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(54) INCREASING MASKING LAYER ETCH RATE AND SELECTIVITY

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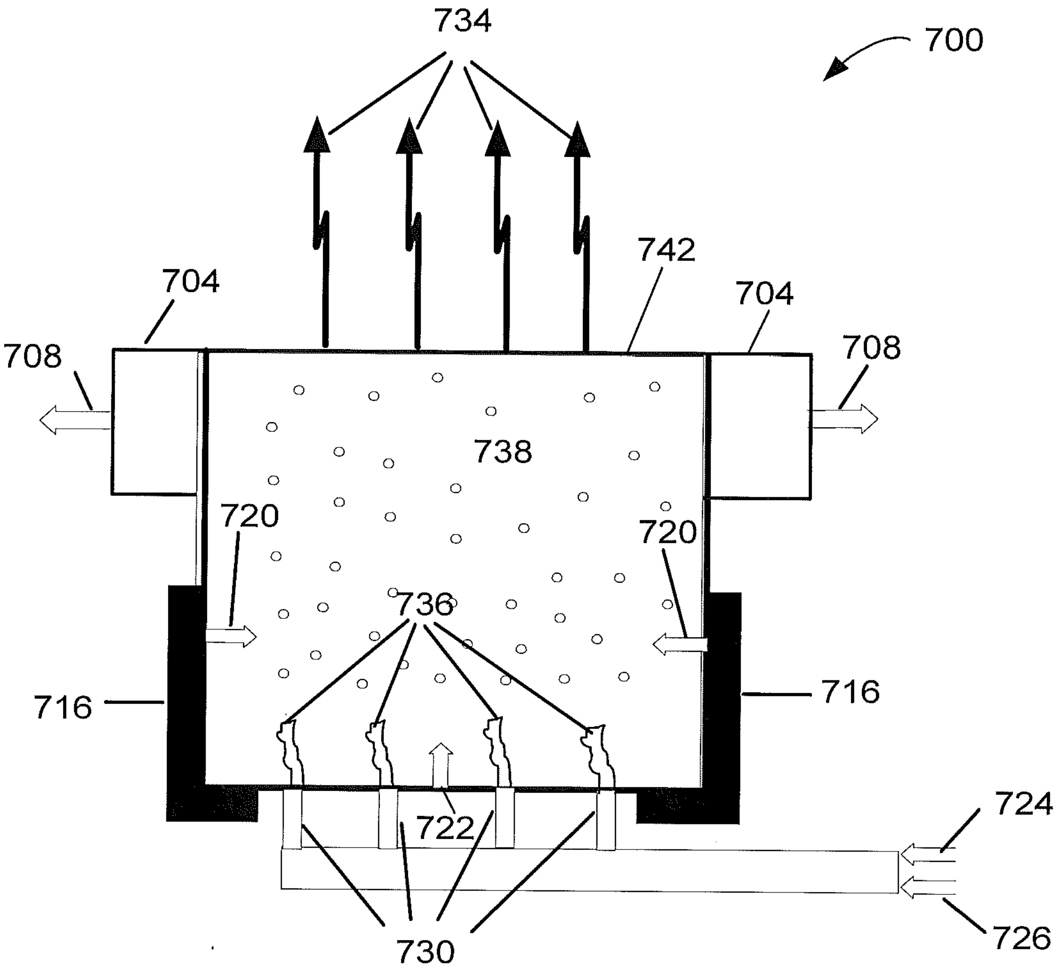
(57) ABSTRACT

Provided is a method and system for increasing etch rate and etch selectivity of a masking layer on a substrate, wherein the system comprises a plurality of substrates containing the masking layer and a layer of silicon or silicon oxide, an etch processing chamber configured to process the plurality of substrates, the processing chamber containing a treatment liquid for etching the masking layer, and a boiling apparatus coupled to the processing chamber and configured to generate a supply of steam water vapor mixture at elevated pressure, wherein the steam water vapor mixture is introduced into the processing chamber at a controlled rate to maintain a selected target etch rate and a target etch selectivity ratio of the masking layer to silicon or silicon oxide.



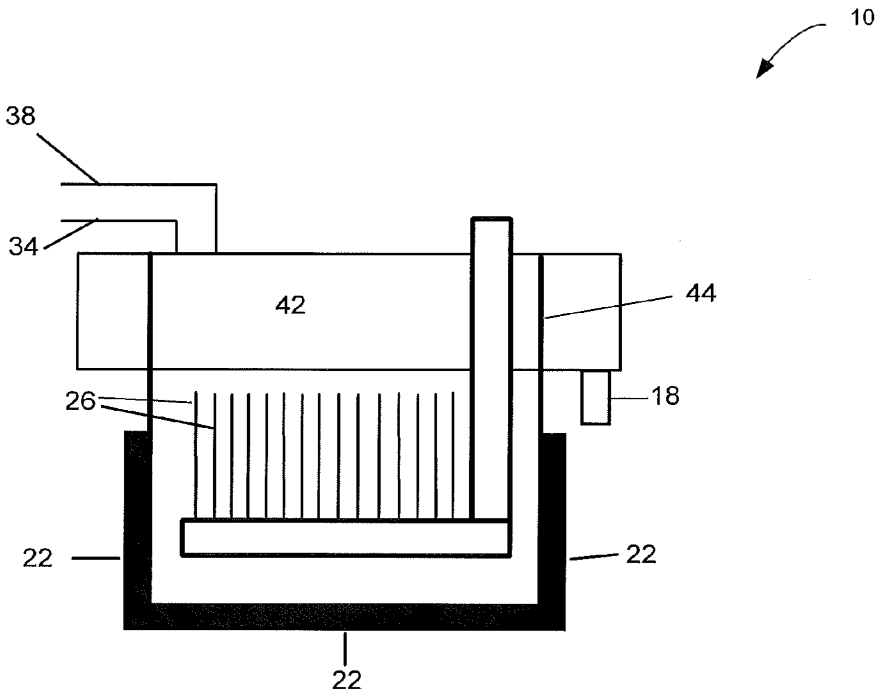


FIG. 1 Prior Art

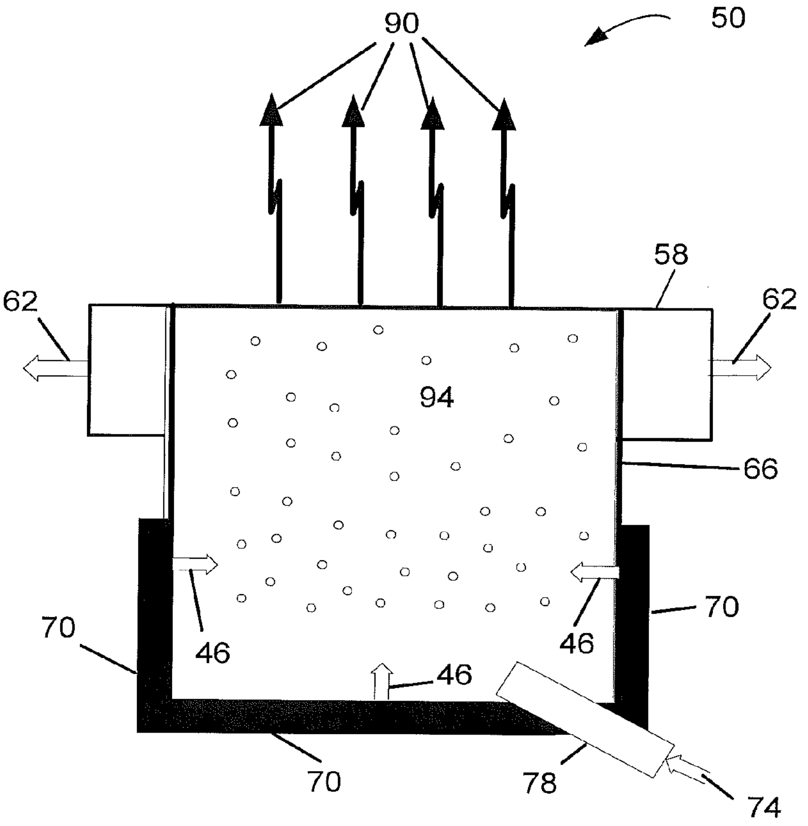


FIG. 2 Prior Art

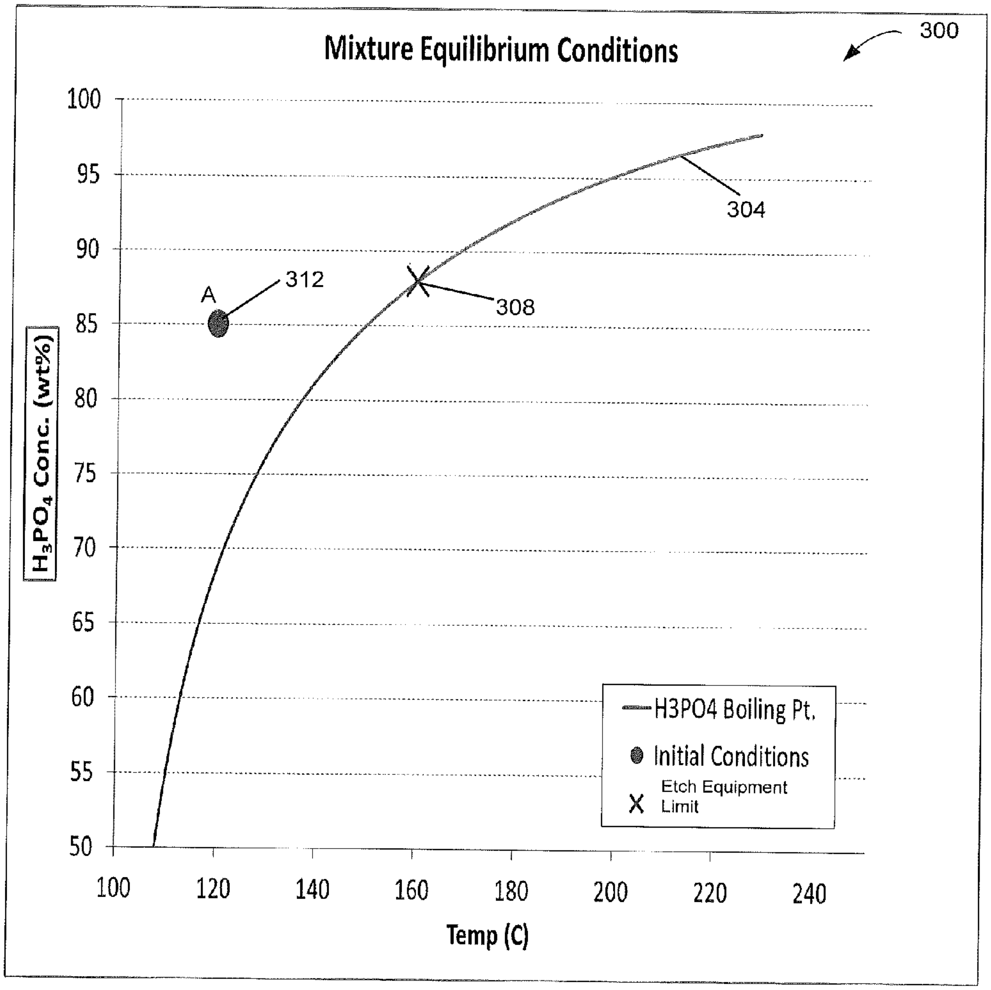

300
Mixture Equilibrium Conditions
100
95
90
85
80
75
70
65
60
55
50
H_3PO_4 Conc. (wt%)
A
312
308
304
100
120
140
160
180
200
220
240
Temp (C)
H3PO4 Boiling Pt.
Initial Conditions
Etch Equipment Limit

