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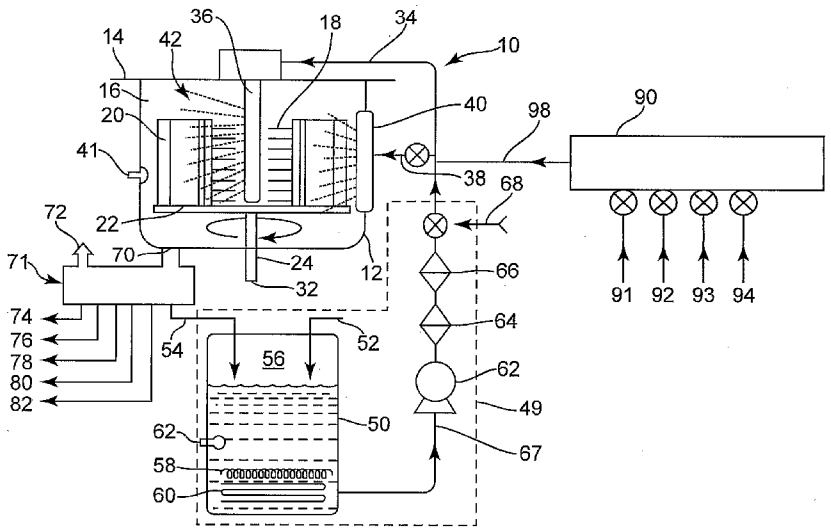
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(54) **Title:** PROCESS FOR REMOVING MATERIAL FROM SUBSTRATES



(57) **Abstract:** A method of removing materials, and preferably photoresist, from a substrate (18) comprises dispensing a liquid sulfuric acid composition comprising sulfuric acid and/or its desiccating species and precursors and having a water/ sulfuric acid molar ratio of no greater than 5:1 onto an material coated substrate in an amount effective to substantially uniformly coat the material coated substrate. The substrate is preferably heated to a temperature of at least about 9O°C, either before, during or after dispensing of the liquid sulfuric acid composition. After the substrate is at a temperature of at least about 9O°C, the liquid sulfuric acid composition is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition above the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor. The substrate is then preferably rinsed to remove the material .

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PROCESS FOR REMOVING MATERIAL FROM SUBSTRATES

This application claims the benefit of U.S. Provisional Application Serial No. 60/739,727, filed November 23, 2005, entitled "PROCESS FOR REMOVING ORGANIC MATERIAL" which application is incorporated herein by reference in its entirety.

Field of the Invention

The present invention relates to methods for removing material from substrates. More specifically, the present invention relates to removal of materials, and preferably photoresist materials, from substrates using sulfuric acid and water vapor.

Background of the Invention

Advances in electronic technology cause integrated circuits to be formed on substrates such as silicon wafers with ever increasing packing density of active components. The formation of circuits is carried out by sequential application, processing, and selective removal of various components from the substrate. Various compositions have been developed for removal of specific classes of components from substrates in semiconductor wafer technologies. For example, a composition commonly denoted SC-1, which contains a mixture of NH_4OH(29 wt%)/H_2O_2(30 wt%)/water at a volume ratio of about 1:1:5 (or at somewhat higher dilution ratios), is typically used to remove particles and to reoxidize hydrophobic silicon surfaces. Similarly, a composition commonly denoted SC-2, which contains a mixture of HCl(37 wt%)/H_2O_2(30 wt%)/water at a volume ratio of about 1:1:5 (or at somewhat higher dilution ratios), is typically used to remove metals. An additional composition, commonly called a Piranha composition, comprises H_2SO_4(98 wt %)/H_2O_2(30 wt%) at a volume ratio of about 2:1 to 20:1, and is typically used to remove organic contamination or some metal layers.

Photoresist materials are used in many circuit manufacturing processes to assist in formation of sequential layers. In stages of the manufacturing process, these photoresist

materials are often removed, preferably without substantial damage to the substrate, including structures formed thereon. Photoresists are conventionally removed using organic solvents, such as n-methyl-pyrrolidone ("NMP"), glycol ether, amine, or dimethyl sulfoxide ("DMSO"). Alternatively, photoresist materials have been removed using hot chemical removal with a chemical etching agent such as sulfuric acid and hydrogen peroxide, or using dry reactive removal generally known as photoresist plasma ashing. US Patent No. 5,785,875 discloses a method for removing photoresist material by carrying out a wet acid etch by fully submerging the wafers within an hydrous acid, and draining the etching agent from the chamber while inserting a heated solvent vapor. The solvent is, for example acetone, alcohols, or another solvent, but preferably comprises isopropyl alcohol, and is heated to the range of between about 50° C. and about 100° C. Traditional wet chemical processes used to remove photoresist rely on concentrated sulfuric acid combined with hydrogen peroxide (Piranha or "Sulfuric-Peroxide Mix" or SPM) or ozone (sulfuric-ozone mix or "SOM"). Alternatively, photoresists can be removed under certain conditions by using ozone dissolved in DI water or by mixing ozone gas with water vapor at elevated temperatures.

It would be desirable to identify alternative techniques and compositions for treatment to remove materials, especially organic materials, and most especially photoresist materials from substrates such as semiconductor wafers.

Summary of the Invention

It has been determined that applying sulfuric acid and/or its desiccating species and precursors (e.g. sulfur trioxide (SO_3), thiosulfuric acid ($H_2S_2O_3$), peroxosulfuric acid (H_2SO_5), peroxydisulfuric acid ($H_2S_2O_8$), fluorosulfuric acid (HSO_3F), and chlorosulfuric acid (HSO_3Cl)) to photoresist coated substrates in an immersion bath environment, even at elevated temperature, is not effective in removal of harshly treated photoresist. In view of this it has surprisingly been found that sulfuric acid and desiccating sulfuric acid species and

precursors can be effective in removing materials, especially organic materials and most especially photoresist materials from the surface of substrates when a liquid sulfuric acid composition having a water/sulfuric acid molar ratio of no greater than about 5:1 is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition above the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor . In an embodiment of the present invention, the liquid sulfuric acid composition is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition above both (i) the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor and (ii) the temperature of the water vapor. In a preferred embodiment, a liquid sulfuric acid composition having a water/sulfuric acid molar ratio of no greater than about 5:1 is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition on the substrate surface above both (i) the on-substrate temperature of the liquid sulfuric acid composition prior to exposure to the water vapor and (ii) the temperature of the water vapor. The present method is particularly significant in the case of removal of photoresist materials, even in the case when the photoresist is baked onto the substrate or when the photoresist is heavily ion implanted, under certain process conditions.

For purposes of brevity, liquid sulfuric acid compositions as discussed herein will be understood to comprise sulfuric acid and/or its desiccating sulfuric acid species and precursors, and discussions regarding sulfuric acid contained in these liquid compositions will likewise be understood to describe corresponding compositions comprising sulfuric acid and/or its desiccating sulfuric acid species and precursors. Examples desiccating sulfuric acid species and precursors of sulfuric acid include sulfur trioxide (SO_3), thiosulfuric acid ($H_2S_2O_3$), peroxosulfuric acid (H_2SO_5), peroxydisulfuric acid ($H_2S_2O_8$), fluorosulfuric acid (HSO_3F), and chlorosulfuric acid (HSO_3Cl). In an embodiment of the

present invention, a desiccating species of sulfuric acid is a complex of sulfuric acid with an oxidizing agent.

In the method of removing materials, preferably organic materials and more preferably photoresist, from a substrate as provided herein, a substrate having material on a surface thereof is placed in a treatment chamber. A liquid sulfuric acid composition is dispensed onto the substrate in an amount and manner effective to substantially uniformly coat the substrate surface. For purposes of the present invention, the water/sulfuric acid molar ratio is calculated for compositions comprising the desiccating sulfuric acid species and precursors based on the molar ratio in the final mixture of water to the moles present of the desiccating sulfuric acid species or precursor.

In one embodiment of the present invention, the substrate is pretreated with a pretreatment liquid to facilitate providing a surface wherein a liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1, when applied to the surface, will substantially uniformly coat on the surface. For purposes of the present invention, a liquid sulfuric acid composition is considered to substantially uniformly coat the substrate if, when sufficient liquid sulfuric acid composition is applied to the surface to completely coat the surface, substantially no beading up of the liquid sulfuric acid composition (i.e. no discontinuities of the liquid on the surface) is observed. The pretreatment composition in one embodiment comprises application of sufficient liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1 to modify the surface characteristics of the substrate, so that a subsequent (or continuing) application of liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1 will substantially uniformly coat the substrate. Optionally, other surface modifying components may be used in the pretreatment liquid, such as surfactants or solvents that act to modify the surface characteristics of the substrate as desired.

In another aspect of the present invention, it has been found that the effectiveness and efficiency of removal of materials from the surface of a substrate is particularly enhanced wherein the liquid sulfuric acid composition has a water/sulfuric acid molar ratio of no greater than about 3:1, or no greater than about 2:1. In a preferred embodiment of the present invention, it has been found that the effectiveness and efficiency of removal of materials from the surface of a substrate is particularly enhanced wherein the liquid sulfuric acid composition having a water/sulfuric acid molar ratio of no greater than about 1:2. In an embodiment of the invention, the liquid sulfuric acid composition does not contain water. For ease in obtaining materials, however, and embodiment of the invention contemplates that the liquid sulfuric acid composition will contain at least as much water as is conventionally present in the raw materials. In another embodiment of the present invention, the liquid sulfuric acid composition has a water/sulfuric acid molar ratio of from about 1:2 to about 1:4.

Stated another way, preferably the liquid sulfuric acid has a concentration by volume greater than about 50 vol% , more preferably greater than 80 vol% , and most preferably greater than 90 vol%. For purposes of the present invention, when volume ratios of sulfuric acid are discussed, it is intended that the content of sulfuric acid is calculated based on 98 wt% sulfuric acid source. Thus, a sulfuric acid/water composition comprising sulfuric acid in a content of 50% by volume comprises 50 vol% of 98 wt% sulfuric and 50 vol% water.

