherein the plasma is formed in a plurality of elongated, concentric tubes which define chambers in which the free radicals are formed.

24. The method of Claim 23 wherein the plasma is formed in a field created by applying RF power to an induction coil disposed concentrically about the tubes.

25. The method of Claim 21 wherein the step of combining the free radicals includes the step of cooling the free radicals to promote formation of the chemical species.

26. The method of Claim 21 wherein the step of combining the free radicals includes use of a catalyst which promotes formation of the chemical species.

27. In a method of generating a chemical species *in situ* at a point of use: creating free radicals, and combining the free radicals to form the chemical species at the point of use.

28. The method of Claim 27 wherein free radicals of nitrogen and oxygen are obtained from a precursor gas and combined to form N_xO_y , where x and y are positive integers.

29. The method of Claim 27 wherein NO is formed by admitting free radicals of N_2 and O_2 into a chamber, and striking a plasma in the chamber to combine the N_2 and the O_2 to form NO.

30. The method of Claim 27 wherein NO_2 is converted to NO and O_2 and combined with hydrogen to form nitric acid (HNO_3).



31. The method of Claim 27 wherein free radicals of nitrogen and hydrogen are obtained from ammonia (NH_3) and combined with oxygen in the presence of a catalyst to form nitric acid (HNO_3).
32. The method of Claim 31 wherein the catalyst is platinum.
33. The method of Claim 27 wherein free radicals of nitrogen and hydrogen are obtained from ammonia (NH_3) and combined with oxygen.
34. The method of Claim 27 wherein O_2 is combined with SO_2 to form SO_3 .
35. The method of Claim 27 wherein a species selected from the group consisting of hydrogen and oxygen (H_2 and O_2) and water (H_2O) is reacted with a species selected from the group consisting of S, SO, SO_2 and combinations thereof to form sulfuric acid (H_2SO_4).
36. The method of Claim 35 wherein the species selected from the group consisting of hydrogen and oxygen (H_2 and O_2) and water (H_2O) is reacted the species selected from the group consisting of S, SO, SO_2 and combinations thereof in the presence of a catalyst.
37. The method of Claim 36 wherein the catalyst is platinum.
38. The method of Claim 27 wherein a precursor containing fluorine and chlorine is combined with an oxidizing agent to form hydrochloric acid (HCl) and hydrofluoric acid (HF).
39. The method of Claim 27 wherein hydrochloric acid (HCl) is formed from a precursor containing carbon, hydrogen and chlorine.



40. The method of Claim 27 wherein hydrofluoric acid (HF) is formed from a precursor containing carbon, hydrogen and fluorine.
41. The method of Claim 27 wherein polysilicon is formed from a precursor selected from the group consisting of silane (Si_xH_y) alone and silane in combination with hydrogen.
42. The method of Claim 27 wherein silicon nitride is formed from a silane (Si_xH_y) precursor and a nitrogen containing species.
43. The method of Claim 27 wherein a TEOS precursor is used in the formation of a conformal coating.
44. The method of Claim 43 wherein ozone is used in combination with the TEOS precursor.
45. The method of Claim 27 wherein a MX_m precursor is used in the formation of a metal film, where M is the metal, X is a halogen species, and m is the stoichiometric number.
46. The method of Claim 45 wherein the MX_m precursor is used in the presence of a reducing species.
47. The method of Claim 27 wherein a precursor containing nitrogen and sulfur is used in conjunction with hydrogen and oxygen to generate mixed acids.
48. The method of Claim 27 wherein H_2 and O_2 are reacted to form steam for use in the stripping of photoresist.