FIG. 3

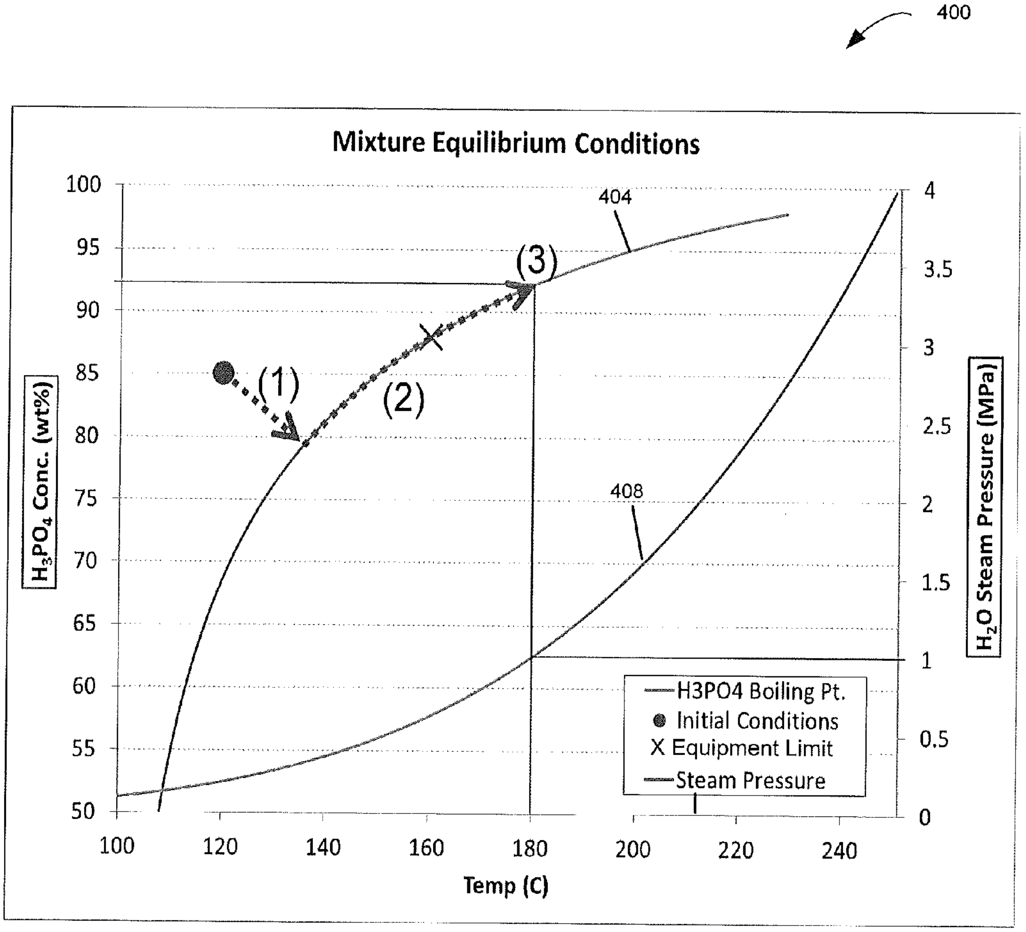

400
Mixture Equilibrium Conditions
100
95
90
85
80
75
70
65
60
55
50
H_3PO_4 Conc. (wt%)
100
120
140
160
180
200
220
240
Temp (C)
4
3.5
3
2.5
2
1.5
1
0.5
0
H_2O Steam Pressure (MPa)
404
408
(1)
(2)
(3)
H3PO4 Boiling Pt.
● Initial Conditions
X Equipment Limit
Steam Pressure

FIG. 4A

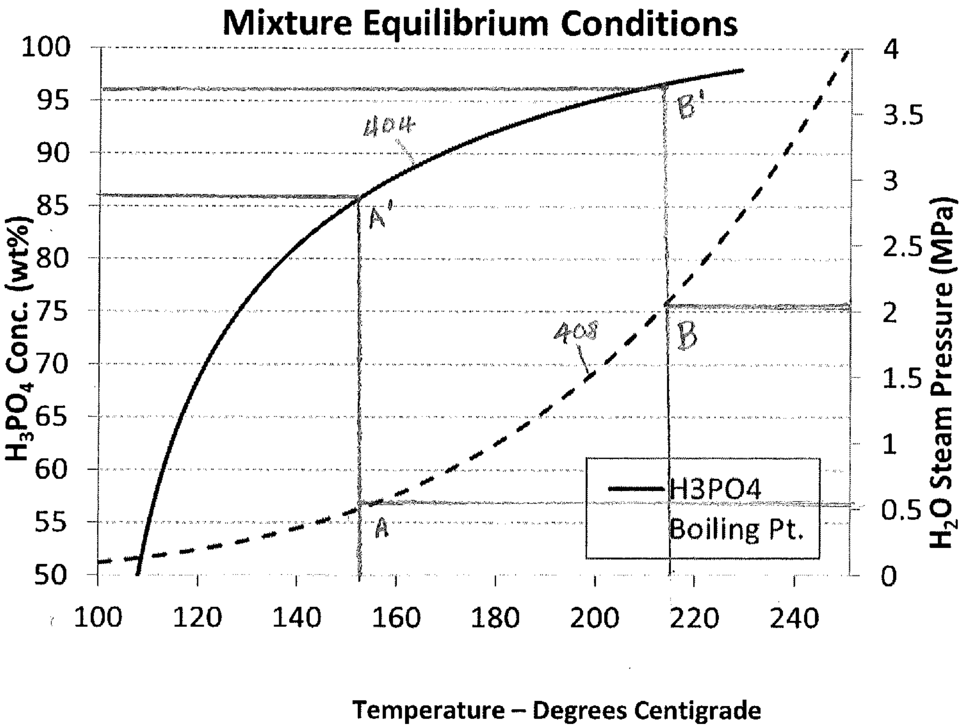

Mixture Equilibrium Conditions
100
95
90
85
80
75
70
65
60
55
50
H_3PO_4 Conc. (wt%)
4
3.5
3
2.5
2
1.5
1
0.5
0
H_2O Steam Pressure (MPa)
100
120
140
160
180
200
220
240
Temperature – Degrees Centigrade
404
408
A'
A
B'
B
H3PO4
Boiling Pt.

FIG. 4B

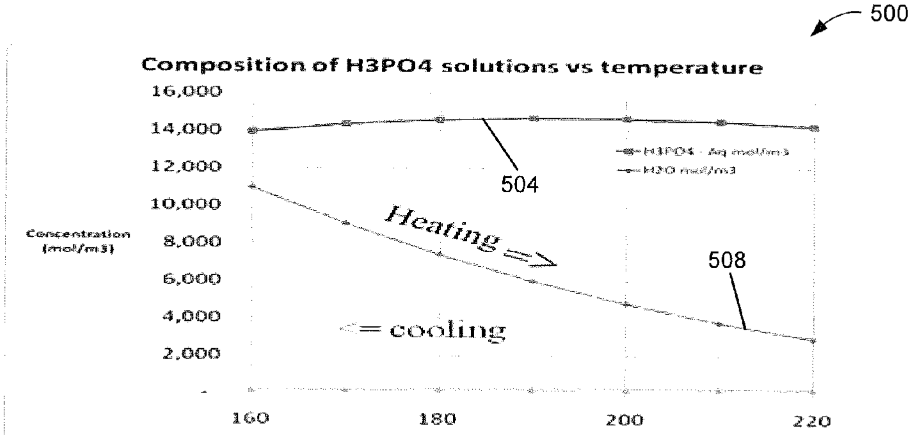

500
Composition of H3PO4 solutions vs temperature
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
Concentration (mol/m3)
H3PO4 - Aq mol/m3
H2O mol/m3
504
Heating =>
508
<= cooling
160
180
200
220
Temperature (°C)

FIG. 5A

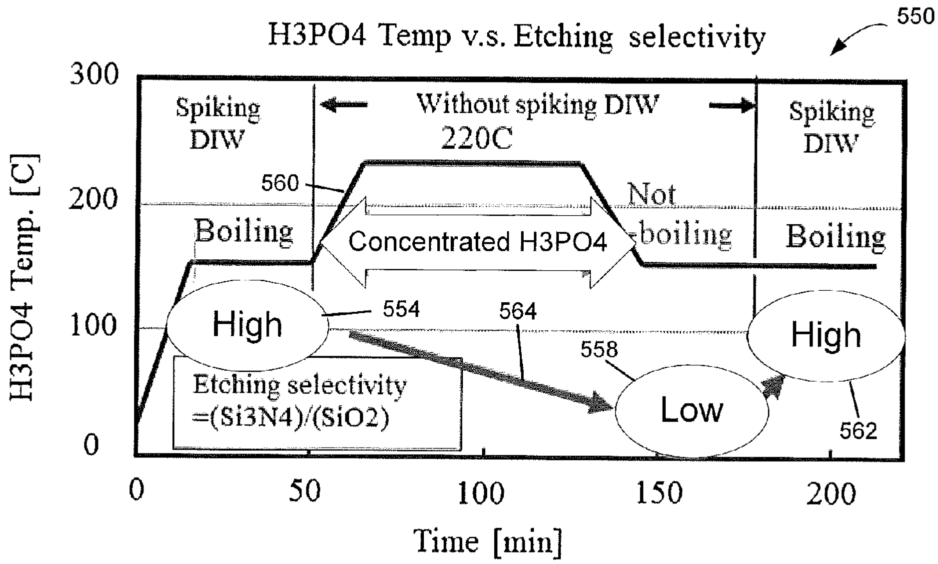

550
H3PO4 Temp v.s. Etching selectivity
300
200
100
0
H3PO4 Temp. [C]
Spiking DIW
Without spiking DIW
220C
Spiking DIW
560
Boiling
Concentrated H3PO4
Not boiling
Boiling
High
554
564
558
Low
High
562
Etching selectivity =(Si3N4)/(SiO2)
0
50
100
150
200
Time [min]