Preferably, the substrate is heated to a temperature of at least about 90°C, either before, during or after dispensing of the liquid sulfuric acid composition. The liquid sulfuric acid composition is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition on the substrate surface above the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor . In an embodiment of the present invention, the liquid sulfuric acid composition is exposed to

water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition on the substrate surface above both (i) the temperature of the on-substrate liquid sulfuric acid composition prior to exposure to the water vapor and (ii) the temperature of the water vapor. Either after or between steps of the above described treatment, the substrate is preferably rinsed.

It has been found that the amount of water present in the liquid sulfuric acid composition prior to or as applied to the substrate is important to the effectiveness of the removal of undesired material. Specifically, it has been found that sulfuric acid compositions that initially contain too much water are less able to strip resist when exposed to water vapor. While not being bound by theory, it is believed that these diluted sulfuric acid compositions are either less able to take up water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition above the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor, or the chemical activity of the composition is decreased by the water, or both.

In embodiments where the substrate is at an ambient processing temperature below the boiling point of water (particularly in a temperature range of about 20-60°C), the temperature of the liquid sulfuric acid composition is substantially increased upon addition of water vapor. Surprisingly, it further has been found that even when the substrate and/or the sulfuric acid composition is at a high temperature (e.g. greater than about 90°C), and particularly at a temperature at or above 100°C, the water vapor is taken up by the liquid sulfuric acid composition even though the temperature of the liquid sulfuric acid composition is near or above the boiling point of water. While not being bound by theory, it is believed that the liquid sulfuric acid has a desiccating effect, thereby causing water from the water vapor to be condensed into the liquid sulfuric acid composition and releasing the energy corresponding roughly to the heat of vaporization stored in the water vapor.

Brief Description of the Drawings

FIG. 1 is a graph showing the resulting temperature rise when liquid water or H_2O_2 (30 wt%) is added to H_2SO_4 (98 wt%).

FIG. 2 is a graph showing the temperature rise when liquid water is added to a blend of H_2SO_4 (98 wt%)/water as a function of the fraction of H_2SO_4 (98 wt%) in the solution.

FIG. 3A shows a schematic view of a batch spray processor that can be used to carry out the process of the present invention.

FIG. 3B shows one representative mode of practice of using the processor shown in FIG. 1A.

FIG. 4 is graph showing the temperature of the liquid composition of sulfuric acid/hydrogen peroxide as cast onto the side wall of the processing chamber during runs of a comparative process and of a process of the present invention.

FIG. 5 is a graph showing the maximum measured on-wafer temperatures of the sulfuric acid/hydrogen peroxide composition during runs of a comparative process, and after exposure to water vapor in a process of the present invention. Also shown are the temperatures of the sulfuric acid/hydrogen peroxide compositions as blended, before being dispensed.

FIG. 6 is a graph showing the difference between the maximum measured on-wafer temperatures of the sulfuric acid/hydrogen peroxide composition after exposure to water vapor and the temperature of the sulfuric acid/hydrogen peroxide compositions as blended during runs of a comparative process, and of a process of the present invention. Also shown are the averaged temperatures of the sulfuric acid/hydrogen peroxide composition as blended, before being dispensed.

FIG. 7 shows a schematic view of a single-wafer processor that can be used to carry out the process of the present invention.

FIG. 8 shows a system for directing a spray using a three orifice nozzle.

Detailed Description

The above mentioned and other advantages of the present invention, and the manner of attaining them will become more apparent, and the invention itself will be better understood by reference to the following description of the embodiments of the invention taken in conjunction with the accompanying drawings.

For purposes of the present invention, water vapor is defined as water in the gaseous form, and distinguished from small droplets of water commonly called "mist." Because mist is water that is condensed in the form of small droplets, there is essentially no net warming effect when mist settles on a surface that would correspond to a heat of vaporization. For purposes of the present invention, steam is vaporized water at or above the boiling point of water, which depends on the pressure, e.g. 100°C if the pressure is 1 atmosphere. When steam is provided at a temperature greater than the boiling point of water, is it called superheated steam. Water vapor optionally may be provided from compositions comprising components in addition to water, such as dissolved gasses such as ozone, or inert gasses such as nitrogen. It is contemplated that water vapor may be supplied to the sulfuric acid composition in any manner, either essentially pure, or in compositions, either above, or below or at 100° C, and having pressures or partial pressures of water vapor either above, below or at 1 atm. The method of the present invention may be used to process multiple wafer-like objects simultaneously, as occurs with batches of wafers when being processed in a spray processing tool such as the MERCURY® or ZETA® spray processors commercially available from FSI International, Inc., Chaska, MN, or the Magellan® system, also commercially available from FSI International, Chaska, Minnesota. The present invention may also be used in single wafer processing applications where the wafers are either moving or fixed, or in batch applications where the wafers are substantially stationary.

With reference to the figures, wherein like numerals are used to label like components throughout the several figures:

FIG. 1 shows the resulting temperature when 20° C H_2SO_4(98 wt%) is mixed with 20° C liquid water or 20° C H_2O_2(30 wt%) in a rapidly stirred beaker. In region A, at H_2SO_4 volume fractions between approximately 100% and 57%, the H_2SO_4/water blend increases in temperature with increasing water content. In region B, at fractions between approximately 56% and 36%, the H_2SO_4/water blend decreases slowly in temperature with increasing water content. In region C, at fractions between approximately 35% and 10%, the temperature of the blend decreases rapidly with increasing water content. The temperature profile of H_2SO_4 mixed with H_2O_2 follows the same trend, but with a slightly lower maximum temperature. A maximum temperature rise of approximately 110° (130° C final temperature) is obtained with an H_2SO_4/water blend that is a blend of approximately 57 vol% H_2SO_4 and 43 vol% H_2O_2. Also shown on the top axis is the H_2O to H_2SO_4 mole ratio of the water:H_2SO_4 blend. The boundaries between regions A and B is approximately 2:1 water:H_2SO_4, and between B and C is approximately 5:1.

FIG. 2 shows the derivative of the water-added curve from FIG. 1. This shows the rise in temperature for each percent increase in water content as a function of the fraction of H_2SO_4 in the solution. There is an almost linear decrease in dT/dWater from 100% to 37% H_2SO_4 fraction. While not being bound by theory, it is believed that the temperature increase of the solution (the heat of mixing) is being caused by the heat of hydration as water molecules coordinate around each sulfuric acid molecule. In the present invention, this strong attraction between the water and sulfuric molecules drives the desiccant action that draws water vapor from the atmosphere and into the sulfuric acid composition, even when the temperature of the sulfuric acid composition is above the boiling point of water. At approximately 55 vol% sulfuric acid, the heat of hydration is balanced by the thermal load of the added water, and additional added water has a net cooling effect on the blend.

At approximately 37 vol% H_2SO_4, the hydration of H_2SO_4 appears to be complete. As shown in the upper x-axis of FIGs. 1 and 2 show the mole ratio of water:H_2SO_4 in the solution. The hydration appears to be complete when approximately 5 moles of water are present for each mole of H_2SO_4.

In contrast to FIG. 1, the present invention adds water to the sulfuric acid composition by condensation of water vapor into the composition. This results in the heating of the composition not only by the heat of mixing between H_2SO_4 and H_2O, but also by the water's heat of vaporization that is regained when the water condenses into the sulfuric acid composition. Compared to adding liquid water to H_2SO_4, the thermal contribution from water vapor's heat of vaporization allows larger temperature increases for a given amount of dilution.

FIGS. 3A and 3B show one example of equipment useful for carrying out the process of the present invention. FIG. 3A shows a schematic view of a batch spray processor 10 showing main system components including chemical mixing manifold 90, recirculation tank 50, and process bowl 12. The equipment 10 is a schematic representation of a spray processing tool such as that included in a MERCURY® or ZETA® spray processor commercially available from FSI International, Inc., Chaska, MN. Equipment 10 generally includes a bowl 12 and lid 14 defining a processing chamber 16. Wafer-like objects 18 are positioned in carriers 20 (e.g., TEFLON® cassettes), which in turn are held upon rotating turntable 22 by turntable posts (not shown). Turntable 22 is coupled to motor-driven shaft 24. Water or nitrogen may be supplied from supply line(s) 32 and dispensed into processing chamber 16 through the turntable posts (not shown). One or more chemicals may also be supplied from supply line(s) 34 and dispensed into processing chamber 16 directly onto the wafers 18 and/or directly onto turntable 22 through center spray post 36 or onto the wafers via the side spray post 40 via line(s) 38.

For example, a supply line 34 can be fluidly coupled to a chemical recirculation system 49. The recirculation system can include chemical supply lines 67 and 68. Chemical supply line 67 can include filters 64 and 66, pump 62, and be fluidly coupled to recirculation supply tank 50. The recirculation supply tank can be supplied with process chemical from recirculation drain 54 and fresh chemical makeup 52. A nitrogen blanket 56 can be used in the headspace of tank 50. To control temperature of the process chemical in tank 50, tank 50 can include a heating coil 58, cooling coil 60, and temperature probe 41. Chemical supply line 68 can supply, e.g., nitrogen and DI water rinse. After supplying chemical to processing chamber 16, any unused chemical can enter drain 70 and pass into drain manifold 71. From the drain manifold, the chemical can be directed to a variety of outlets such as recirculation drain 54, exhaust 72, DI drain 74, auxiliary 76, auxiliary 78, auxiliary 80, and auxiliary 82.