49. The method of Claim 48 wherein an acid selected from the group consisting of HF, H₂SO₄ and HNO₃ is generated *in situ* and combined with the steam.
50. The method of Claim 27 wherein O₂ is combined with SO₂ to form SO₃ for use in stripping organic photoresist.
51. The method of Claim 27 wherein N₂O is converted to NO₂ for use in stripping photoresist.
52. The method of Claim 27 wherein N₂O is converted to NO and NO₂ for use in nitriding an oxide film to act as a barrier to ion penetration.
53. The method of Claim 27 wherein a MX_m precursor is used in the presence of an oxidizing species in the formation of a metal oxide film, where M is the metal, X is a halogen species, and m is the stoichiometric number.
54. The method of Claim 52 wherein the oxidizing species is selected from the group consisting of O₂ and H₂O and combinations thereof.
55. The method of Claim 27 wherein H₂ and O₂ are reacted to form steam for growing an SiO₂ layer on Si.
56. The method of Claim 27 wherein polysilicon is formed from a member of the group consisting of silane (Si_xH_y) precursor, a species containing hydrogen, and combinations thereof.
57. The method of Claim 27 wherein hydrofluoric acid (HF) is formed from a precursor containing nitrogen, hydrogen and fluorine.



58. The method of Claim 27 wherein hydrofluoric acid (HF) is formed from a precursor selected from the group consisting of a precursor containing nitrogen, hydrogen and fluorine and a precursor containing carbon, fluorine and hydrogen and combinations thereof for use in removing native oxide from silicon.

59. In a method of devolitizing products on the surface of a silicon wafer, the steps of:

forming hydrofluoric acid (HF) from a precursor selected from the group consisting of a precursor containing nitrogen, hydrogen and fluorine, a precursor containing carbon, fluorine and hydrogen, O₂, H₂ and combinations thereof;

forming nitric acid (HNO₃) from a precursor containing nitrogen, hydrogen and oxygen;

forming sulfuric acid (H₂SO₄) with a species selected from the group consisting of S, SO, SO₂ and combinations thereof;

forming hydrochloric acid (HCl) is from a precursor containing carbon, hydrogen and chlorine;

combining the HF with the HNO₃, H₂SO₄ and HCl to form reaction products;

solvating the products on the surface of the wafer with an aqueous solution containing the reaction products at temperature low enough that a thin film of water will condense on the wafer surface;

raising the temperature of the wafer to evaporate the aqueous solution; and

spinning the wafer to further assist in removal of the aqueous solution.

60. In a method of devolitizing products on the surface of a silicon wafer, the steps of:

forming hydrofluoric acid (HF) from a precursor selected from the group consisting of a precursor containing nitrogen, hydrogen and fluorine,



- 5 a precursor containing carbon, fluorine and hydrogen, O₂, H₂ and combinations thereof;

combining the hydrofluoric acid with hydrogen, nitrogen and oxygen to form HNO₃ and steam;

- 10 solvating the products on the surface of the wafer with a solution containing the HNO₃ and steam at temperature low enough that a thin film of water will condense on the wafer surface;

raising the temperature of the wafer to evaporate the solution; and spinning the wafer to further assist in removal of the solution.

61. In a method of devolitizing products on the surface of a silicon wafer, the steps of:

- 5 forming hydrofluoric acid (HF) from a precursor selected from the group consisting of a precursor containing nitrogen, hydrogen and fluorine, a precursor containing carbon, fluorine and hydrogen, O₂, H₂ and combinations thereof;

combining the hydrofluoric acid with hydrogen, nitrogen and oxygen to form HNO₃ and steam;

- 10 solvating the products on the surface of the wafer with an aqueous solution containing the HNO₃ and the steam at temperature low enough that a thin film of water will condense on the wafer surface;

raising the temperature of the wafer to evaporate the aqueous solution; and

- 15 spinning the wafer to further assist in removal of the aqueous solution.

62. In a method of devolitizing products on the surface of a silicon wafer, the steps of:

- 5 forming hydrofluoric acid (HF) from a precursor selected from the group consisting of a precursor containing nitrogen, hydrogen and fluorine, a precursor containing carbon, fluorine and hydrogen, O₂, H₂ and combinations thereof;



combining the hydrofluoric acid with SiO_2 to form a reaction products;

10 solvating the products on the surface of the wafer with an aqueous solution containing the reaction product at temperature low enough that a thin film of water will condense on the wafer surface;

raising the temperature of the wafer to evaporate the aqueous solution; and

15 spinning the wafer to further assist in removal of the aqueous solution.