FIG. 5B

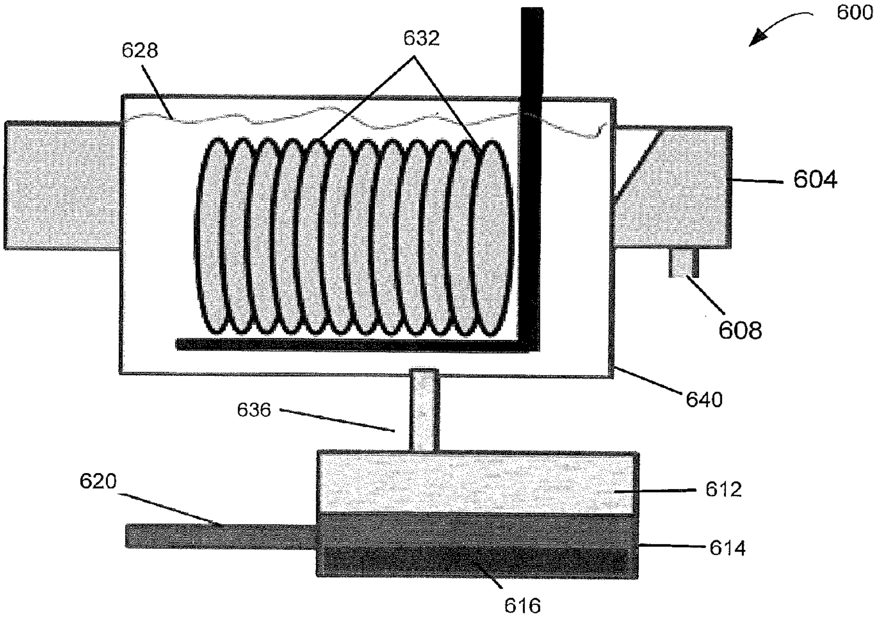

600
628
632
604
608
640
636
620
612
614
616

FIG. 6A

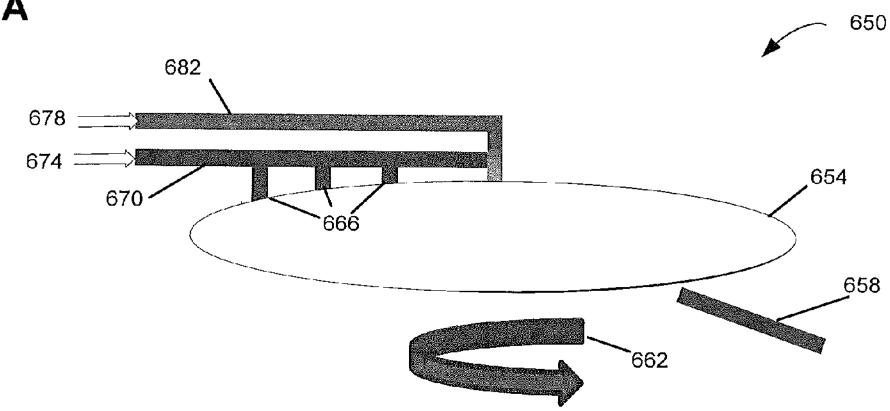

650
682
678
674
670
666
654
658
662

FIG. 6B

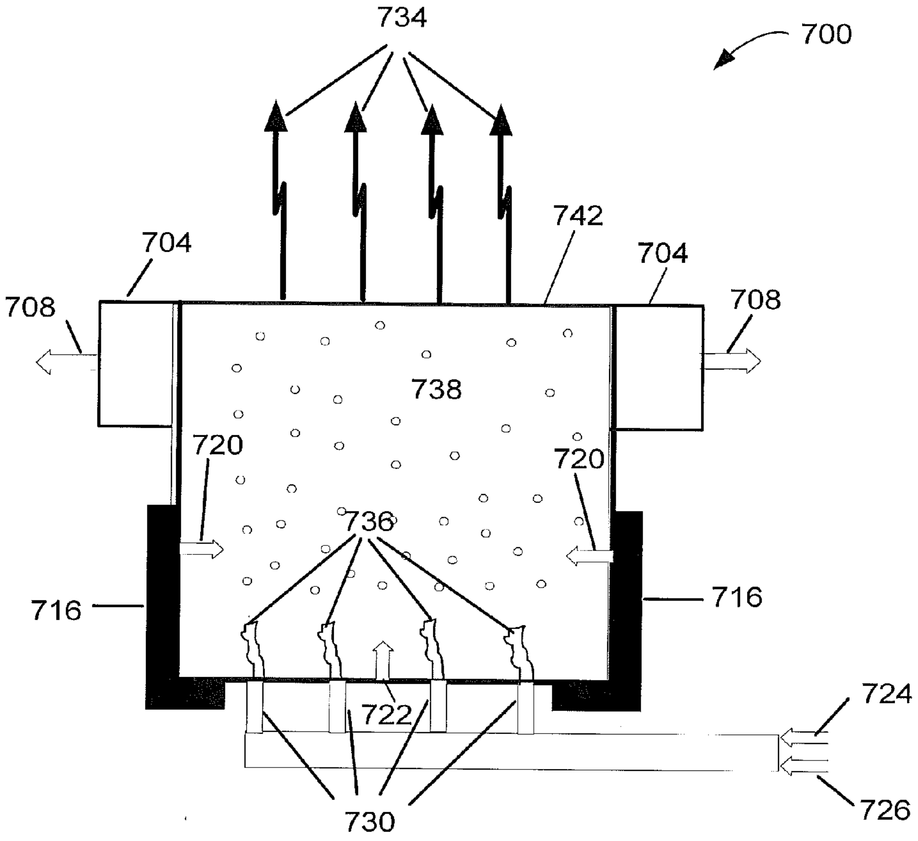

734
700
742
704
704
708
708
738
720
720
736
716
716
724
722
726
730

FIG. 7A

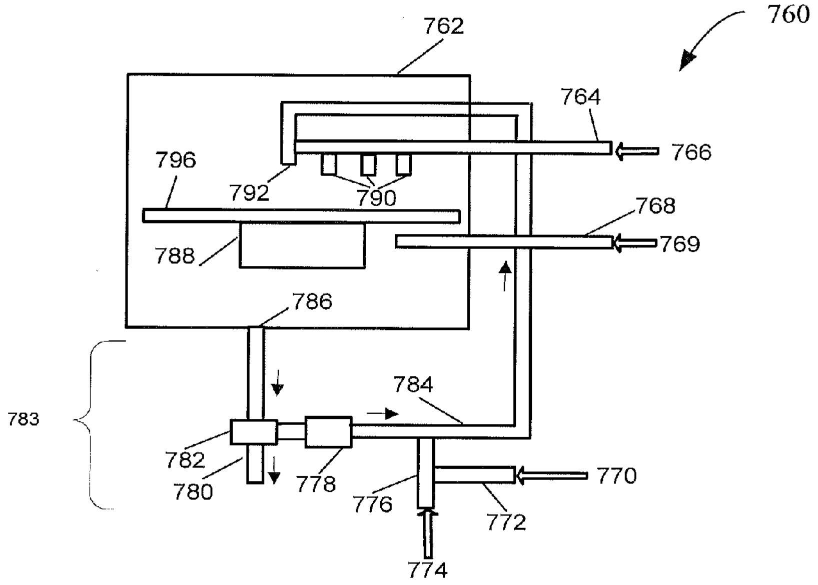

760
762
764
766
796
792
790
768
769
788
786
783
784
782
778
780
776
770
772
774

FIG. 7B

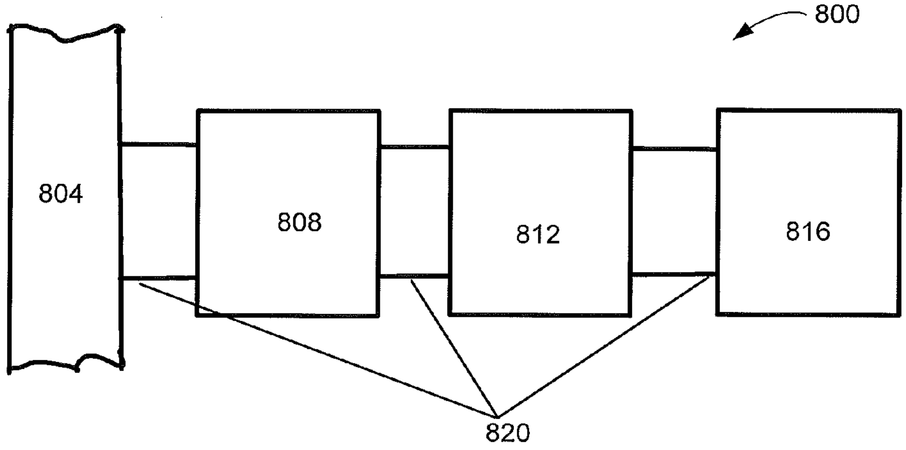


FIG. 8A

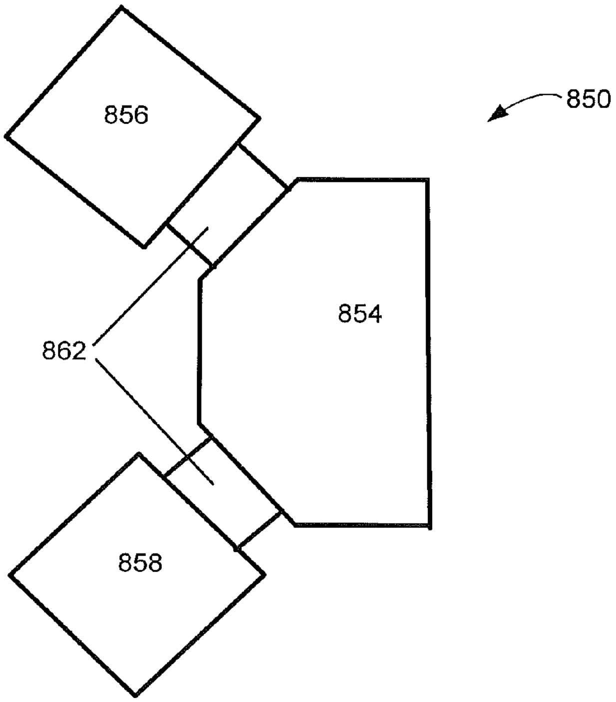


FIG. 8B

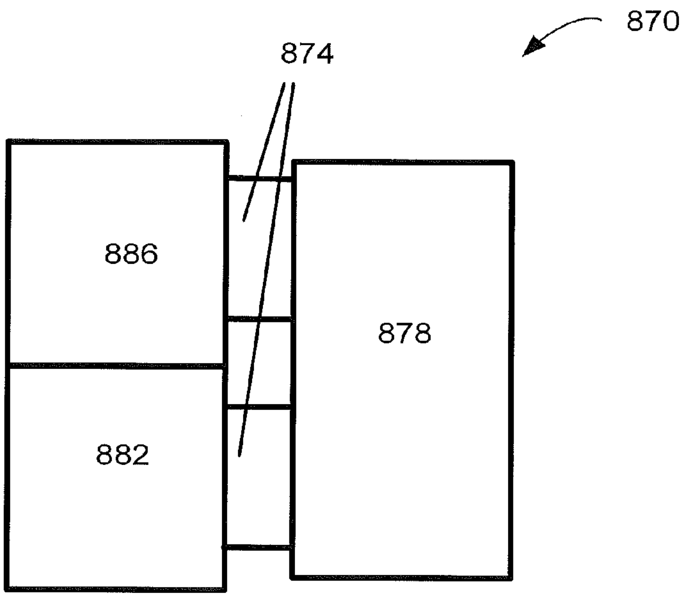


FIG. 8C

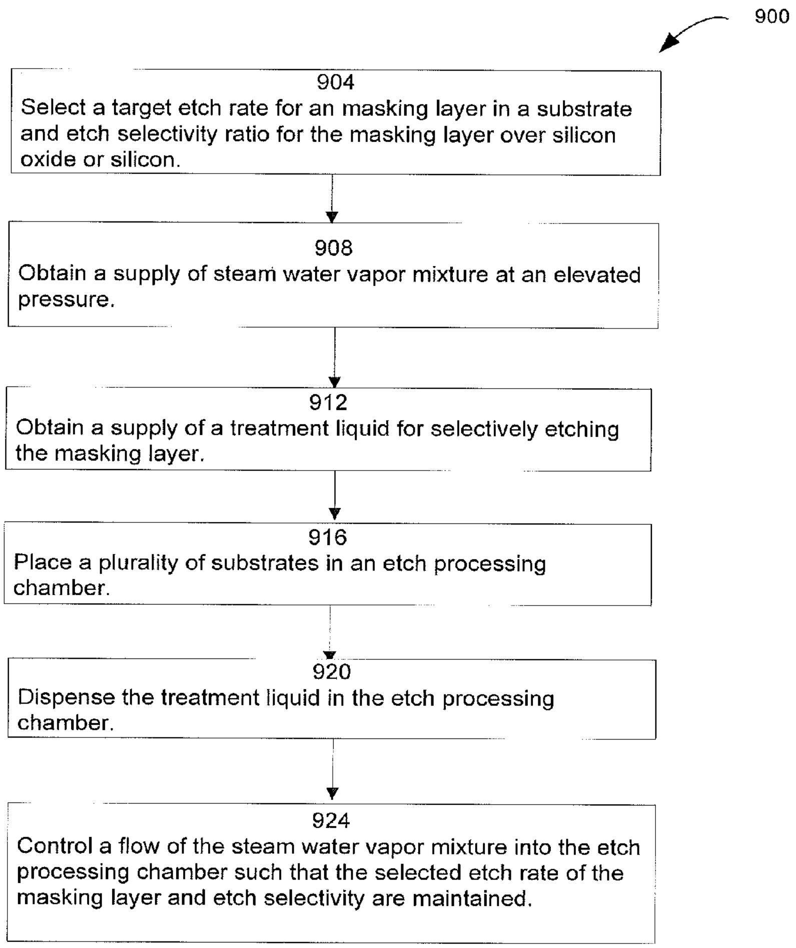

900
904
Select a target etch rate for an masking layer in a substrate and etch selectivity ratio for the masking layer over silicon oxide or silicon.
908
Obtain a supply of steam water vapor mixture at an elevated pressure.
912
Obtain a supply of a treatment liquid for selectively etching the masking layer.
916
Place a plurality of substrates in an etch processing chamber.
920
Dispense the treatment liquid in the etch processing chamber.
924
Control a flow of the steam water vapor mixture into the etch processing chamber such that the selected etch rate of the masking layer and etch selectivity are maintained.

FIG. 9

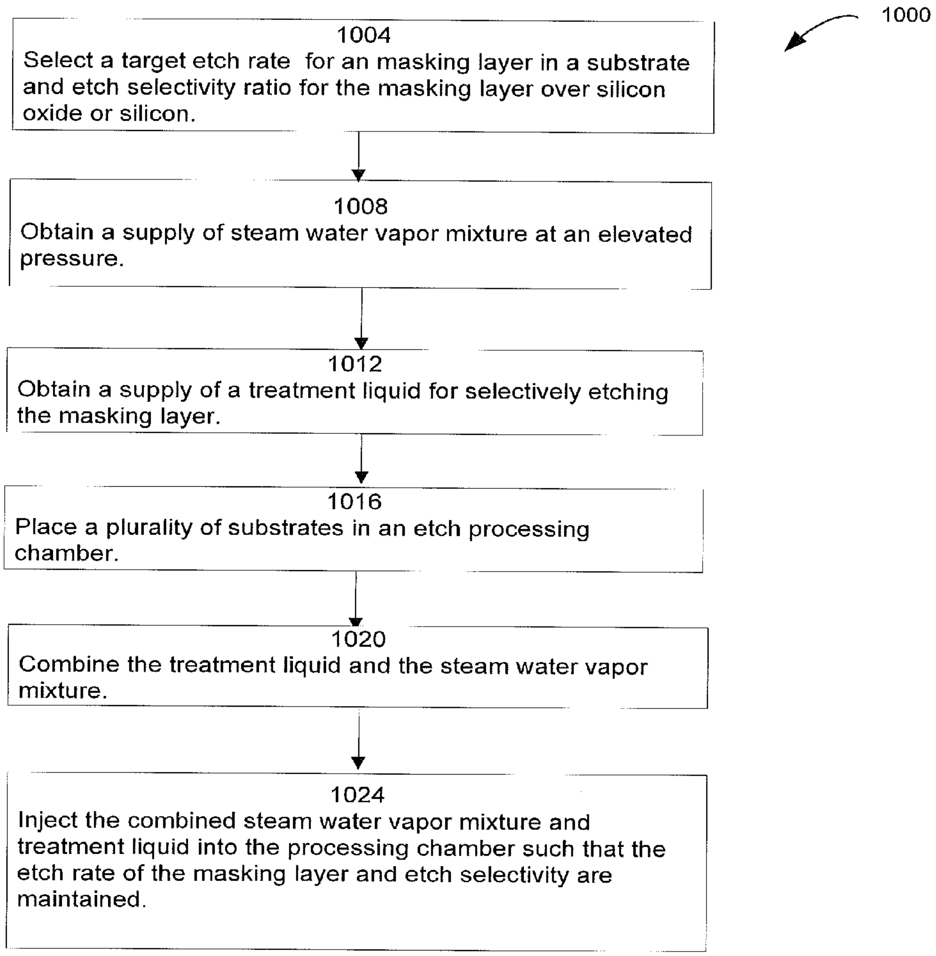

1000
1004
Select a target etch rate for an masking layer in a substrate and etch selectivity ratio for the masking layer over silicon oxide or silicon.
1008
Obtain a supply of steam water vapor mixture at an elevated pressure.
1012
Obtain a supply of a treatment liquid for selectively etching the masking layer.
1016
Place a plurality of substrates in an etch processing chamber.
1020
Combine the treatment liquid and the steam water vapor mixture.
1024
Inject the combined steam water vapor mixture and treatment liquid into the processing chamber such that the etch rate of the masking layer and etch selectivity are maintained.