Supply line 34 can also be fluidly coupled to a fresh chemical blending manifold 90. In the manifold, controlled flows of fresh chemicals from lines 91-94 are mixed to form a desired blend that is sent to the center spray post 36 via line(s) 98 and 34 or to the side spray post 40 via lines 98 and 38. Optionally, the chemical blend can be heated by an in-line infra-red heater in line 98 (heater not shown). Alternately, one or more of the feed chemicals can be heated by an infra-red heater placed in one or more of lines 91-94.

The configuration and use of equipment 10 has been further described in U.S. Pat. Nos. 5971368; 6,235,641; 6,274,506; and 6,648,307, as well as in Assignee's co-pending U.S. Patent Application titled ROTARY UNIONS, FLUID DELIVERY SYSTEMS, AND RELATED METHODS in the names of Benson et al., filed March 12, 2004, and having U.S. Serial No. 10/799,250, said co-pending application being incorporated herein by reference in its entirety.

FIG. 3B shows one representative mode of practice of using the equipment 10 in accordance with the present invention. A liquid sulfuric acid composition 42 is dispensed

onto wafers 18 from center spray post 36 and/or side spray post 40 (not shown) in an amount effective to substantially uniformly coat the organic material coated substrate. This substantially uniform coating may be facilitated by pretreatment, for example, using the same apparatus, with a pretreatment liquid to provide a surface wherein a liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1, when applied to the surface, will substantially uniformly coat on the surface. As noted above, the pretreatment composition may for example be a preapplication of liquid sulfuric acid composition to modify the surface characteristics of the substrate, so that a subsequent (or continuing) application of liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1 will substantially uniformly coat the substrate. Optionally, other surface modifying components may be used in the pretreatment liquid, such as surfactants or solvents that act to modify the surface characteristics of the substrate as desired. Additional components may be added to provide chemical modification of the pretreatment solution. For example, a minor amount of acid may be added to an aqueous pretreatment solution.

After (or while, or before) the liquid sulfuric acid composition 42 is dispensed, hot water 44 is dispensed onto turn table 22. Evaporation of a portion of the hot water 44 increases the water vapor content (humidity) of the chamber atmosphere. Wafers 18 have been coated with an organic material that is to be removed. In preferred embodiments, the organic material is photoresist material. Organic materials that are challenging to remove include photoresist that has been baked on by exposure to heat during previous wafer processing steps. Organic materials that are particularly challenging to remove are those that have been heavily ion implanted during previous wafer processing steps. The methods of the present invention are particularly and surprisingly effective in the removal of heavily ion implanted photoresist materials.

The liquid sulfuric acid composition 42 has a water/sulfuric acid molar ratio of no greater than about 5:1. Thus, the liquid sulfuric acid composition is limited in water content. In one embodiment, the liquid sulfuric acid composition may comprise a solvent that does not substantially interfere with the coordination of subsequently added water vapor with sulfuric acid, as discussed in more detail herein. Preferred such solvents are inert with respect to the substrate to be treated (e.g. the wafer), such as fluorine based liquids. An example of such inert solvents include the Fluorinert™ solvents commercially available from 3M, St. Paul, MN. It should be noted that the above mentioned molar ratio recites the water/sulfuric acid molar ratio, and not the solvent/sulfuric acid ratio. This underscores that the solvent that does not substantially interfere with the coordination of subsequently added water vapor with sulfuric acid does not factor into this ratio of the present inventive embodiment.

More preferably, the liquid sulfuric acid composition is highly concentrated. Preferably, the liquid sulfuric acid composition is dispensed at a sulfuric acid concentration of at least about 80 vol%, more preferably at least about 90 vol%, and most preferably at least about 94 vol%. As shown in FIGs 1 and 2, these high H_2SO_4 concentrations result in the largest temperature rise per unit of water vapor condensed into the H_2SO_4 composition.

In an embodiment of the present invention, the liquid sulfuric acid composition 42 comprises hydrogen peroxide. The hydrogen peroxide serves as an oxidant that assists in breaking down organic species to CO_2 and water. Hydrogen peroxide is conveniently provided in a water-containing solution blended with concentrated sulfuric acid to provide a liquid sulfuric acid composition having water/sulfuric acid molar ratio of no greater than about 5:1. Advantageously, mixing of concentrated sulfuric acid with a water-containing hydrogen peroxide solution generates heat by an exothermic reaction, and so the resulting liquid sulfuric acid composition comprising hydrogen peroxide can be provided at elevated temperature while using less energy from a dedicated heat source to heat the composition.

This exothermic reaction is normally a significant source of heat for the composition. However, in the present invention the reaction between the sulfuric acid composition and water vapor provides the desired heat, and excess additions of water-based hydrogen peroxide can inhibit this sulfuric-vapor reaction. Therefore, with the knowledge of the effect of vapor in concentrated sulfuric acid compositions as described herein, the skilled artisan can now adjust the H_2O_2 concentration to simultaneously optimize the heat generated by the H_2SO_4-vapor reaction while supplying sufficient reactants to oxidize organics.

In an aspect of the present invention, an oxidizing agent can be introduced into the treatment chamber before, during or after dispense of the liquid sulfuric acid composition. For example, hydrogen peroxide can be mixed with the liquid concentrated sulfuric acid prior to introduction of the liquid sulfuric acid composition into the treatment chamber, or alternatively during or after dispense of the liquid sulfuric acid composition in the treatment chamber. Mixing of the hydrogen peroxide with the liquid concentrated sulfuric acid can be accomplished by the use of static mixers or active mixing techniques, or can be merely contacting one solution with the other, with mixing being accomplished by mere diffusion. Other agents, such as ozone, may be similarly incorporated in the liquid sulfuric acid composition as desired. Water-free oxidants such as ozone may be superior to H_2O_2 as they will not dilute the H_2SO_4 composition. For example, oxidants other than H_2O_2 may be utilized in the inventive sulfuric-vapor process. For instance, ozone, nitric acid, the chromate ion (Cr^{+6}), or the ceric ion (Ce^{+4}) may be incorporated in the process as described herein. In particular, these species might be added to H_2SO_4 in an anhydrous form, so that the H_2SO_4 remains relatively undiluted. Other oxidants may also be used.

Preferably, the liquid sulfuric acid composition is dispensed at a temperature of at least about 90°C, and more preferably from about from about 90°C to about 150°C. In another embodiment, the liquid sulfuric acid composition is preferably dispensed at a temperature of from about 95°C to about 120°C. In another embodiment, the liquid sulfuric

acid composition is dispensed at a temperature of at least about 130°C prior to exposure to the water vapor, and more preferably from about 130°C to about 200°C. The introduction of the liquid sulfuric acid composition 42 wets the wafer surfaces with the sulfuric acid chemistry. Preferably liquid sulfuric acid composition 42 is applied to the wafer in an amount to provide sufficient sulfuric acid functionality to remove the organic material coated on wafer 18. Preferably, the liquid sulfuric acid composition is dispensed onto the organic material coated substrate to a thickness of at least about 5 microns, more preferably to a thickness of at least about 10 microns. In an embodiment of the present invention, the liquid sulfuric acid composition is dispensed onto the organic material coated substrate to a thickness of from about 10 microns to about 140 microns, and preferably to a thickness of from about 10 microns to about 60 microns.

In one embodiment, wafers 18 are provided at a temperature below the boiling point of water, such as at a temperature of from about 20 to about 60°C. Wafers 18 are preferably heated to a temperature of at least about 90°C., either before, during or after dispensing of the liquid sulfuric acid composition. More preferably, wafers 18 are heated to a temperature of from about 90°C to about 150°C. In another embodiment, the wafers are heated to a temperature of from about 95°C to about 120°C. This heating can be carried out, for example, by heating the chamber using radiant heat, introduction of hot water or other liquid solution to the wafer with substantial removal of the heated liquid prior to application of the concentrated sulfuric acid composition, introduction of heated gases to the chamber, and the like. If a liquid is used to heat the wafer by direct contact to the wafer, sufficient amount of the liquid is removed from the wafers prior to introduction of the concentrated sulfuric acid composition so that the concentrated sulfuric acid composition maintains the desired level of sulfuric acid concentration prior to the exposure of the liquid sulfuric acid composition to water vapor.

In one embodiment of the present invention, the wafers can be preheated by submerging one or more wafers into a heated bath of liquid, quickly draining the contents of the bath (e.g. a "quickdump" procedure) and conducting the remaining treatment steps as described below. The bath liquid can be, for example, DI water, DI water containing sulfuric acid, sulfuric acid/hydrogen peroxide mixture, an inert fluid (such as a fluorocarbon), sulfuric acid/ozone mixture, and the like. This embodiment can provide substantial benefit in enhancing throughput of the treatment process by more efficiently heating the wafers. An example of a particularly suitable process system that can be used to employ this embodiment is the Magellan® system commercially available from FSI International, Chaska, Minnesota,

Water vapor is introduced to the chamber in any appropriate manner. As shown in FIG. 3B, heated DI water 44 is splashed down onto the rotating turntable 22 from the bottom 46 of center spray post 36. In this "splashdown" approach, water vapor is generated. Alternatively, water vapor can be generated inside the treatment chamber by any appropriate alternative water vapor generation technique, such as by heating and/or agitating water in the treatment chamber.

In yet another alternative, the water vapor can be generated outside of the treatment chamber and introduced to the treatment chamber in the desired water vapor form. For instance, externally produced water vapor could be supplied to the chamber as a gas, or as component of a mixture of gasses. In one embodiment, vapor could be produced by bubbling a gas (eg. N_2) through a column of water (preferably hot water). In another embodiment, the gas could pass over the surface of a quantity of water. In another embodiment, the gas could pass through an irrigated packed column as commonly used in chemical engineering. In another embodiment, substantially pure water vapor could be produced by boiling liquid water. The gaseous products from any of these alternatives could be further heated. Other embodiments are also possible.

Preferably, the water vapor is introduced so that it is exposed to the wafers at a water vapor temperature of from about 70°C to about 150°C. More preferably, the water vapor is introduced so that it is exposed to the wafers at a water vapor temperature of from about 80°C to about 110°C. In a particularly advantageous embodiment, the water vapor is introduced so that it is exposed to the wafers at a water vapor temperature of from about 85°C to about 98°C. This embodiment is advantageous because the water vapor is is easy to generate by the "splashdown" approach described above. Because the water is not at the boiling point, control of entry of the stream of water without undue spattering is easier to accomplish. In different advantageous embodiment, the water vapor is introduced so that it is exposed to the wafers at a water vapor temperature of about 100°C. This embodiment is relatively easy to carry out by boiling water under conventional conditions to form steam either inside or outside the treatment vessel by conventional steam forming apparatus.

In another embodiment, the water vapor is provided at a temperature greater than the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor. This embodiment provides the benefit of direct heating of the liquid sulfuric acid composition by direct heat transfer, as well as the transfer of energy upon condensation of the water vapor into the liquid sulfuric acid as discussed above. In an embodiment, the water vapor is provided at a temperature greater than about 150°C for this purpose.

Optionally, the water vapor can additionally comprise another agent, such as hydrogen peroxide or ozone, as desired.

The water vapor is introduced into the treatment chamber in an amount effective to increase the temperature of the liquid sulfuric acid composition abovethe temperature of the liquid sulfuric acid composition prior to exposure to the water vapor, and preferably additionally above the temperature of the water vapor. In an embodiment of the present invention, the liquid sulfuric acid composition is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition on the substrate

surface above both (i) the temperature of the on-substrate liquid sulfuric acid composition prior to exposure to the water vapor and (ii) the temperature of the water vapor. Surprisingly, even when the temperature of the liquid sulfuric acid composition is near or even above the boiling point of water, the water vapor still associates with the liquid sulfuric acid composition in a manner to increase the temperature of the liquid sulfuric acid composition, thereby enhancing the organic material removing effectiveness of the increase the temperature of the liquid sulfuric acid composition.

Preferably, sufficient liquid sulfuric acid composition and water vapor are present and mixed to increase the temperature of the liquid sulfuric acid composition by at least about 20°C, more preferably by at least about 40°C, and more preferably by at least about 60°C. This is particularly significant since the liquid sulfuric acid composition is in place on the wafer, which itself acts as a heat sink and absorbs substantial energy to maintain a temperature that is close to the temperature of the liquid sulfuric acid composition. The temperature of the liquid sulfuric acid composition on the substrate surface can be determined by any appropriate measuring technique. For purposes of the present invention, an appropriate temperature approximation can be made by using temperature probe 41 to measure the temperature of liquid cast onto the treatment vessel walls during spinning of the wafer carriers on turntable 22. To carry out this measurement, a temperature probe may be positioned within the treatment vessel. In one embodiment, a color-changing temperature indicating material may be used to indicate the maximum temperature reached in the treatment vessel.

The exposure of the liquid sulfuric acid composition to water vapor can be carried out at any time effective to increase the temperature of the liquid sulfuric acid composition when in place on the organic material coated substrate. In one embodiment, water vapor is introduced to the treatment chamber during the dispense of the liquid sulfuric acid composition. It will be appreciated that in this embodiment, the temperature of the liquid

sulfuric acid composition may begin to increase even prior to contact of the composition with the substrate. In this embodiment, the increase of the temperature of the liquid sulfuric acid composition upon exposure to water vapor as discussed above can be taken to be the difference between the temperature of the liquid sulfuric acid composition at dispense and the maximum temperature of the liquid sulfuric acid composition after exposure to water vapor.

In another embodiment of the present invention, the liquid sulfuric acid composition is provided to the wafers not in a continuous stream, but rather in in a plurality of discrete pulses. These pulses are preferably short (i.e. from about 3-10 seconds in length), and at high flow (i.e. at a flow rate of about 2-8 lpm). There preferably is a time period of about 5 to 20 seconds between pulses with no flow of liquid.. When operating with pulsed liquid flow, water vapor optionally is only introduced during the pulse, reducing the amount of water vapor that is flushed from the chamber during the present process. Likewise, water vapor can be optionally introduced during the pulse, to enhance the temperature rise of the sulfuric acid composition before its contact with the substrate, or between pulses, to emphasize the heating of the composition while on the substrate.

In another embodiment, the dispense of the liquid sulfuric acid composition is stopped prior to introduction of the water vapor. In an aspect of this embodiment, the substrate is provided with a coating of the liquid sulfuric acid composition that is relatively stagnant. Optionally, rotation of the substrate is slowed to a rate of less than about 20 rpm or stopped during and/or after dispense of the liquid sulfuric acid composition, and during exposure of the liquid sulfuric acid composition to the water vapor. This process is carried out to promote maintenance of this coating (or "pooling") of liquid sulfuric acid composition on the substrate. While not being bound by theory, it is believed that because the liquid sulfuric acid composition exhibits little bulk motion especially during exposure of the liquid sulfuric acid composition to the water vapor, the liquid tends to dissolve and/or

otherwise remove the undesired materials on the surface of the substrate at a comparable rate across all points on the substrate. This enhanced uniformity may be due to uniform exposure of the liquid sulfuric acid composition to the water vapor. Additionally or alternatively, the enhanced uniformity of removal of undesired material (in particular, removal of SiO_2) may be due to uniform saturation rates of the liquid sulfuric acid composition by the dissolved undesired material across the coating. The dispense of the liquid sulfuric acid composition may further be modified by varying the thickness of the liquid sulfuric acid composition layer by varying the flow rate, dispense time, and the rate of removal of the liquid sulfuric acid composition by centrifugal force. Further, the aggressiveness of removal of undesired material may be increased by ramping off the spent sulfuric acid solution mixture after the vapor step, applying a fresh layer of sulfuric acid solution mixture, and re-introducing vapor into the chamber.

As noted above, the liquid sulfuric acid composition 42 is dispensed onto wafers 18 from spray posts 36 and/or 40. In certain configurations of wafer treatment equipment, positioning of the spray posts and direction of flow of fluid from the posts have been found to impact the performance of the present process. In certain wafer treatment apparati having a fixed spray post configuration, dispensed fluid tends to be deposited in a manner leading to heavy concentrations of liquid at portions of the wafer. For example, liquids dispensed from the center spray post 36 tend to be deposited on the substrate at heavy concentrations near the center spray post. Also, at some orientations of the turntable 22, a large fraction of the liquid from the center spray post can pass between the wafers and be wasted. Advantageously, superior deposition efficiency and uniformity can be achieved by using the side-bowl spray post 40 (SBSP.) But spray dispensed by the SBSP normal to the face of the chamber, directly toward the turn table's axis of rotation, also tends to deposit liquid excessively near the center spray post. The normal spray further wastes liquid that passes between the wafers at some orientations of the turn table. Superior deposition patterns may

be observed by angling the spray of liquids from the spray posts (and particularly the SBSP) off normal from the major surface of the chamber and/or away from the center of the turntable. While angled spray results in a less "focused" deposition near the CSP, no individual angle suffices for uniform coverage. The angle of spray in an embodiment of the invention is stationary. In another embodiment of the invention, the turntable holding the substrate(s) is rotating during dispense of the liquid sulfuric acid composition onto the surface of the substrate, and the liquid sulfuric acid composition is dispensed by spraying the liquid at a varying angle relative to the turntable in a sweeping motion. In one aspect of this embodiment, the angle of spray varies during a single dispense of the liquid sulfuric acid composition. In another aspect of this embodiment, the angle of spray varies from one dispense of the liquid sulfuric acid composition to the next when a plurality of liquid dispenses are carried out in a treatment cycle.

Varying the angle of spray of the liquid sulfuric acid composition (or "sweeping") results in varying the location of the spray's focus, leading to more uniform liquid deposition. Varying the spray's angle of incidence on the wafer-carrier system also reduces the effects of shadowing by structural members of the cassette and turntable. It is possible to vary the angle of the spray in many ways including, for instance, rotating the spray mechanism or spraying through multiple spray mechanisms at varying angles.

A preferred method and apparatus of varying the direction of the SBSP's 40 spray is shown in FIG. 8, which shows a system 120 for directing a spray using a three orifice nozzle 122. In this nozzle, a central orifice 124 is provided with liquid from a liquid source (not shown) under sufficient pressure to eject a stream 126 of liquid therefrom. Gas orifice 130 is provided with a gas from gas source 134 through control valve 136. The gas is provided at a regulated pressure to eject a stream of gas 138 from orifice 130 that simultaneously deflects and atomizes the spray. Similarly, gas orifice 140 is provided with a gas from gas source 144 through control valve 146. The gas is provided at a regulated pressure to eject a

stream of gas 148 from orifice 140 that simultaneously deflects and atomizes the spray. The spray direction can be adjusted by modifying the flow of gas streams 138 and 148 to impart a direction to the flow of the liquid spray. Finer gradations of gas flow allow finer adjustment of the spray direction. Equal flows from the two gas sources result in a spray pattern centered perpendicular to the face of the spray mechanism. The spray can be deflected discretely (e.g. 10 seconds at +20°, then 10 seconds at +30°, etc.), or swept continuously. The gas flows can be modulated over a continuous range, such as by mass flow controllers, or discretely, as by multiple orifices. This system 120 is particularly advantageous for use in treatment of semiconductor wafers, because it provides excellent directional and force control of spray of liquid. Furthermore, this excellent control is provided without the need to install an apparatus having moving parts in the treatment chamber. The minimization of the amount of moving parts in treatment chambers is desirable because moving parts increases the likelihood of introduction of small particles in the chamber due to frictional wear of moving components. Additionally, service of equipment is greatly simplified if the equipment is not located in the treatment chamber.