FIG. 10

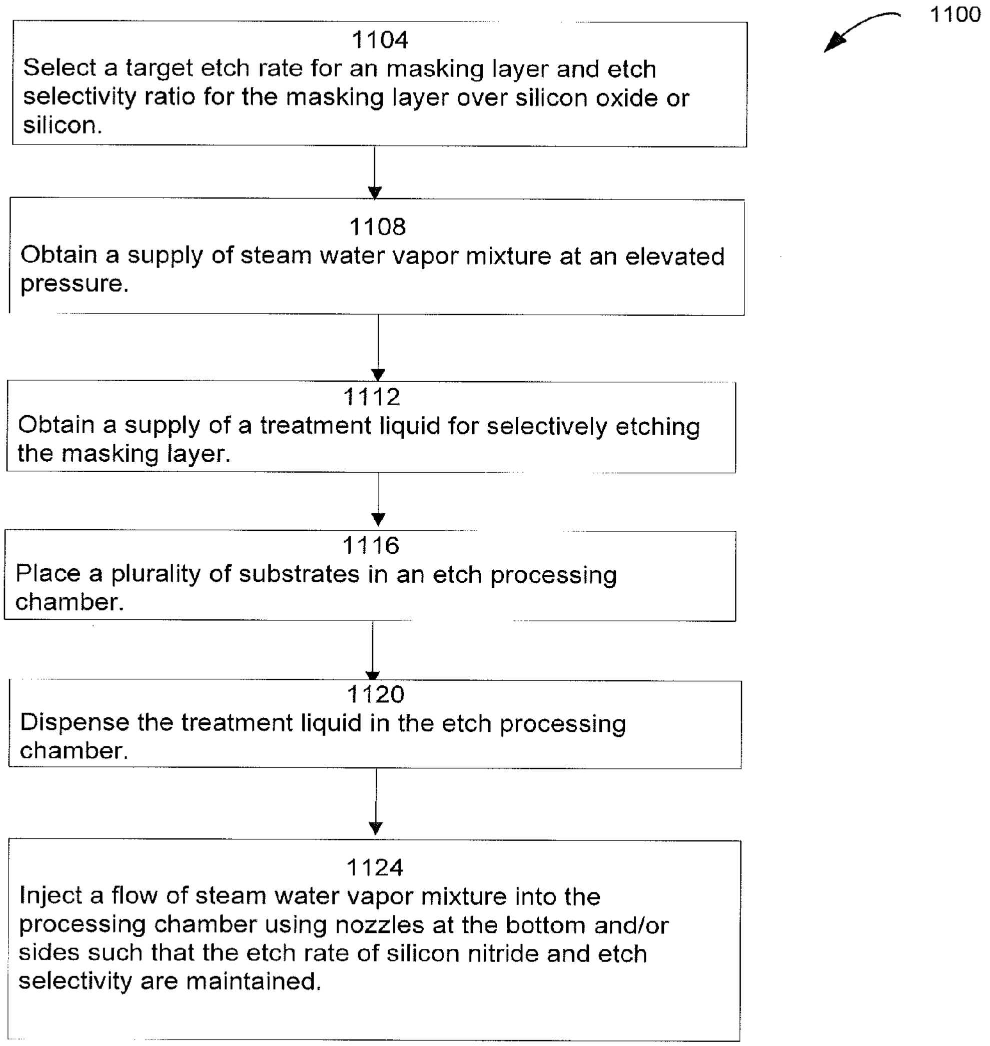

1100
1104
Select a target etch rate for an masking layer and etch selectivity ratio for the masking layer over silicon oxide or silicon.
1108
Obtain a supply of steam water vapor mixture at an elevated pressure.
1112
Obtain a supply of a treatment liquid for selectively etching the masking layer.
1116
Place a plurality of substrates in an etch processing chamber.
1120
Dispense the treatment liquid in the etch processing chamber.
1124
Inject a flow of steam water vapor mixture into the processing chamber using nozzles at the bottom and/or sides such that the etch rate of silicon nitride and etch selectivity are maintained.

FIG. 11

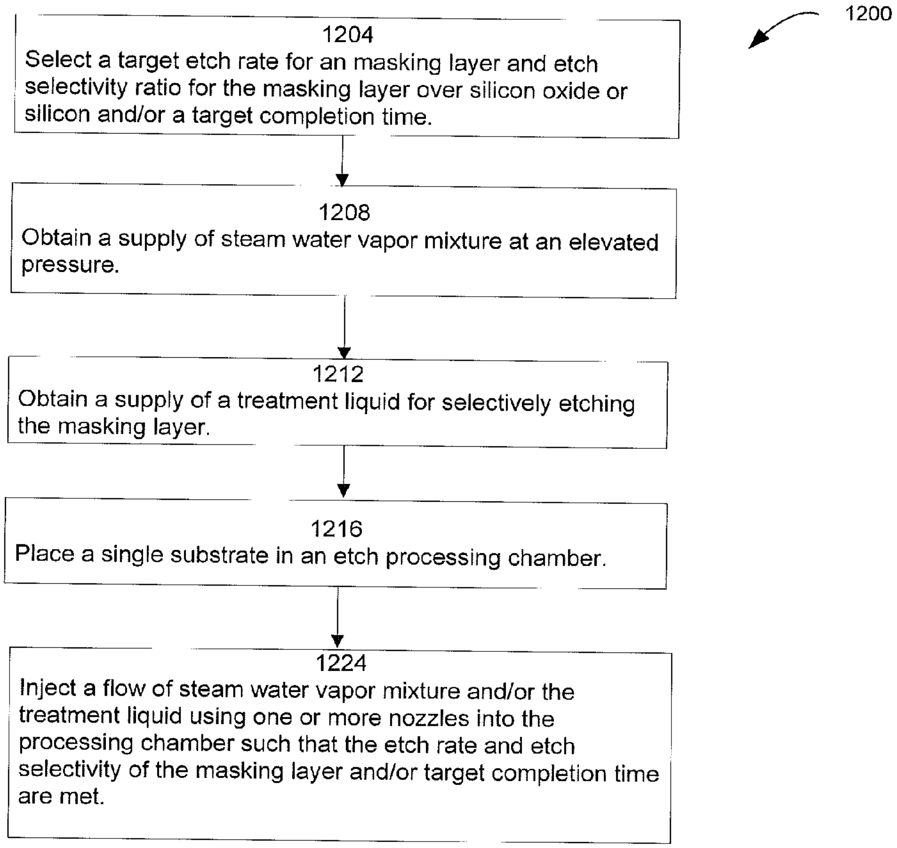

1200
1204
Select a target etch rate for an masking layer and etch selectivity ratio for the masking layer over silicon oxide or silicon and/or a target completion time.
1208
Obtain a supply of steam water vapor mixture at an elevated pressure.
1212
Obtain a supply of a treatment liquid for selectively etching the masking layer.
1216
Place a single substrate in an etch processing chamber.
1224
Inject a flow of steam water vapor mixture and/or the treatment liquid using one or more nozzles into the processing chamber such that the etch rate and etch selectivity of the masking layer and/or target completion time are met.

FIG. 12

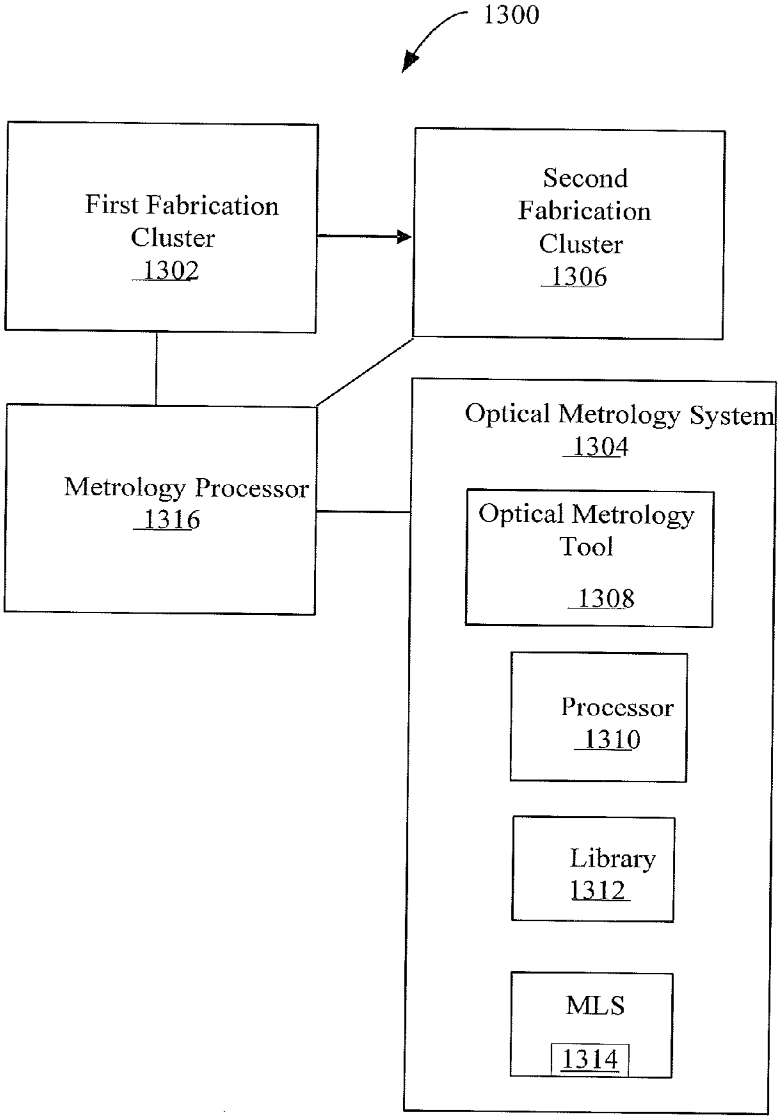

1300
First Fabrication Cluster
1302
Second Fabrication Cluster
1306
Metrology Processor
1316
Optical Metrology System
1304
Optical Metrology Tool
1308
Processor
1310
Library
1312
MLS
1314

FIG. 13

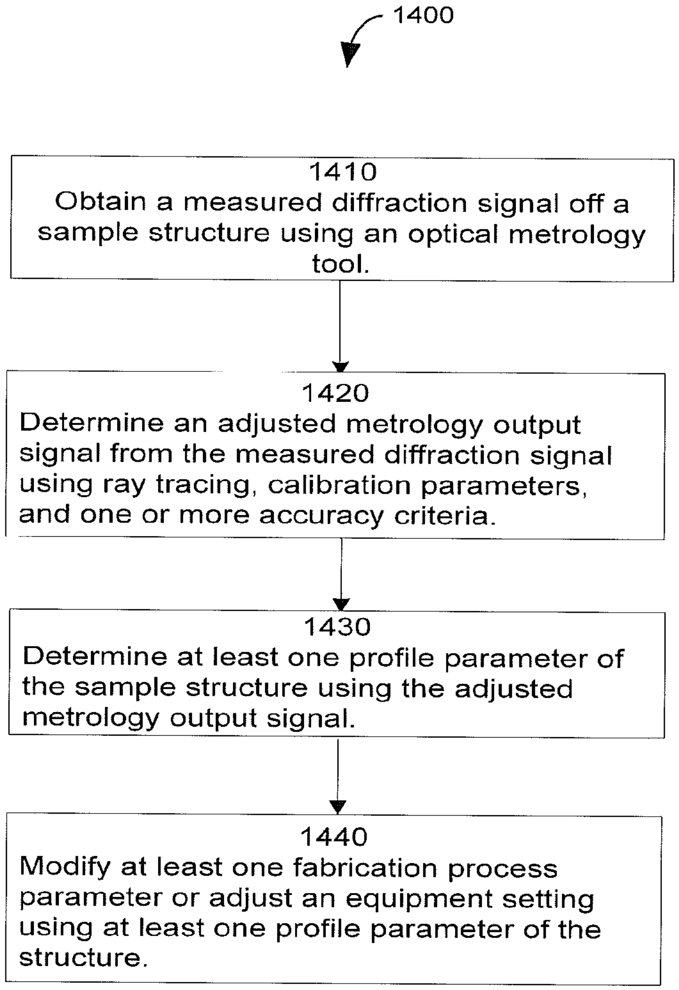

1400
1410
Obtain a measured diffraction signal off a sample structure using an optical metrology tool.
1420
Determine an adjusted metrology output signal from the measured diffraction signal using ray tracing, calibration parameters, and one or more accuracy criteria.
1430
Determine at least one profile parameter of the sample structure using the adjusted metrology output signal.
1440
Modify at least one fabrication process parameter or adjust an equipment setting using at least one profile parameter of the structure.

FIG. 14

INCREASING MASKING LAYER ETCH RATE AND SELECTIVITY

BACKGROUND

[0001] 1. Field

[0002] The present application generally relates to the design of an etch treatment system and method for increasing etch rate and selectivity of etching a masking layer using a batch etch process.

[0003] 2. Related Art

[0004] Current methods in the production of complementary metal oxide semiconductor (CMOS) transistors require masking layers to separate and protect active device regions such as dielectric, metal interconnect, strain, source/drain, and the like. Silicon nitride (Si_3N_4) or silicon oxide (SiO_x, wherein x is greater than 0) is often used as a masking layer due to its electrical and morphological similarity to silicon dioxide (SiO_2), as well as because silicon nitride is easily bonded to SiO_2. Generally, silicon nitride is used as an etch-stop layer but in certain cases, such as in a "dual damascene" process, the silicon nitride must be etched away without altering the carefully-controlled thickness of the silicon dioxide underlayer. In such instances, the etch selectivity of silicon nitride to silicon oxide, calculated as the etch rate of silicon nitride divided by the etch rate of silicon oxide, ideally is as high as possible to improve the process margin. As devices continue to shrink, the thickness of masking layers and underlayers shrink in tandem. Etch selectivity for ultra-thin layers will become more of a challenge in the future.

[0005] Current techniques for selectively etching silicon nitride may use differing chemistries and approaches. Both dry-plasma etching as well as aqueous-chemistry etch are used in the removal of silicon nitride. Aqueous chemistry materials can include dilute hydrofluoric Acid (dHF), hydrofluoric acid/ethylene glycol as well as phosphoric acid. The decision for using the different chemistries is governed by the requirement for silicon nitride etch rate and selectivity to oxide. Aqueous chemistry methods are preferable because of the reduced cost of ownership compared to dry techniques. It is well understood the silicon nitride etch rate in phosphoric acid is strongly influenced by temperature, where the etch rate rises in response to a rise in temperature. In a wet-bench configuration such as immersing substrates into a bath of aqueous phosphoric acid solution, the process temperature is limited by the boiling point of the aqueous phosphoric acid solution. The boiling point of the solution is a function of the concentration of water in aqueous phosphoric acid solution as well as the atmospheric pressure. One current method for maintaining temperature is by a feedback-loop-controller that measures the existence of a boiling state, while adjusting the addition of water volume and heater power timing interval to the bath so as to maintain this boiling state at a target temperature, (typical range of target temperatures is from 140 degrees Centigrade to 160 degrees Centigrade). When the aqueous phosphoric acid solution is heated without addition of water, the boiling point of the aqueous phosphoric acid solution rises as the water is evaporated from the solution.

[0006] Increasing the temperature of the phosphoric acid is favorable for increasing the silicon nitride etch rate for production and lower the cost of manufacturing at the expense of lower selectivity because with current phosphoric acid recirculation tanks, the consequence of allowing a high boiling point is to reduce the concentration of water. Water is critical in controlling the selectivity of silicon nitride to silicon oxide or silicon etching. Experimental evidence shows that a non-boiling state (i.e., low water content) at elevated temperature does not result in a favorable etch selectivity. Conversely, to improve selectivity, it would be preferable to have a high concentration of water, (i.e., dilute the acid further), however this is not practical. Increasing the concentration of water in the bath reduces the boiling point of the acid mixture. At lower temperature, the etch rate of the silicon nitride falls significantly due to the strong Arrhenius relationship of the silicon nitride etch rate with temperature.

[0007] In the current art, for example, Morris, in U.S. Pat. No. 4,092,211, discloses a method for controlling within a boiling aqueous phosphoric acid solution the etch rate of a silicon oxide insulator layer which is employed in masking a silicon nitride insulator layer. The method employs the deliberate addition of a silicate material to the boiling aqueous phosphoric acid solution. In addition, Bell et al., in U.S. Pat. No. 5,332,145, disclose a method for continuously monitoring and controlling the compositions of low-solids soldering fluxes that employ a solvent with a specific gravity closely matched to the specific gravity of the flux composition. Desirable in the art are methods and systems that can maintain a high etch rate for a masking layer and also maintain a high selectivity of etching the masking layer over the silicon or silicon oxide. There is a need for batch etch treatment systems and methods and single substrate systems and methods that can meet the goals of etch rate, etch selectivity, etch time, and/or cost of ownership.

SUMMARY

[0008] Provided is a method and system for increasing etch rate and etch selectivity of a masking layer on a substrate, wherein the system comprises a plurality of substrates containing the masking layer and a layer of silicon or silicon oxide, an etch processing chamber configured to process the plurality of substrates, the processing chamber containing a treatment liquid for etching the masking layer, and a boiling apparatus coupled to the processing chamber and configured to generate a supply of steam water vapor mixture at elevated pressure, wherein the steam water vapor mixture is introduced into the processing chamber at a controlled rate to maintain a selected target etch rate and a selected target etch selectivity ratio of the masking layer to silicon or silicon oxide.

BRIEF DESCRIPTION OF DRAWINGS

[0009] FIG. **1** is an architectural diagram illustrating prior art method of etching silicon nitride in a batch etch process.

[0010] FIG. **2** depicts an exemplary architectural diagram illustrating a prior art batch etch treatment system using a water supply and heaters for etching silicon nitride.

[0011] FIG. **3** depicts an exemplary graph of the boiling point of phosphoric acid as a function of phosphoric acid concentration and temperature.

[0012] FIG. **4**A is an exemplary graph of the boiling point of phosphoric acid as a function of phosphoric acid concentration and temperature and an exemplary graph of steam pressure as a function of temperature for mixture equilibrium conditions in an etch treatment system.

[0013] FIG. **4**B is an exemplary graph of the boiling point of phosphoric acid as a function of phosphoric acid concentration and temperature and an exemplary graph of steam pressure as a function of temperature for mixture equilibrium conditions at two steam pressures in an etch treatment system.

[0014] FIG. **5**A depicts an exemplary graph of the composition of phosphoric acid solutions as a function of temperature.

[0015] FIG. **5**B depicts an exemplary graph of etch selectivity of phosphoric acid solutions as a function of time and temperature in an etch treatment system.

[0016] FIG. **6**A depicts an exemplary schematic representation of batch etch treatment system according to an embodiment of the present invention.

[0017] FIG. **6**B depicts an exemplary schematic representation of a single substrate etch treatment system according to an embodiment of the present invention.

[0018] FIG. **7**A is an exemplary schematic representation of batch etch treatment system using nozzles to dispense the steam according to an embodiment of the present invention.

[0019] FIG. **7**B depicts an exemplary schematic representation of a single substrate etch treatment system including a treatment liquid recycling system according to an embodiment of the present invention.

[0020] FIGS. **8**A, **8**B, and **8**C are exemplary schematic representations of a transfer system for an etch treatment system in several embodiments of the present invention.

[0021] FIG. **9** is an exemplary flowchart of a method for increasing etch rate and etch selectivity for a masking layer of a substrate for a batch etch treatment system using a treatment liquid and steam in an embodiment of the present invention.

[0022] FIG. **10** is an exemplary flowchart of a method for increasing etch rate and selectivity for a masking layer of a substrate for a batch etch treatment system using a combined treatment liquid and steam in an embodiment of the present invention.

[0023] FIG. **11** is an exemplary flowchart of a method for increasing etch rate and selectivity for a masking layer of a substrate for a batch etch treatment system using injection nozzles in an embodiment of the present invention.

[0024] FIG. **12** is an exemplary flowchart for a method for increasing etch rate and selectivity for a masking layer of a substrate in a single substrate etch treatment system in an embodiment of the present invention.

[0025] FIG. **13** is an exemplary schematic representation of a process control system for controlling a fabrication cluster using an etch treatment system configured to increase etch rate and etch selectivity in an embodiment of the present invention.

[0026] FIG. **14** is an exemplary flowchart of a method for controlling a fabrication cluster using an etch treatment system configured to increase etch rate and etch selectivity in an embodiment of the present invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENT(S)

[0027] In order to facilitate the description of the present invention, a semiconductor substrate is utilized to illustrate an application of the concept. The methods and processes equally apply to other workpieces such as a wafer, disk, or the like. Similarly, aqueous phosphoric acid is utilized to illustrate a treatment liquid in the present invention. As mentioned below, other treatment liquids can alternatively be used.

[0028] Referring to FIG. **1**, an architectural diagram **10** illustrating prior art method of etching silicon nitride in a batch etch treatment system where the etch chemicals (etchants) are dispensed using one or more input streams, **34** and **38**, onto the etch processing chamber **44** where a plurality of substrates **26** are positioned. The etchants may be reused or recycled or disposed of using the overflow tank **42** and overflow spout **18**. Heaters **22** can be provided for example by having heaters on the sides or at the bottom of the process chamber **44**. The heaters **22** may be external or inline.

[0029] FIG. **2** depicts an exemplary architectural diagram illustrating a prior art batch etch treatment systems **50** for etching silicon nitride comprising etch processing chamber **66** and spill tank **58**. As above, heaters **70** may be provided in the front, back, and below etch processing chamber **66**; these heaters **70** may be external or inline, and may provide the heat flux in **46** into an aqueous solution **94** in the process chamber **66**. The heat flux out comprises conduction **62** and evaporation of the water **90**. If the heat flux in is greater than the heat flux out due to evaporation and conduction, the temperature of the aqueous solution will increase until boiling occurs. The boiling point is fixed by the acid concentration and atmospheric pressure. During boiling, an increase in heat boils the water away faster. To maintain a constant boiling temperature for the aqueous solution **94**, the process chamber controller (not shown) must regulate the heaters **70** and water supply **74** injected through supply line **78** at the same time. If the water supply in is greater than the water loss due to evaporation, the temperature of the aqueous solution decreases, diluting the acid and lowering the boiling point. Conversely, if the water supply in is less than the water loss due to evaporation, the temperature of the aqueous solution increases, concentrating the acid and raising the boiling point.

[0030] It is well understood that the silicon nitride etch rate in phosphoric acid is strongly influenced by temperature, wherein the etch rate rises in response to a rise in temperature. The chemical reactions for etching silicon nitride and for etching silicon dioxide are as follows:

$$Si_3N_4+4H_3PO_4+12H_2O\rightarrow 3Si(OH)_4+4NH_4H_2PO_4 \quad (1)$$

$$SiO_2+2H_2O\rightarrow Si(OH)_4 \quad (2)$$

[0031] In a wet-bench configuration when immersing substrates into a bath of aqueous phosphoric acid solution (aqueous solution), such as in the Tokyo Electron Limited (TEL) EXPEDIUS line of tools, the process temperature is limited by the boiling point of the aqueous solution. The boiling point of the aqueous solution is a function of the concentration of water in acid as well as the atmospheric pressure, and can be described by the Clausius-Clapeyron relation and Raoult's law. The Clausius-Clapeyron equation for the liquid-vapor boundary can be expressed as:

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \quad \text{Equation 3.0}$$

wherein

ln is natural logarithm,

T_1 and P_1 are a corresponding temperature (in Kelvins or other absolute temperature units) and vapor pressure,

T_2 and P_2 are the corresponding temperature and pressure at another point,

ΔH_{vap} is the molar enthalpy of vaporization, and

R is the as constant (8.314 J mol^{-1} K^{-1}).

[0032] Raoult's law states the vapor pressure of an ideal solution is dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution. Once the components in the solution have reached equilibrium, the total vapor pressure p of the solution is:

$$p=p_A^{*}x_A+p_B^{*}x_B+\ldots \qquad \text{Equation 4.0}$$

and the individual vapor pressure for each component is

$$p_i=p_i^{*}x_i$$

[0033] where:

p_i is the partial pressure of the component i in mixture

p^*_i is the vapor pressure of the pure component i, and

x_i is the mole fraction of the component i in solution (in mixture).

[0034] An example of equilibrium states for phosphoric acid and water is provided in FIG. **5**A. The current TEL EXPEDIUS method for maintaining temperature is by a feedback-loop-controller that measures the existence of a boiling state, while adjusting the addition of water volume and heater power timing interval to the bath so as to maintain this boiling state at a target temperature (160 degrees C.). When the aqueous solution is heated without addition of water the boiling point of the aqueous solution rises as the water is evaporated from the solution.