In the case of either stationary or sweeping spray introduction of liquid sulfuric acid composition into the treatment chamber, the direction of the spray preferably is coordinated with the rotation of the substrates in the chamber. In an embodiment of the present invention, spray is angled into the oncoming wafers as they rotate in the chamber on a turntable. That is, the spray from the side-bowl spray post 40 is deflected to the right during clockwise rotation of the turntable and left during counterclockwise rotation.

In another embodiment of the present invention, the effects of shadowing by structural members of the cassette and turntable and/or the overconcentration of liquid at certain locations in the chamber can be ameliorated by placement of deflecting members in the chamber to interrupt or block the flow of the spray in certain directions. These members can be supported by the bowl 12 or lid 14 and thus be substantially stationary, or can be

supported by the turntable 22, and thus be at a substantially fixed location with respect to the rotating wafers.

In embodiments of the present invention, it is contemplated that the substrate may be pretreated to assist in removal of the organic material therefrom. For example, the substrate having organic material coated on a portion thereof can be treated with a surfactant-containing composition prior to dispensing the liquid sulfuric acid composition thereon.

Additional manipulation steps are also contemplated during the described method, such as exposure of the substrate to megasonic energy before, during or after treatment by the liquid sulfuric acid composition.

An apparatus for use in the present method can be prepared by modifying a known programmable spray processing machine such as a centrifugal spray processor of the type commercially available from FSI International, Chaska, Minnesota, under one or more of the trade designations MERCURY® or ZETA®, by providing the chemical reservoirs thereof with the necessary solutions and by configuring the machine's controller with a program as indicated herein. It will be understood that other known batch spray and single wafer spray machines can similarly be modified to carry out the present invention.

In another embodiment, the inventive process could also be applied to one wafer at a time in a "single wafer" mode. FIG. 7 shows one embodiment of such a single wafer process apparatus 100 with a sulfuric acid composition 102 being dispensed on a wafer 103 from a duct 101 as the wafer is supported on a holding chuck (not shown) mounted on the shaft of a motor 104. Water vapor 105 is introduced through duct 106. The apparatus is in a chamber 107 sufficiently closed such that the desired levels of vapor can be maintained at the wafer surface.

In one embodiment, apparatus 100 can be operated with a continuous dispense of sulfuric acid composition from duct 101, with duct 101 either stationary or moving relative

to wafer 103. Vapor can be introduced into the apparatus either before, during, or after the start of the dispense.

In another embodiment, the entire wafer is wetted with the sulfuric acid composition and the dispense stopped, allowing the composition to form a film on the wafer of relatively uniform thickness. In this embodiment, the wafer can be provided with a coating of the liquid sulfuric acid composition that is relatively stagnant as discussed above. Optionally, rotation of the substrate is slowed or stopped to promote maintenance of this coating of liquid sulfuric acid composition on the substrate. Vapor can be introduced into the apparatus either before, during, or after the start of the dispense. Optionally, the dispense can be repeated to provide a fresh supply of reactants to the wafer surface. Optionally, the wafer can be rapidly rotated between dispenses to cast off most of the sulfuric acid composition present on the wafer. Optionally, the wafer can be coated with a thin layer of sulfuric acid composition by moving dispense duct 101 in a manner used in the semiconductor industry to create thin layers of resist.

In an embodiment of the present invention, the sulfuric acid composition arrives at the wafer surface at substantially the temperature at which it left dispense duct 101. In one embodiment, it may be beneficial to break the composition into small droplets that can absorb vapor and heat up before contacting the wafer. Such droplets can be created, for instance, by atomizing the sulfuric acid composition with the vapor composition or with another gas, or by passing the sulfuric acid composition through a spray nozzle, or by other techniques. It may be beneficial to move this source of heated sulfuric acid composition mist over the wafer.

In an embodiment of the present invention, the sulfuric acid composition can be preheated before it leaves the dispense duct 101 by contacting the composition with a gas comprising water vapor. For example, a gas comprising water vapor could be combined with the sulfuric acid composition at a "T" in a heat resistant tube (eg. quartz). This

embodiment offers the advantage that the sulfuric acid composition temperature attained can be much higher than the temperatures of the as-blended sulfuric acid composition or the vapor.

It will be appreciated that the various embodiments of the method as described herein (such as variation in delivery of the sulfuric acid composition) are not limited to use with the specific apparatus of the figures, but rather are applicable to use in all configurations of treatment machines appropriate for use in carrying out the presently described methods. The principles of the present invention will now be described in connection with the following illustrative examples.

Experimental Techniques

A. Sample Preparation

Wafer samples were prepared for evaluation of effectiveness of removal of ion implanted photoresist as follows:

200 mm diameter silicon wafers were coated with Shipley UV6 248 nm photo resist.

Some of the wafers were patterned and others were left with a complete layer of resist (patterned and blanket wafers respectively).

Samples of both patterned and blanket wafers were implanted with arsenic at an energy of 40 keV, and with a dose of either $5x10^{14}$ or $1x10^{15}$ atoms/cm^2 (5E14 or 1E15).

Approximately 2x2 cm fragments of resist coated wafers were cleaved from full patterned and blanket wafers and attached near the center of carrier wafers with high-temperature epoxy. Five resist samples were typically attached to each carrier wafer: blanket resist (no implant), blanket 5E14, patterned 5E14, blanket 1E15, and patterned 1E15.

B. Evaluate Strip Efficiency

After processing, the samples were examined by bright field and darkfield optical microscopy. Table 1 shows the evaluation criteria for both blanket and patterned resist samples. The patterned samples consisted of various lithographic test patterns. Stripping of the arrays of fine lines on the patterned samples and of the blanket film served as measures of the stripping efficiency of a treatment.

Table 1

Score	Explanation, Patterned Resist	Explanation, Blanket Resist
1	Gross lines and some blanket remaining	Only some undercut at edges of sample
2	Some lines and blanket remaining	Whole surface of resist damaged
3	Significant fine lines remaining	Some removal of resist
4	Few fine lines remaining	Small spots of resist remaining
5	No visible residue (bright or dark field)	No visible residue (bright or dark field)

C. Chamber Temperature Measurements

The temperature of the liquid composition of sulfuric acid/hydrogen peroxide as cast onto the side wall of the processing chamber was measured by temperature sensor 41. This temperature was recorded at one second intervals and provides a thermal history of the chamber temperature through the process.

D. On-Wafer Temperature Measurements

Measurements of the maximum on-wafer temperature were made by attaching labels to the wafers with dots that changed color irreversibly at specified elevated temperatures (TL-10 series from Omega Engineering, Stamford, CT). The labels were covered with a 0.7 mm glass sheet attached with high temperature epoxy for protection from the stripping chemistries.

E. Treatment Process

The wafers prepared in the manner described above were treated in a ZETA® spray processing tool commercially available from FSI International, Inc., Chaska, MN under the following conditions:

1. The sample wafer was loaded in slot 13 of a 27 wafer carrier cassette 20 and the other slots filled with bare wafers. This cassette and a second balance cassette were loaded onto the turntable 22. A second sample wafer was loaded into slot 15 if needed.
2. The turntable 22 was rotated at 120 rpm and heated H_2SO_4 (110° C) from the recirculation bath 50 was dispensed on the wafers from both the center 36 and side 40 spray posts for 3 minutes at a flow rate of approximately 5 lpm. 50 cc/min of H_2O_2 was added to the flow during the last approximately 1 minute of the dispense. This step served to both preheat and wet completely the wafers.
3. The turntable was rotated at 120 rpm and a 900 cc/min flow of a mixture of fresh sulfuric acid composition (H_2SO_4 and H_2O_2 - SPM) from the mixing manifold 90 was dispensed from the center spray post 36 for 30 seconds. The H_2SO_4 was preheated to 95° C by an inline IR Heater before the H_2O_2 was added. The blend ratio of the SPM composition varied between treatments as listed in Table 2.
4. The process continued as above in 3. for six minutes except that, in the inventive treatments, approximately 8 lpm of 95° C DI water 44 was dispensed onto the turn table 22 to generate water vapor.
5. After a six minute rinse with DI water, the samples were treated for 75 seconds with an 80° C SC-1 solution (1:1:15 vol ratio of $NH_4OH:H_2O_2:H_2O$).
6. The samples were rinsed in DI water and dried in N_2.

Table 2

Example Treatment Protocol	H_2SO_4/H_2O_2 Blend Ratio	Water Vapor Added	Max on-wafer temperature (° C)	Max side bowl temperature (° C)
1	20:1	Yes	204	159
2 (comparative)	20:1	No	93	60
3	10:1	Yes	154	50
4 (comparative)	10:1	No	62	37
5	5:1	Yes	126	45
6 (comparative)	5:1	No	78	43
7	2.17:1	Yes	145	54
8 (comparative)	2.17:1	No	72	32

Examples

Example 1: Treatment Process E from above was performed twice using a 10:1 blend of SPM with and without the addition of water vapor (Protocols 3 and 4 from Table 2). The temperature of the liquid cast off against the chamber wall was measured by the side bowl temperature sensor 41. FIG. 4 shows the temperature profiles of the two treatments. In both cases, the 5 lpm recirculated flow of H_2SO_4 heated the side bowl sensor to approximately 65° C in the first three minutes of the treatments. From 3 to 9 minutes, the sensor temperature of the "SPM" comparative example dropped approximately 7° C to near 58° C. In contrast, the "SPM + water vapor" inventive example rose by 60° C to 125° C during the same period. The addition of water vapor in the chamber significantly increased the temperature of the cast off liquid.

Example 2: Treatment Process E from above was performed 8 times using the 8 Protocols from Table 2. The maximum temperature of the cast off liquid for each treatment was measured with the side bowl temperature sensor 41 at the end of the SPM dispense step (e.g., the 540 sec. reading from FIG. 4). Maximum on-wafer temperatures were measured with temperature sensing labels. FIG. 5 shows the as-blended temperature of the SPM (calculated from FIG.1) using H_2SO_4 preheated to 95° C by an inline IR Heater, the maximum on-wafer temperature, and the maximum side-bowl temperature for each

treatment. The temperature of the as-blended SPM rose with increasing H_2O_2 concentration (reduced H_2SO_4). The maximum on-wafer and side-bowl temperatures of the comparative examples also rose with increasing H_2O_2 concentration, but stayed well below the as-blended temperature of the SPM.

In contrast, the inventive treatments with water vapor achieved on-wafer temperatures 50 to 100° C higher than the comparative treatments. These inventive temperatures are also substantially higher than either the vapor temperature or the on-wafer SPM temperature in the comparative examples. (The comparative treatments represent the temperature of the SPM on the substrates prior to vapor exposure.)

Further, the temperature increase between comparative and inventive treatments decreased with increasing H_2O_2 concentration. FIG. 6 shows the temperature difference between the as-blended SPM and the maximum on-wafer temperature. The benefit of the inventive vapor process decreases with decreasing H_2SO_4 concentrations. To achieve maximum on-wafer temperatures, high concentrations of H_2SO_4 are desirable.

It is also desirable to increase the temperature of the as-blended liquid by increasing the pre-blend temperature of the H_2SO_4, the H_2O_2 or both. One embodiment would utilize H_2SO_4 from a recirculation tank operating at greater than 95° C.

Example 3: Treatment Process E from above was performed 8 times using the 8 Protocols from Table 2. Carrier wafers with samples of patterned and blanket, 5E14 and 1E15 implanted resist were processed in slot 13 of the cassette. Table 3 shows the results of evaluating the samples per the guidelines in Table 1. In all cases, the comparative treatments (Protocols 2, 4, 6, and 8) failed to thoroughly remove the implanted resist and scored a "1" in all evaluations. In contrast, the inventive treatments (Protocols 1, 3, 5, and 7) removed completely the patterned and blanket 5E14 resist scoring a "5" in all evaluations.

While performing far better than the comparative treatments, these particular protocols of the inventive process were not able to remove completely the 1E15 implanted resists.

Protocols 1, 3, and 5 performed similarly, nearly removing the patterned resist. Protocol 7 performed slightly better on the blanket resist, but far worse on the patterned resist. To achieve maximum strip performance, high concentrations of H_2SO_4 are desirable.

Table 3

Example treatment protocol	5E14 ion implant on patterned resist	5E14 ion implant on blanket resist	1E15 ion implant on pattern resist	1E15 ion implant on blanket resist
1	5	5	4	2
2 (comparative)	1	1	1	1
3	5	5	4	2
4 (comparative)	1	1	1	1
5	5	5	4	2
6 (comparative)	1	1	1	1
7	5	5	1	3
8 (comparative)	1	1	1	1

Example 4: A modified version of Treatment Process E from above was performed on 1E15 blanket and patterned wafer samples. The process was as follows:

A 5 lpm flow of H_2SO_4 from the recirculation tank was dispensed from the center and side spray posts in 4 segments: 45 sec. at 20 rpm clockwise turntable rotation, 45 sec. at 300 rpm clockwise, 45 sec. at 20 rpm counterclockwise, and 45 sec. at 300 rpm counterclockwise.

A 1600 cc/m flow of 10:1 SPM (1500 of 110° C H_2SO_4 from the recirulation tank and 150 cc/m of fresh 20° C H_2O_2) was dispensed from the center and side spray posts in two segments: 120 sec. at 120 rpm clockwise, 120 sec. at 120 rpm counterclockwise. 8 lpm of 95° C water was dispensed on the turntable to create water vapor.

A 1000 cc/m flow of fresh 9:1 SPM (900 of 95° C H_2SO_4 and 100 of 20° C H_2O_2) was dispensed from the center spray post in two segments: 180 sec. at 120 rpm clockwise, 180 sec. at 120 rpm counterclockwise. 8 lpm of 95° C water was dispensed on the turntable to create water vapor.

The combination of increased chemical exposure time, increased temperature, and the reversing of rotation resulted in complete removal of the patterned and blanket 1E15 implanted resist (all scores of "5").

Example 5: In some cases, no oxidant need be added to the sulfuric acid composition as unimplanted or lightly implanted resist can often be removed by H_2SO_4 alone. As an example, a 5 lpm flow of 95°C H_2SO_4 from the recirculation tank was dispensed from the center and side spray posts for 3 minutes at 120 rpm. This treatment removed completely unimplanted blanket resist.

All percentages and ratios used herein are volume percentages and volume ratios unless otherwise indicated. All temperatures recited are assuming an ambient pressure of one atmosphere. It will be understood that if the treatment process is carried out at a different pressure, the temperatures of the various components involved in the process can be adjusted accordingly. All publications, patents and patent documents cited are fully incorporated by reference herein, as though individually incorporated by reference.

Numerous characteristics and advantages of the invention meant to be described by this document have been set forth in the foregoing description. It is to be understood, however, that while particular forms or embodiments of the invention have been illustrated, various modifications, including modifications to shape, and arrangement of parts, and the like, can be made without departing from the spirit and scope of the invention.

CLAIMS:

1. A method of removing material from a substrate, comprising

a) placing a substrate having material on a surface thereof in a treatment chamber;

b) dispensing a liquid sulfuric acid composition comprising sulfuric acid and/or its desiccating species and precursors onto the substrate surface in an amount effective to substantially uniformly coat the substrate surface; and

c) exposing the liquid sulfuric acid composition to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition above the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor ; wherein the liquid sulfuric acid composition at the time of exposure to water vapor has a water/sulfuric acid molar ratio of no greater than about 5:1.

2. The method of claim 1, wherein the liquid sulfuric acid composition is exposed to water vapor in an amount effective to increase the temperature of the liquid sulfuric acid composition on the substrate surface above both (i) the temperature of the on-substrate liquid sulfuric acid composition prior to exposure to the water vapor and (ii) the temperature of the water vapor.

3. The method of claim 1, wherein the liquid sulfuric acid composition at the time of exposure to water vapor has a water/sulfuric acid molar ratio of no greater than about 2:1.

4. The method of claim 1, wherein the liquid sulfuric acid composition at the time of exposure to water vapor has a water/sulfuric acid molar ratio of no greater than about 1:2.

5. The method of claim 1, wherein an oxidizing agent is introduced into the treatment chamber during or after dispense of the liquid sulfuric acid composition.

6. The method of claim 5, wherein the oxidizing agent is hydrogen peroxide.

7. The method of claim 5, wherein the oxidizing agent is ozone

8. The method of claim 1, wherein the substrate surface is treated with a surfactant containing composition prior to dispensing the liquid sulfuric acid composition thereon.

9. The method of claim 1, wherein either before, during or after dispensing of the liquid sulfuric acid composition but prior to exposing the liquid sulfuric acid composition to water vapor, the substrate is heated to a temperature of at least about 90°C.

10. The method of claim 1, wherein the water vapor is provided at a temperature of from about 80°C to about 110°C.

11. The method of claim 1, wherein the water vapor is provided at a temperature of about 100°C.

12. The method of claim 1, wherein the water vapor is provided at a temperature greater than the temperature of the liquid sulfuric acid composition prior to exposure to the water vapor.

13. The method of claim 1, wherein the liquid sulfuric acid composition is dispensed at a temperature of at least about 130°C prior to exposure to the water vapor.

14. The method of claim 1, wherein the liquid sulfuric acid composition is dispensed at a temperature of from about 130°C to about 200°C prior to exposure to the water vapor.

15. The method of claim 1, wherein the material is a photoresist.

16. The method of claim 1, wherein the dispense of the liquid sulfuric acid composition is stopped prior to exposure of the liquid sulfuric acid composition to the water vapor.

17. The method of claim 1, wherein the liquid sulfuric acid composition is dispensed onto the substrate surface in a plurality of discrete pulses.

18. The method of claim 1, wherein the substrate is not moving or is rotating at a rate of less than about 20 rpm during and/or after dispense of the liquid sulfuric acid composition, and during exposure of the liquid sulfuric acid composition to the water vapor.

19. The method of claim 1, wherein the substrate is rotating during dispense of the liquid sulfuric acid composition onto the surface of the substrate, and the liquid sulfuric acid composition is dispensed by spraying the liquid at an angle that is off normal from the center of rotation of the substrate.

20. The method of claim 1, wherein the substrate is rotating during dispense of the liquid sulfuric acid composition onto the surface of the substrate, and the liquid sulfuric acid composition is dispensed by spraying the liquid at a varying angle relative to the center of rotation of the substrate in a sweeping motion.

21. The method of claim 1, wherein the angle of spray varies during a single dispense of the liquid sulfuric acid composition.

22. The method of claim 1, wherein the angle of spray varies from one dispense of the liquid sulfuric acid composition to the next when a plurality of liquid dispenses are carried out in a treatment cycle.