[0035] Increasing the temperature of the phosphoric acid is favorable for increasing the silicon nitride etch rate for production and lower cost of manufacturing at the expense of lower selectivity because with current phosphoric acid recirculation tanks, the consequence of allowing a high boiling point is to reduce the concentration of water. Water is critical in controlling the selectivity of silicon nitride to SiO2 etching [Chemical Reactions in Equations 1, 2]. Experimental evidence shows that a non-boiling state (i.e., low water content) at elevated temperature does not result in a favorable etch selectivity as shown in FIG. **5**B. Conversely, to improve selectivity, it would be preferable to have a high concentration of water (i.e., dilute the acid further); however, this is not practical. Increasing the concentration of water in the bath reduces the boiling point of the aqueous solution. At lower temperature, the etch rate of the silicon nitride falls significantly due to the strong Arrhenius relationship of the silicon nitride etch rate with temperature.

[0036] The term treatment liquid shall be used for the rest of the specification in order to highlight that a solvent used can be water or some other solvent. The present invention is focused on a novel method for increasing the delivery temperature of the treatment liquid to the silicon nitride to increase the silicon nitride etch rate while also maintaining high water content to maintain optimum silicon nitride etch selectivity over silicon or silicon dioxide. The high temperature is achieved by pressurized steam injection into a stream of phosphoric acid before being dispensed on a stationary or rotating single substrate. Condensation of the steam liberates the latent heat energy into the phosphoric acid providing an efficient transfer to heat the phosphoric acid. An additional benefit is that the phosphoric acid is automatically always saturated with water. Water is necessary to maintain a high silicon nitride etch selectivity over silicon dioxide. For a single pass process, it is necessary to have phosphoric acid supplied with dissolved silica to assist with selectivity control. For a recycle process, silica can be supplied in the native phosphoric acid or by cycling of blanket silicon nitride substrates through the etch treatment system (this is a common process used in batch etch treatment systems, also known as phosphoric acid baths). In an embodiment, a steam jet may also be utilized to preheat the substrate to ensure etch uniformity from center to edge on the substrate.

[0037] The problem solved by this invention, among others, is the improvement of the silicon nitride etch rate process using a treatment liquid, for example, phosphoric acid, to enable a single substrate process to be practical and cost effective. Phosphoric acid processing is typically seen as a "dirty process" and is typically followed by a standard clean 1 (SC1) step to remove particles that remain. Single substrate etch processes are inherently cleaner than batch etch processes because the mechanism of defect/particle redeposition and/or backside to frontside contamination can be avoided. Silicon nitride etch processes are slow (30-60 Angstrom/min, or A/min) in hot phosphoric acid at 16° C. If the etch rate of silicon nitride can be increased to over 180 A/min, it would make silicon nitride processing on single substrate process tools feasible. With the use of direct steam injection to heat the silicon nitride, high process temperatures can be achieved while maintaining the saturated water content required for high silicon nitride etch selectivity over silicon or silicon dioxide.

[0038] In one embodiment, a boiling apparatus, fed liquid water at ambient temperature, is used to generate a supply of steam water vapor mixture at elevated pressure. The temperature of the steam water vapor mixture can be controlled by the resulting pressure inside the boiler. The steam water vapor mixture is then piped into the chemical delivery line of the hot phosphoric acid to the single substrate processing chamber. The steam water vapor mixture will provide a source of heat and moisture to the bath, thus elevating the bath above standard boiling temperature and introducing an excess of water vapor in both the vapor and liquid phase to maintain nitride etch selectivity over silicon dioxide and silicon.

[0039] In another embodiment, the steam water vapor mixture is combined with the treatment liquid at high pressure prior to entering the etch processing chamber. Sufficient pressure must be maintained to avoid boiling in the supply delivery line. The treatment liquid will then commence rapid boiling upon entering the etch processing chamber at ambient pressure. In another embodiment, multiple nozzles can be used above the substrate. The first nozzle introduces the heated phosphoric acid, the second or more nozzle(s) introduces jets of high temperature steam water vapor mixture to preheat the substrate surface prior to introduction of the phosphoric acid to help with maintaining uniform temperature across the substrate and consequently ensuring etch uniformity. In this embodiment, the nozzle position and number of nozzles can be positioned to maximize the efficiency of heat delivery and treatment liquid to the substrate. The steam water vapor mixture can also be injected onto the backside of the substrate to maintain temperature uniformity.

[0040] FIG. **3** depicts an exemplary graph **300** of the boiling point of phosphoric acid as a function of phosphoric acid concentration and temperature at one atmosphere pressure. The temperature and concentration of the treatment liquid are two key factors that determine the etch rate and silicon nitride etch selectivity over the silicon or silicon oxide. FIG. **3** depicts a boiling point curve **304** of the temperature of a batch etch process for silicon nitride versus the concentration of the phosphoric acid. Referring to the boiling point curve **304**, assuming the treatment liquid is at an initial set of conditions A, for example, the treatment liquid has a phosphoric acid concentration of 85 percent by weight at about 120 degrees Centigrade. The treatment liquid is heated until a boiling point is reached as represented by the point X, labeled **308**, which is a point in the boiling point curve **304** that also represents the control limit of an exemplary etch treatment system. As mentioned above, the temperature of the treatment liquid is increased in order to increase the etch rate while maintaining a target silicon nitride etch selectivity and maintaining etch uniformity at the same time.

[0041] FIG. **4**A is an exemplary graph **400** comprising the boiling point curve **404**, represented on the left vertical axis, of phosphoric acid as a function of phosphoric acid concentration at one atmosphere pressure and a steam pressure curve **408**, represented on the right vertical axis, as a function of temperature for mixture equilibrium conditions in an etch treatment system. The phosphoric acid concentration is expressed as the percent weight of phosphoric acid in the aqueous solution. Assume a set of initial conditions of the treatment liquid at point (**1**) represented by a dot, corresponding to a composition of 85% phosphoric acid by weight and a temperature of 120 degrees Centigrade (C). The treatment liquid is heated up and reaches boiling temperature represented by the dotted line portion of the boiling point curve **404**. Heating may utilize inline or external heaters or by injecting steam water vapor mixture onto the etch treatment liquid. In one embodiment, the etch treatment system has a limit high temperature represented as point (**2**) on boiling point curve **404** with a corresponding temperature of 160 degrees C. A combination of steam and water vapor (steam water vapor mixture) is pumped into the bottom of the etch treatment system until the treatment liquid reaches a point (**3**) corresponding substantially to a composition of 92% phosphoric acid by weight, a temperature of 180 degrees C. and a steam pressure at approximately 1.0 mega Pascals (MPa). Other combinations of steam water vapor mixtures with aqueous phosphoric acid can be tested to determine the etch rate and etch selectivity of silicon nitride that meet the objectives of an application. Pressure for the steam water vapor mixture can be in the range from 0.2 to 2.0 MPa.

[0042] Referring to FIG. **4**B, assume a pressure of 0.5 MPa is selected as the target pressure for steam water vapor mixture. The corresponding temperature of the mixture (point A on the steam pressure curve **408**) is about 152 degrees C. As the steam water vapor mixture is injected onto the treatment liquid in a bath or a single substrate etch treatment system, the boiling point is determined by the vertical line connecting point A to point A' of the boiling point curve **404**, resulting in a corresponding phosphoric acid concentration at equilibrium of about 86%. If the selected target pressure is 2.0 MPa, the corresponding temperature of the mixture (point B on the steam pressure curve **408**) is about 214 degrees C. Using the same approach, the boiling point is determined by the vertical line connecting point B to point B' of the boiling point curve **404**, resulting in a corresponding phosphoric acid concentration at equilibrium of about 96%. Thus, a flow rate and pressure of the steam water vapor mixture can be used as variables for controlling a temperature of the treatment liquid, which affects the boiling point temperature of the treatment liquid, and further resulting in a concentration of phosphoric acid in the treatment liquid. The equilibrium phosphoric acid concentration and temperature of the treatment liquid affects the etch rate and etch selectivity.

[0043] FIG. **5**A depicts an exemplary graph **500** comprising a first curve **504** of the composition of phosphoric acid solutions expressed as aqueous moles per cubic meter (Aq. mols/m3) and a second curve **508** for water expressed as mols/m3) as a function of temperature in degrees C. As the treatment liquid is heated up in the range of 160 to 220 degrees C., the concentration of phosphoric acid is basically flat, whereas the water concentration goes down due to evaporation as the temperature goes up. To further illustrate the changes to etch selectivity of the treatment liquid, FIG. **5**B depicts an exemplary graph **550** of etch selectivity of phosphoric acid solutions as a function of time and temperature of the treatment liquid in an etch treatment system. At the beginning of the test, the treatment liquid, (aqueous phosphoric acid) was boiling, and deionized water (DIW) was used to spike the treatment liquid, etch selectivity of silicon nitride to silicon dioxide **554** was high. After 50 minutes, spiking with DIW was stopped and the temperature of the treatment liquid crested at about 220 degrees C., leveled at roughly the same temperature before going lower after heater power was reduced. The etch selectivity also went down from high to low, **554** to **558**, as can be seen with the downward slope of etch selectivity curve **564**. After resuming the spiking of the treatment liquid with DIW, the treatment liquid went into a boiling state and the etch selectivity went from low to high, **558** to **562**. The inventors found that the treatment liquid can be advantageous at a range of 160 to 200 degrees C. and preferably about 180 degrees C. for a treatment liquid using aqueous phosphoric acid.

[0044] FIG. **6**A depicts an exemplary schematic representation of batch etch treatment system **600** according to an embodiment of the present invention. A plurality of substrates **632** are positioned in an etch processing chamber **640**. A treatment liquid **628** is introduced into the etch processing chamber **640** and excess treatment liquid goes into an overflow container **604** and can be disposed via a discharge spout **608**. A steam generator **614** is supplied with input liquid via delivery line **620** and is heated by heater **616** which produces a steam water vapor mixture **612**. The steam water vapor mixture **612** is dispensed by a connection **636** onto the bottom of the etch processing chamber **640**. Using a controller (not shown), the batch etch treatment system **600** is configured to meet a selected etch process rate and a Fselected etch selectivity ratio by controlling flow rates of the treatment liquid **628** and the steam water vapor mixture **612**, which may or may not be pressurized to high pressure. Pressure for the steam water vapor mixture can be in the range from 0.2 to 2.0 MPa.

[0045] FIG. **6**B depicts an exemplary schematic representation of a single substrate etch treatment system **650** according to an embodiment of the present invention. A single substrate **654** is mounted on stage **662** configured to keep the substrate **654** stationary or to rotate the substrate **654** while a treatment liquid **678** is dispensed from supply line **682** and the steam water vapor mixture **674** is dispensed from supply delivery line **670**. The steam water vapor mixture **674** is delivered through supply delivery line **670** across the substrate **654** via nozzles **666** arranged so as to effect uniform processing across the substrate **654**. Multiple etch treatment system setups similar to single substrate treatment system **650** can be configured in several arrangements such as stacked, orthogonal, or circular arrangements and the like that can be serviced by a common substrate transfer system. Steam may be delivered onto the backside of the substrate **654** via steam delivery line **658** in order to preheat or maintain uniform temperature across the substrate **654**.

[0046] FIG. **7**A is an exemplary schematic representation of a batch etch treatment system **700** using nozzles **730** to dispense the steam water vapor mixture according to an embodiment of the present invention. A treatment liquid **738** can be heated by heaters **716** positioned in a front and back of an etch processing chamber **742**. The heaters **716** may be external or inline, providing a heat flux in **720** to the treatment liquid **738** in the etch processing chamber **742**. Furthermore, an additional heat flux in **722** is provided by the injection of steam water vapor mixture **736** in the treatment liquid **738**, delivered via supply delivery line **726**. The heat flux out comprises conduction **708** and evaporation of the water **734**. If the heat flux in is greater than the heat flux out **708**, **734** due to evaporation and conduction, a temperature of the treatment liquid **738** will increase until boiling occurs. The boiling point is fixed by the treatment liquid **738** concentration and atmospheric pressure. During boiling, an increase in heat boils the water away faster.

[0047] To maintain a constant boiling temperature for the treatment liquid **738**, the process chamber controller (not shown) must regulate the heaters **716** and the injection of steam water vapor mixture through nozzles **730** at the same time. If the supply of steam water vapor mixture is greater than the water loss due to evaporation, the temperature of the treatment liquid **738** decreases, diluting the treatment liquid **738** and lowering the boiling point. Conversely, if the water supply in is less than the water loss due to evaporation, the temperature of the treatment liquid **738** increases, concentrating the acid and raising the boiling point. Placing the nozzles **730** at a bottom of the etch processing chamber **742** provides mixing actions so as to create a uniform temperature profile in the treatment liquid **738**. The treatment liquid **738** can be introduced via the second supply delivery line **724** to the nozzles **730**. Excess treatment liquid **738** goes to a spill tank **704**. The batch etch treatment system **700** provides a way to increase the etch rate of a masking layer, for example, silicon nitride by raising a temperature of the treatment liquid **738**. The target etch selectivity, the ratio of silicon nitride etching over the silicon oxide or silicon, is also maintained by controlling the molarity of the treatment liquid **738**, for example, by adding more or less steam water vapor mixture, and/or increasing or decreasing the temperature of the steam water vapor mixture distributed through the nozzles **730**.