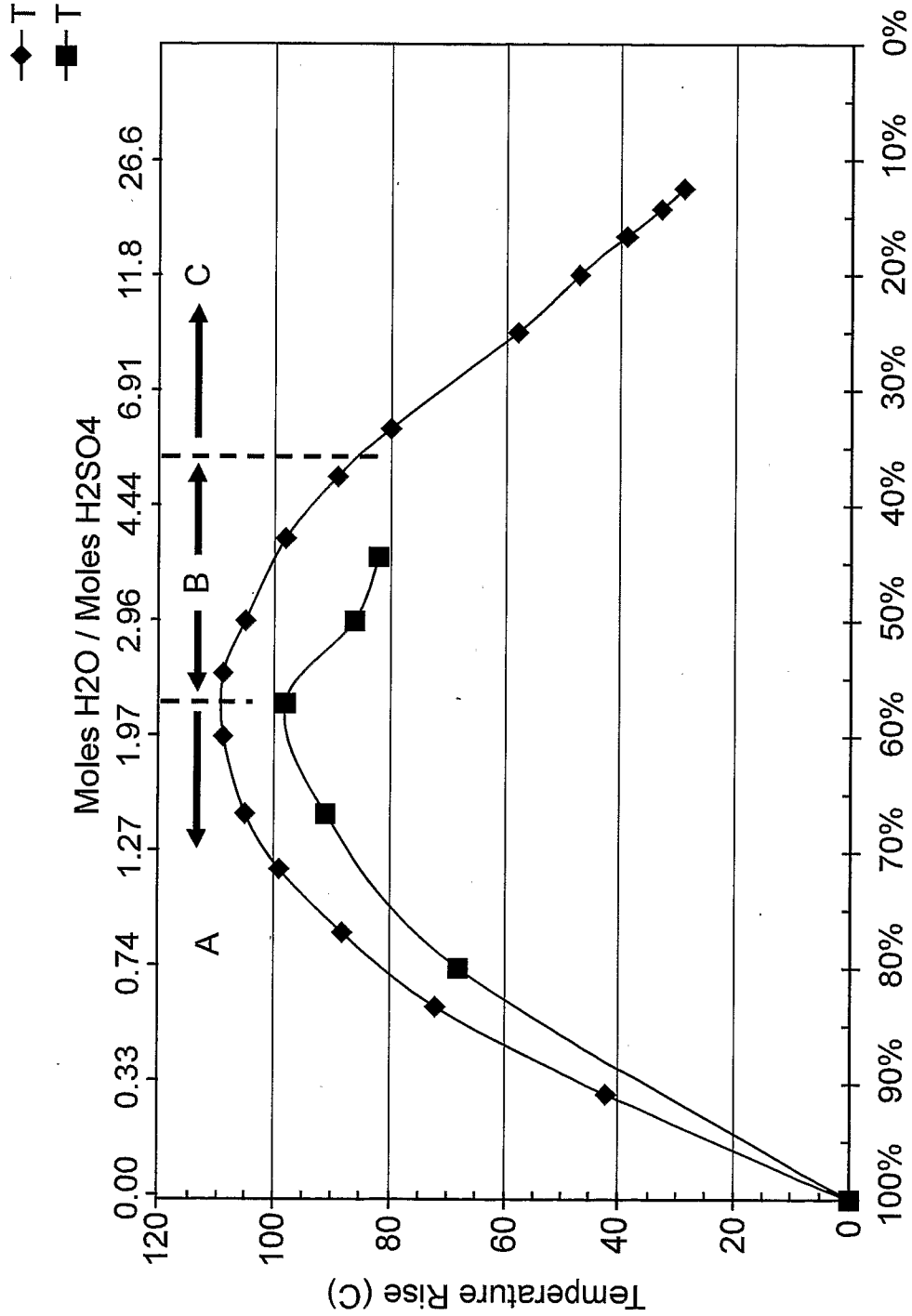

T H2O added
T H2O2 added
Moles H2O / Moles H2SO4
0.00
0.33
0.74
1.27
1.97
2.96
4.44
6.91
11.8
26.6
A
B
C
Temperature Rise (C)
120
100
80
60
40
20
0
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Vol% H2SO4

Fig. 1

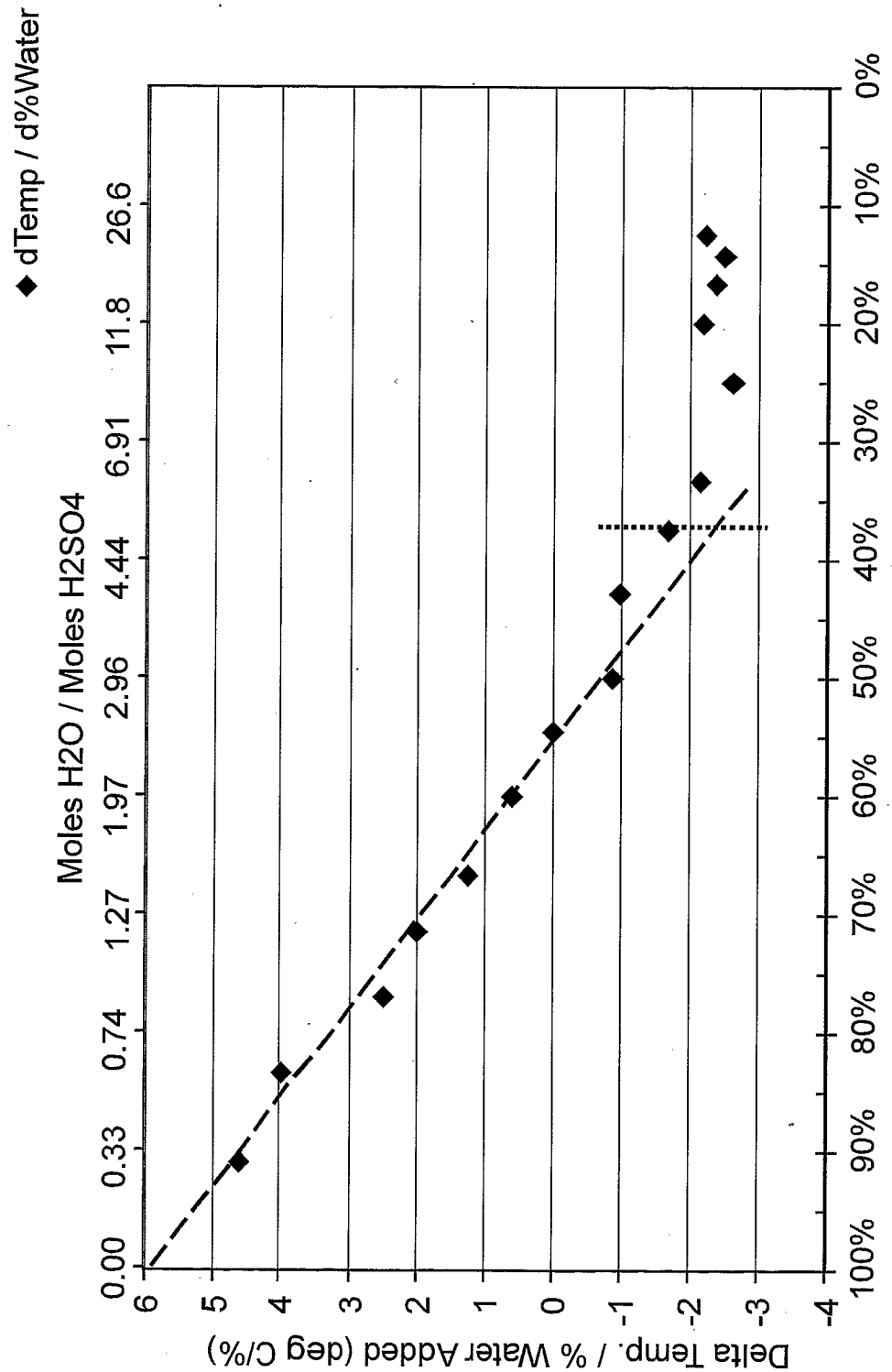

◆ dTemp / d%Water
Moles H2O / Moles H2SO4
0.00 0.33 0.74 1.27 1.97 2.96 4.44 6.91 11.8 26.6
Delta Temp. / % Water Added (deg C/%)
6 5 4 3 2 1 0 -1 -2 -3 -4
Vol% H2SO4
100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%