[0048] FIG. 7B depicts an exemplary schematic representation of a single substrate etch treatment system **760** including a treatment liquid recycling system **783** according to an embodiment of the present invention. Recycling the treatment liquid **774** reduces chemical usage and assist etch selectivity by keeping a high concentration of silica in the treatment liquid to keep the equilibrium of Reaction 2 to the left as will be discussed further below. Referring to the single substrate etch treatment system **760**, a single substrate **796** is positioned on a stage **788** configured to make the substrate **796** stationary or rotating inside the etch processing chamber **762**. A steam water vapor mixture **766** is delivered using supply line **764** and dispensed onto the substrate using nozzles **790**. Steam **769** is dispensed using a steam input line **768** onto the back surface of the substrate **796** to maintain a uniform temperature for the substrate **796**. The steam **769** may be the same as the steam water vapor mixture **766**. The treatment liquid recycling system **783** comprises a drain line **786** coupled to the bottom of the etch processing chamber **762** and goes through a control valve **782** that disposes a portion of the treatment liquid **774** through disposal line **780** and recycles the balance of the treatment liquid **774** through recycle line **784**. An optional heater **778** may be positioned before or after the liquid treatment delivery line **776** to maintain a desired temperature of the recycled treatment liquid **774**. New treatment liquid **774** is introduced onto the recycle line **784** using treatment liquid delivery line **776**.

[0049] Referring to FIG. 7B, dissolved silica assists in maintaining the target silicon nitride etch rate by inhibiting Reaction 2. In one embodiment, dissolved silica ($Si(OH)_4$) is injected onto the treatment liquid **774** using a silica injection line **772** and using delivery line **776**, the amount of silica sufficient to maintain the amount of dissolved silica at a certain target range, for example, 10 to 30 ppm dissolved silica. In one implementation, the dissolved silica can be 20 ppm. In another embodiment, a number of substrates **796** containing silicon nitride is processed in order to obtain a desired amount of dissolved silica in the recycled treatment liquid **774**. One advantage of the present invention using a single substrate treatment system is tolerance for a higher concentration of silica in the treatment liquid. Prior art batch etch treatment systems using phosphoric acid typically shows an increase in defect rate as the concentration of silica went up. A single substrate treatment system is inherently advantageous due to lower defect rate than batch etch treatment systems for the same application, in addition to tolerance of the higher concentration of silica which helps maintain a stable selectivity ratio of the masking layer to the silicon oxide.

[0050] FIGS. **8**A, **8**B, and **8**C are exemplary schematic representations of a transfer system for an etch treatment system in several embodiments of the present invention. According to one embodiment, FIG. **8**A depicts a processing system **800** for performing a non-plasma cleaning process on a substrate or on substrates. The processing system **800** comprises a first treatment system **816**, and a second treatment system **812** coupled to the first treatment system **816**. For example, the first treatment system **816** can comprise a chemical treatment system (or chemical treatment component of a single process chamber), and the second treatment system **812** can comprise a thermal treatment system (or thermal treatment component of a single process chamber).

[0051] Also, as illustrated in FIG. **8**A, a transfer system **808** can be coupled to the first treatment system **816** in order to transfer a substrate or substrates into and out of the first treatment system **816** and the second treatment system **812**, and exchange substrates with a multi-element manufacturing system **804**. The first and second treatment systems **816**, **812**, and the transfer system **808** can, for example, comprise a processing element within the multi-element manufacturing system **804**. For example, the multi-element manufacturing system **804** can permit the transfer of a substrate or substrates to and from processing elements including such devices as etch treatment systems, deposition system, coating systems, patterning systems, metrology systems, etc. In order to isolate the processes occurring in the first and second systems, an isolation assembly **820** can be utilized to couple each system. For instance, the isolation assembly **820** can comprise at least one of a thermal insulation assembly to provide thermal isolation, and a gate valve assembly to provide vacuum isolation. Of course, treatment systems **816** and **812**, and transfer system **808** can be placed in any sequence.

[0052] Alternately, in another embodiment, FIG. **8**B presents a processing system **850** for performing a non-plasma cleaning process on a substrate. The processing system **850** comprises a first treatment system **856**, and a second treatment system **858**. For example, the first treatment system **856**

can comprise a chemical treatment system, and the second treatment system **858** can comprise a thermal treatment system.

[0053] Also, as illustrated in FIG. **8**B, a transfer system **854** can be coupled to the first treatment system **856** in order to transfer a substrate or substrates into and out of the first treatment system **856**, and can be coupled to the second treatment system **858** in order to transfer a substrate or substrates into and out of the second treatment system **858**. Additionally, transfer system **854** can exchange a substrate or substrates with one or more substrate cassettes (not shown). Although only two process systems are illustrated in FIG. **8**B, other process systems can access transfer system **854** including such devices as etch treatment systems, deposition systems, coating systems, patterning systems, metrology systems, etc. In order to isolate the processes occurring in the first and second systems, an isolation assembly **862** can be utilized to couple each system. For instance, the isolation assembly **862** can comprise at least one of a thermal insulation assembly to provide thermal isolation, and a gate valve assembly to provide vacuum isolation. Additionally, for example, the transfer system **854** can serve as part of the isolation assembly **862**.

[0054] Alternately, in another embodiment, FIG. **8**C presents a processing system **870** for performing a non-plasma cleaning process on a substrate or on substrates. The processing system **870** comprises a first treatment system **886**, and a second treatment system **882**, wherein the first treatment system **886** is stacked atop the second treatment system **882** in a vertical direction as shown. For example, the first treatment system **886** can comprise a chemical treatment system, and the second treatment system **882** can comprise a thermal treatment system.

[0055] Also, as illustrated in FIG. **8**C, a transfer system **878** can be coupled to the first treatment system **886** in order to transfer a substrate or substrates into and out of the first treatment system **886**, and can be coupled to the second treatment system **882** in order to transfer a substrate or substrates into and out of the second treatment system **882**. Additionally, transfer system **878** can exchange a substrate or substrates with one or more substrate cassettes (not shown). Although only two process systems are illustrated in FIG. **8**C, other process systems can access transfer system **878** including such devices as etch treatment systems, deposition systems, coating systems, patterning systems, metrology systems, etc. In order to isolate the processes occurring in the first and second systems, an isolation assembly **874** can be utilized to couple each system. For instance, the isolation assembly **874** can comprise at least one of a thermal insulation assembly to provide thermal isolation, and a gate valve assembly to provide vacuum isolation. Additionally, for example, the transfer system **878** can serve as part of the isolation assembly **874**. As illustrated above, the chemical treatment system and the thermal treatment system may comprise separate process chambers coupled to one another. Alternatively, the chemical treatment system and the thermal treatment system may be a component of a single process chamber.

[0056] FIG. **9** is an exemplary flowchart for a method **900** for increasing etch rate and etch selectivity for a masking layer of a substrate for a batch etch treatment system using a treatment liquid and steam water vapor mixture in an embodiment. In step **904**, a target etch rate and target etch selectivity ratio for the masking layer over silicon oxide or silicon are selected. The masking layer can be silicon nitride, gallium nitride or aluminum nitride and the like. In step **908**, a supply of steam water vapor mixture at an elevated pressure is obtained. The steam water vapor mixture may be provided by an inline steam generator or from a general purpose steam source in the fabrication cluster. In step **912**, a supply of a treatment liquid for selectively etching a masking layer is obtained. The treatment liquid can include phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol and the like. In step **916**, a plurality of substrates is placed in the etch processing chamber. In step **920**, the treatment liquid is dispensed in the etch processing chamber, wherein dispensing can be performed using a supply delivery line or a using nozzle. In step **924**, a flow of steam water vapor mixture is injected into the etch processing chamber, wherein the flow rate of the steam water vapor mixture is controlled to achieve the target etch rate for the masking layer and target etch selectivity of the masking layer over the silicon oxide or silicon. The flow rate of the steam water vapor mixture can be correlated to data based on treatment liquid concentration, temperature of the aqueous solution, and steam pressure as shown in FIGS. **4**A and **4**B. As mentioned in the description of FIG. **4**B, a flow rate and pressure of the steam water vapor mixture can be used as variables for controlling a temperature of the treatment liquid, which affects the boiling point temperature of the treatment liquid and further resulting in a concentration of phosphoric acid in the treatment liquid. The equilibrium phosphoric acid concentration and temperature affects the etch rate and etch selectivity.

[0057] FIG. **10** is an exemplary flowchart for a method **1000** for increasing etch rate and etch selectivity for a masking layer of a substrate in a batch etch treatment system using a combined treatment liquid and steam water vapor mixture. In step **1004**, a target etch rate and target etch selectivity for the masking layer over silicon oxide or silicon are selected. The masking layer can be silicon nitride, gallium nitride, or aluminum nitride and the like. In step **1008**, a supply of steam water vapor mixture at an elevated pressure is obtained. The supply may be provided by an inline steam generator or from a general purpose steam source in the fabrication cluster. In step **1012**, a supply of a treatment liquid for selectively etching a masking layer is obtained. The treatment liquid can include phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol and the like. In step **1016**, a plurality of substrates is placed in the etch processing chamber. In step **1020**, the treatment liquid is combined with the steam water vapor mixture in a mixing tank or in a supply delivery line. Sufficient pressure must be maintained to avoid boiling in the supply delivery line. The treatment liquid will commence rapid boiling upon entering the etch processing chamber at ambient pressure.

[0058] Referring to FIG. **10**, in step **1024**, a flow of the combined steam water vapor mixture and treatment liquid is injected into the etch processing chamber, wherein the flow rate of the steam water vapor mixture is controlled to achieve the target etch rate for the masking layer and target etch selectivity of the masking layer over the silicon oxide or silicon. As mentioned above, the flow rate of the steam water vapor mixture can be correlated to data based on treatment liquid concentration, temperature of the aqueous solution, and steam pressure as shown in FIGS. **4**A and **4**B. As mentioned in the description of FIG. **4**B, a flow rate and pressure of the steam water vapor mixture can be used as variables for controlling a temperature of the treatment liquid, which affects the boiling point temperature of the treatment liquid and further resulting in a concentration of phosphoric acid in the treatment liquid. The equilibrium phosphoric acid concentration and temperature affects the etch rate and etch selectivity.

[0059] The correlation can be used to determine the flow rate needed to meet the target etch rate and target etch selectivity. In one embodiment, the steam water vapor mixture and treatment liquid are combined in a supply delivery line before entering the etch processing chamber. In another embodiment, the steam water vapor mixture and treatment liquid are combined immediately before exiting the supply delivery line in the etch processing chamber.

[0060] FIG. **11** is an exemplary flowchart for a method **1100** for increasing etch rate and etch selectivity for a masking layer of a substrate in a batch etch treatment system using a plurality of nozzles positioned at a bottom and sides of the etch processing chamber. In step **1104**, a target etch rate and target etch selectivity for the masking layer over silicon oxide or silicon are selected. The masking layer can be silicon nitride, gallium nitride, or aluminum nitride and the like. In step **1108**, a supply of steam water vapor mixture at an elevated pressure is obtained. The supply may be provided by an inline steam generator or from a general purpose steam source in the fabrication cluster. In step **1112**, a supply of a treatment liquid for selectively etching a masking layer is obtained. The treatment liquid can include phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol and the like. In step **1116**, a plurality of substrates is placed in the etch processing chamber. In step **1120**, the treatment liquid is dispensed in the etch processing chamber.

[0061] In step **1124**, a flow of the combined steam water vapor mixture and treatment liquid is injected into the etch processing chamber using the plurality of nozzles, wherein the flow rate of the steam water vapor mixture is controlled to achieve the target etch rate for the masking layer and target etch selectivity of the masking layer over the silicon oxide or silicon. The plurality of nozzles can be positioned in the bottom and/or on the sides of the etch processing chamber. Arrangements of the plurality of nozzles can be varied to ensure temperature uniformity and consequently etching uniformity. As mentioned above, the flow rate of the steam water vapor mixture can be correlated to data based on treatment liquid concentration, temperature of the aqueous solution, and steam pressure as shown in FIGS. **4**A and **4**B. As mentioned in the description of FIG. **4**B, a flow rate and pressure of the steam water vapor mixture can be used as variables for controlling a temperature of the treatment liquid, which affects the boiling point temperature of the treatment liquid and further resulting in a concentration of phosphoric acid in the treatment liquid. The equilibrium phosphoric acid concentration and temperature affects the etch rate and etch selectivity.

[0062] FIG. **12** is an exemplary flowchart for a method for increasing etch rate and etch selectivity for a layer of a substrate in a single substrate etch treatment system. In step **1204**, a target etch rate and target etch selectivity for the masking layer over silicon oxide or silicon, and/or target completion time are selected. The masking layer can be silicon nitride, gallium nitride, or aluminum nitride and the like. In step **1208**, a supply of steam water vapor mixture at an elevated pressure is obtained. The supply may be provided by an inline steam generator or from a general purpose steam source in the fabrication cluster. In step **1212**, a supply of a treatment liquid for selectively etching a masking layer is obtained. The treatment liquid can include phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol and the like. In step **1216**, a single substrate is placed in the etch processing chamber. In one embodiment, two or more etch processing chambers can be configured such that these chambers can be supplied with the treatment liquid, supplied with steam water vapor mixture, and loaded with and unloaded of substrates. In step **1220**, the treatment liquid is dispensed in the etch processing chamber, wherein dispensing can be performed using a supply delivery line or a nozzle. In step **1224**, a flow of steam water vapor mixture and/or treatment liquid is injected into the etch processing chamber using one or more nozzles while the substrate is spinning. Alternatively, the substrate can be stationary while the nozzles are made to rotate.

[0063] Referring to FIG. **12**, in one embodiment, the treatment liquid and steam water vapor mixture are combined in the supply delivery line prior to entry into the etch processing chamber or after entry into the etch processing chamber but prior to exit out of the nozzle. Sufficient pressure must be maintained in order to avoid boiling in the supply delivery line. The treatment liquid will then commence rapid boiling upon entering the processing chamber at ambient pressure. In another embodiment, multiple nozzles can be used above the substrate. The first nozzle introduces the heated phosphoric acid, the second or more nozzle(s) introduce jets of high temperature steam to preheat the substrate surface prior to introduction of the phosphoric acid to help maintain uniform temperature across the substrate and ensure etch uniformity. In another embodiment, the nozzle position and number of nozzles can be positioned to maximize the efficiency of heat delivery and treatment liquid to the substrate. In still another embodiment, steam water vapor mixture can also be injected onto the backside of the substrate to maintain temperature uniformity.

[0064] FIG. **13** is an exemplary block diagram of a system **1300** for determining and utilizing profile parameters of a structure on a substrate after etch processing where the profile parameter values are used for automated process and equipment control. System **1300** includes a first fabrication cluster **1302** and optical metrology system **1304**. System **1300** also includes a second fabrication cluster **1306**. For details of an optical metrology system used to determine profile parameters of a structure on a substrate, refer to U.S. Pat. No. 6,943,900, titled GENERATION OF A LIBRARY OF PERIODIC GRATING DIFFRACTION SIGNALS, issued on Sep. 13, 2005, which is incorporated herein by reference in its entirety. Although the second fabrication cluster **1306** is depicted in FIG. **13** as being subsequent to first fabrication cluster **1302**, it should be recognized that second fabrication cluster **1306** can be located prior to first fabrication cluster **1302** in system **1300**, for example, in the manufacturing process flow.

[0065] A photolithographic process, such as exposing and/or developing a photoresist layer applied to a substrate, can be performed using first fabrication cluster **1302**. In one exemplary embodiment, optical metrology system **1304** includes an optical metrology tool **1308** and processor **1310**. Optical metrology tool **1308** is configured to measure a diffraction signal off the sample structure. Processor **1310** is configured to use the measured diffraction signal measured by the optical metrology tool and adjust using a signal adjuster, generating an adjusted metrology output signal. Furthermore, processor **1310** is configured to compare the adjusted metrology output signal to the simulated diffraction signal. As mentioned above, the simulated diffraction is determined using an optical metrology tool model using ray tracing, a set of profile parameters of the structure and numerical analysis based on the Maxwell equations of electromagnetic diffraction. In one exemplary embodiment, optical metrology system **1304** can also include a library **1312** with a plurality of simulated diffraction signals and a plurality of values of one or more profile parameters associated with the plurality of simulated diffraction signals. As described above, the library can be generated in advance; metrology processor **1310** can compare an adjusted metrology output signal to the plurality of simulated diffraction signals in the library. When a matching simulated diffraction signal is found, the one or more values of the profile parameters associated with the matching simulated diffraction signal in the library is assumed to be the one or more values of the profile parameters used in the substrate application to fabricate the sample structure.

[0066] System **1300** also includes a metrology processor **1316**. In one exemplary embodiment, processor **1310** can transmit the one or more values of the one or more profile parameters to metrology processor **1316**. Metrology processor **1316** can then adjust one or more process parameters or equipment settings of the first fabrication cluster **1302** based on the one or more values of the one or more profile parameters determined using optical metrology system **1304**. Metrology processor **1316** can also adjust one or more process parameters or equipment settings of the second fabrication cluster **1306** based on the one or more values of the one or more profile parameters determined using optical metrology system **1304**. As noted above, second fabrication cluster **1306** can process the substrate before or after fabrication cluster **1302**. In another exemplary embodiment, processor **1310** is configured to train machine learning system **1314** using the set of measured diffraction signals as inputs to machine learning system **1314** and profile parameters as the expected outputs of machine learning system **1314**.

[0067] FIG. **14** is an exemplary flowchart of a method for controlling a fabrication cluster using an etch treatment system configured to increase etch rate and etch selectivity. Using the system described in FIG. **13**, after etch processing using the systems and methods described in relation to FIGS. **3** to **12**, the structure in the substrate can be measured using the method as depicted with the exemplary block diagram **1400** of a system for determining and utilizing profile parameters for automated process and equipment control. In step **1410**, a measured diffraction signal off a sample structure is obtained using an optical metrology tool. In step **1420**, a metrology output signal is determined from the measured diffraction signal using ray tracing methodology, calibration parameters of the optical metrology device, and one or more accuracy criteria or other scatterometry methodologies such as regression, library matching or machine learning systems. In step **1430**, at least one profile parameter of the sample structure is determined using the metrology output signal. In step **1440**, at least one fabrication process parameter or an equipment setting is modified using at least one profile parameter of the structure.

[0068] Referring to FIGS. **6**A and **6**B, a controller (not shown) can be used to control the flow rates of the treatment liquid and steam water vapor mixture, pressure of the treatment liquid, sequencing of the use of the nozzles in the batch or single substrate etch application. A program stored in the memory of the controller can be utilized to activate the inputs to the aforementioned components of the etch treatment systems **600 650** (FIGS. **6**A and **6**B) according to a process recipe in order to perform the method of increasing the etch rate and etch selectivity of the masking layer compared to silicon or silicon oxide. One example of controller **1090** is a DELL PRECISION WORKSTATION 610TH, available from Dell Corporation, Austin, Tex. A controller can be locally located relative to the etch treatment systems **600 650**, or it can be remotely located relative to the etch treatment systems **600 650**, via an internet or intranet. Thus, the controller can exchange data with the etch treatment systems **600 650**, using at least one of a direct connection, an intranet, or the internet. The controller can be coupled to an intranet at a customer site (i.e., a device maker, etc.), or coupled to an intranet at a vendor site (i.e., an equipment manufacturer). Furthermore, another computer (i.e., controller, server, etc.) can access the controller of the etch treatment systems **600 650** to exchange data via at least one of a direct connection, an intranet, or the internet.

[0069] Although exemplary embodiments have been described, various modifications can be made without departing from the spirit and/or scope of the present invention. For example, the invention was illustrated and described utilizing etching of a masking layer on a substrate, specifically, silicon nitride. Other masking materials or insulating layers can be processed using the same methods and systems described in the specification. Therefore, the present invention should not be construed as being limited to the specific forms shown in the drawings and described above. Accordingly, all such modifications are intended to be included within the scope of this invention.

What is claimed:

1. A system for increasing etch rate and etch selectivity of a masking layer on a substrate, the system comprising:

a plurality of substrates containing the masking layer and a layer of silicon or silicon oxide;

an etch processing chamber configured to process the plurality of substrates, the etch processing chamber containing a treatment liquid for etching the masking layer in the plurality of substrates; and

a boiling apparatus coupled to the processing chamber and configured to generate a supply of steam water vapor mixture at elevated pressure;

wherein the steam water vapor mixture is introduced into the etch processing chamber at a flow rate sufficient to maintain a selected target etch rate and a selected target etch selectivity ratio of the masking layer to silicon or silicon oxide.

2. The system of claim **1**, where the masking layer comprises one of silicon nitride, gallium nitride, or aluminum nitride.

3. The system of claim **2**, wherein the treatment liquid is an aqueous phosphoric acid solution.

4. The system of claim **2**, wherein the selected target etch selectivity ratio is in the range from 10:1 to 1000:1.

5. The system of claim **3**, wherein a temperature of the aqueous phosphoric acid solution is in the range of 160 to 220 degrees Centigrade.

6. The system of claim **2**, wherein the steam water vapor mixture at elevated pressure and a treatment liquid are combined at high pressure prior to entering the etch processing chamber.

7. The system of claim **2**, wherein the steam water vapor mixture at elevated pressure and a treatment liquid are combined at high pressure prior to exiting supply delivery lines to the etch processing chamber.

8. The system of claim **2**, wherein:

the flow rate and pressure of the steam water vapor mixture are controlled to maintain the selected target etch rate and the selected target etch selectivity ratio of silicon nitride to silicon or silicon oxide.

9. The system of claim **1**, wherein:

the steam water vapor mixture at elevated pressure is introduced into the etch processing chamber using nozzles fitted along a bottom and a side of the etch processing chamber; and

the steam water vapor mixture is introduced at a controlled rate to maintain the selected target etch rate and the selected target etch selectivity ratio of the masking layer to silicon or silicon oxide.

10. The system of claim **1**, wherein the treatment liquid includes one of phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol.

11. The system of claim **1** wherein the flow rate and pressure of the steam water vapor mixture are controlled to cause a temperature of the treatment liquid, causing in turn a boiling point temperature of the treatment liquid and further causing an equilibrium concentration and temperature of the treatment liquid to achieve the target etch rate and the target etch selectivity ratio.

12. A method of increasing etch rate and etch selectivity of a masking layer on a substrate, the method comprising:

fabricating a plurality of substrates containing the masking layer and a layer of silicon or silicon oxide;

obtaining a supply of steam water vapor mixture at an elevated pressure;

obtaining a supply of a treatment liquid for selectively etching the masking layer over the silicon or silicon oxide at a set etch rate and a set etch selectivity ratio;

placing the plurality of substrates into an etch processing chamber;

combining the treatment liquid and the steam water vapor mixture; and

injecting the combined treatment liquid and the steam water vapor mixture into the etch processing chamber;

wherein a flow of the combined treatment liquid and the steam water vapor mixture is configured to maintain the set etch rate and the set etch selectivity ratio of the masking layer to silicon or silicon oxide.

13. The method of claim **12**, where the masking layer comprises silicon nitride.

14. The method of claim **13**, wherein the treatment liquid comprises an aqueous phosphoric acid solution.

15. The method of claim **13**, wherein the set etch selectivity ratio is from 10:1 to 1000:1.

16. The method of claim **13**, wherein a temperature of the aqueous phosphoric acid solution is in the range of 160 to 180 degrees Centigrade.

17. The method of claim **13**, wherein the steam water vapor mixture at elevated pressure and the treatment liquid are combined at high pressure prior to entering the etch processing chamber.

18. The method of claim **13**, wherein:

the injecting the combined treatment liquid and the steam water vapor mixture uses nozzles fitted along a bottom and/or sides of the etch processing chamber; and

the steam water vapor mixture is introduced at a controlled rate to maintain the set etch selectivity ratio of silicon nitride to silicon or silicon oxide.

19. The method of claim **13**, wherein the treatment liquid includes one of phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol.

20. The method of claim **19**, wherein the masking layer includes one of silicon nitride, gallium nitride, or aluminum nitride.

21. The method of claim **20** wherein flow rate and pressure of the steam water vapor mixture are controlled to cause a temperature of the treatment liquid, causing in turn a boiling point temperature of the treatment liquid and further causing an equilibrium concentration and temperature of the treatment liquid to achieve the target etch rate and the target etch selectivity ratio.

22. A method of increasing etch rate and selectivity of etching silicon nitride on a substrate, the method comprising:

placing a plurality of substrates containing a masking layer of silicon nitride and a layer of silicon or silicon oxide into an etch processing chamber;

combining a treatment liquid and a steam water vapor mixture under elevated pressure; and

injecting the combined treatment liquid and the steam water vapor mixture into the etch processing chamber;

wherein a flow of the combined treatment liquid and the steam water vapor mixture are controlled to maintain a target etch rate of the silicon nitride and a target etch selectivity ratio of the silicon nitride to silicon or silicon oxide.

23. The method of claim **22**, wherein the treatment liquid includes one of phosphoric acid, hydrofluoric acid, or hydrofluoric acid/ethylene glycol.

24. The method of claim **23** wherein a flow rate and pressure of the steam water vapor mixture are controlled to cause a temperature of the treatment liquid, causing in turn a boiling point temperature and further causing an equilibrium concentration and temperature of the treatment liquid to achieve the target etch rate and the target etch selectivity ratio.

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