Fig. 2

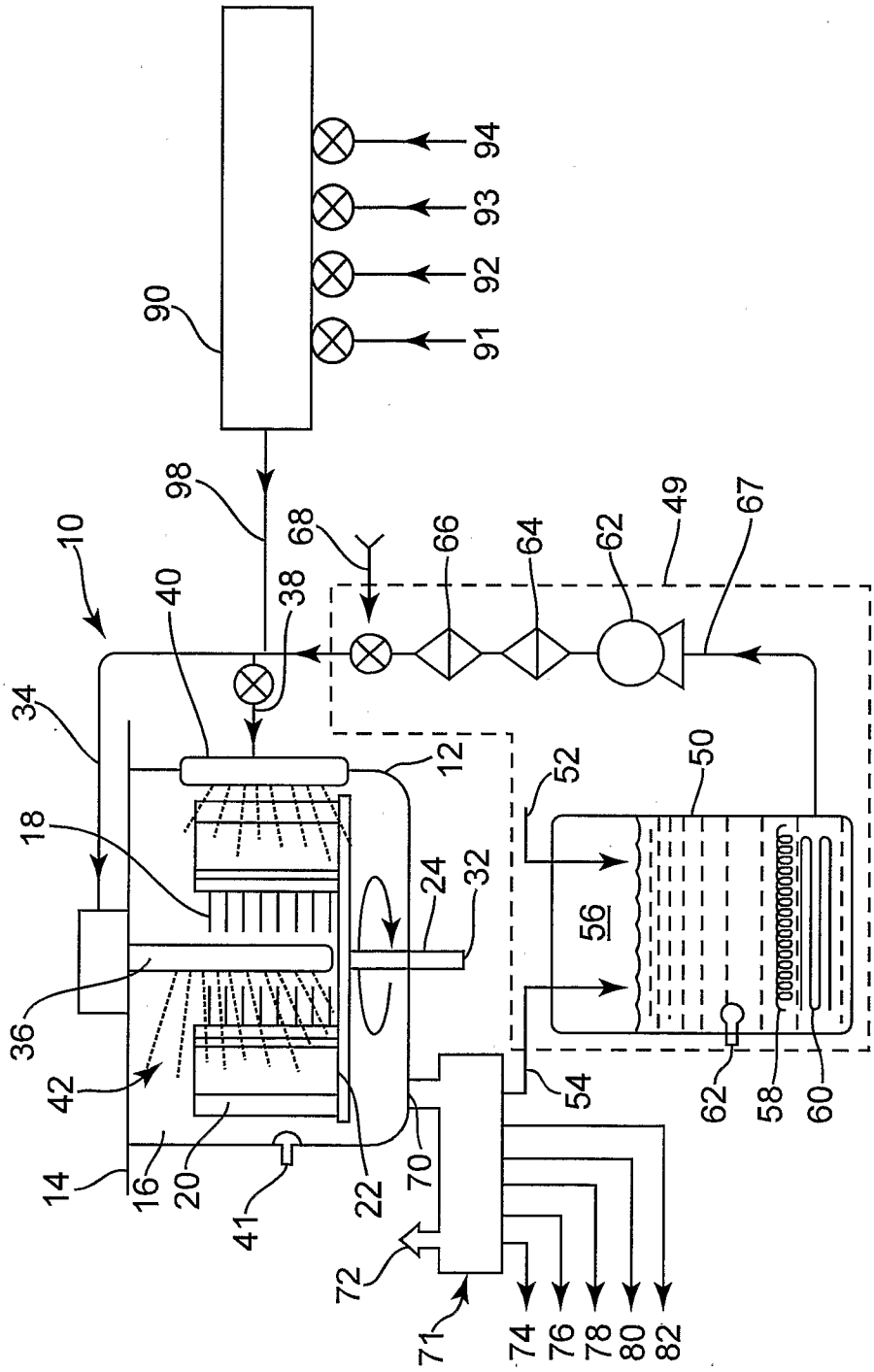

90
91
92
93
94
98
10
68
66
64
62
49
67
40
38
34
12
52
50
18
24
32
56
36
42
14
16
20
41
22
70
54
62
58
60
72
71
74
76
78
80
82

Fig. 3A

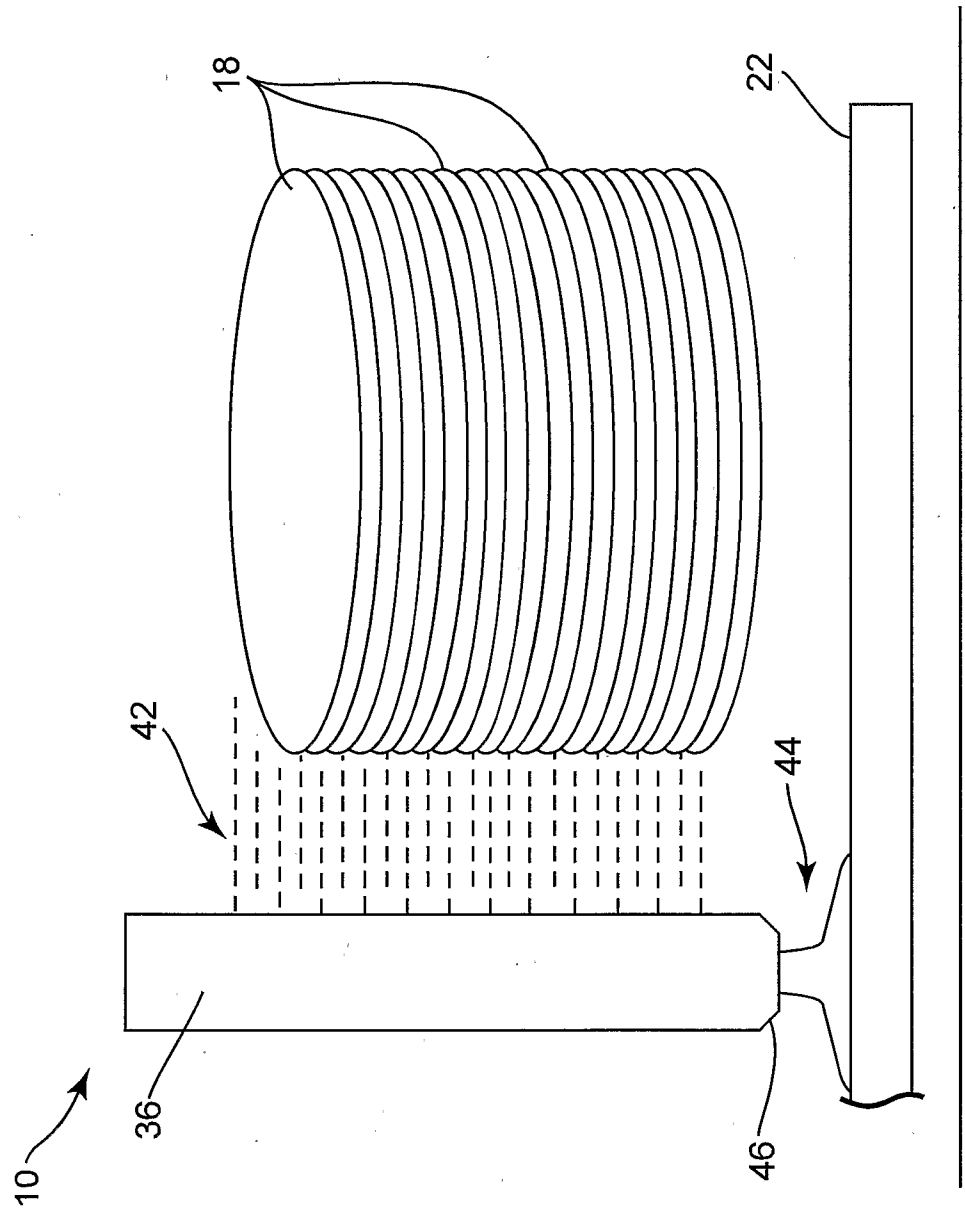


Fig. 3B

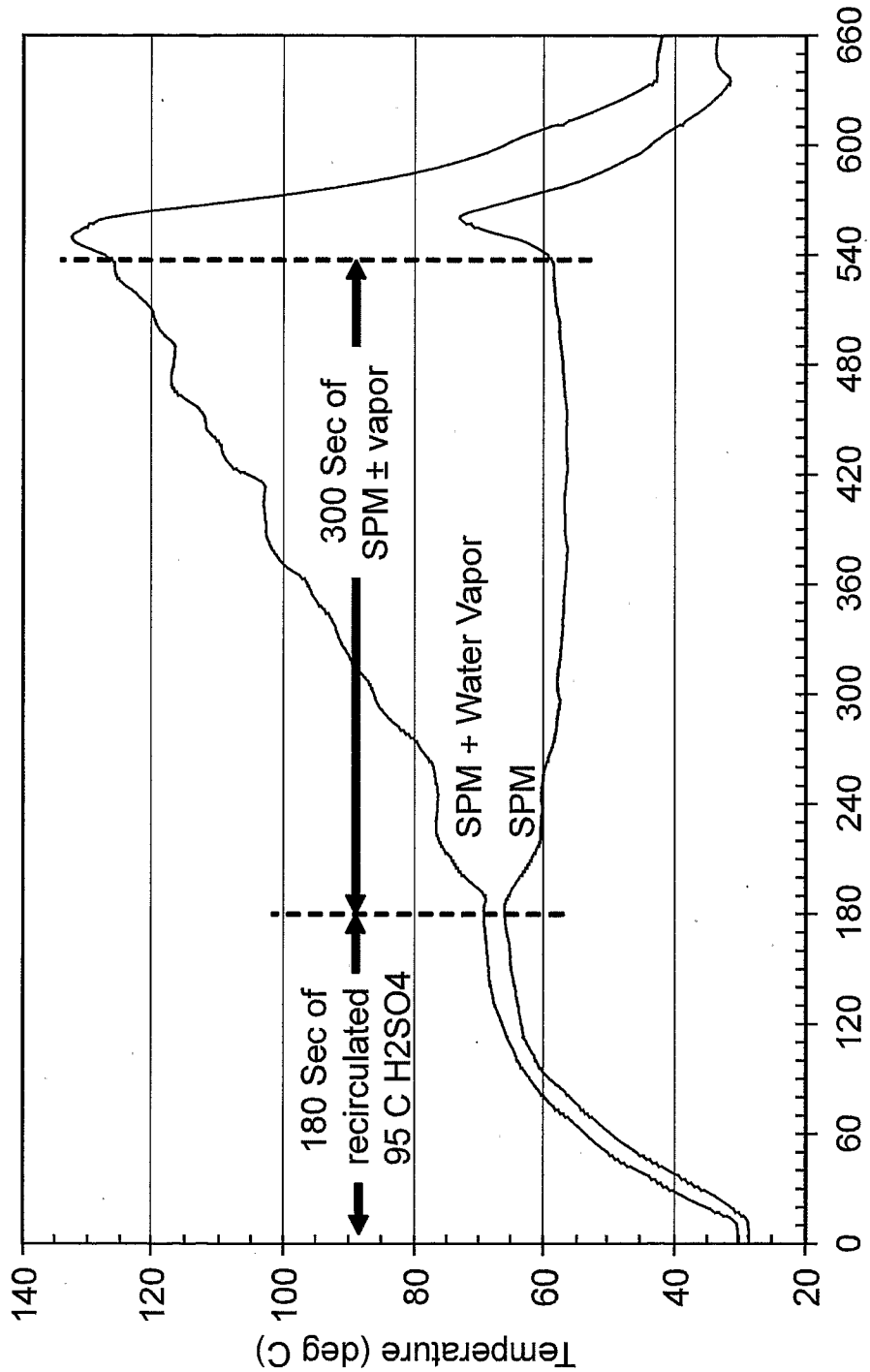

Temperature (deg C)
140
120
100
80
60
40
20
0
60
120
180
240
300
360
420
480
540
600
660
Time (sec)
180 Sec of recirculated 95 C H2SO4
300 Sec of SPM ± vapor
SPM + Water Vapor
SPM

Fig. 4

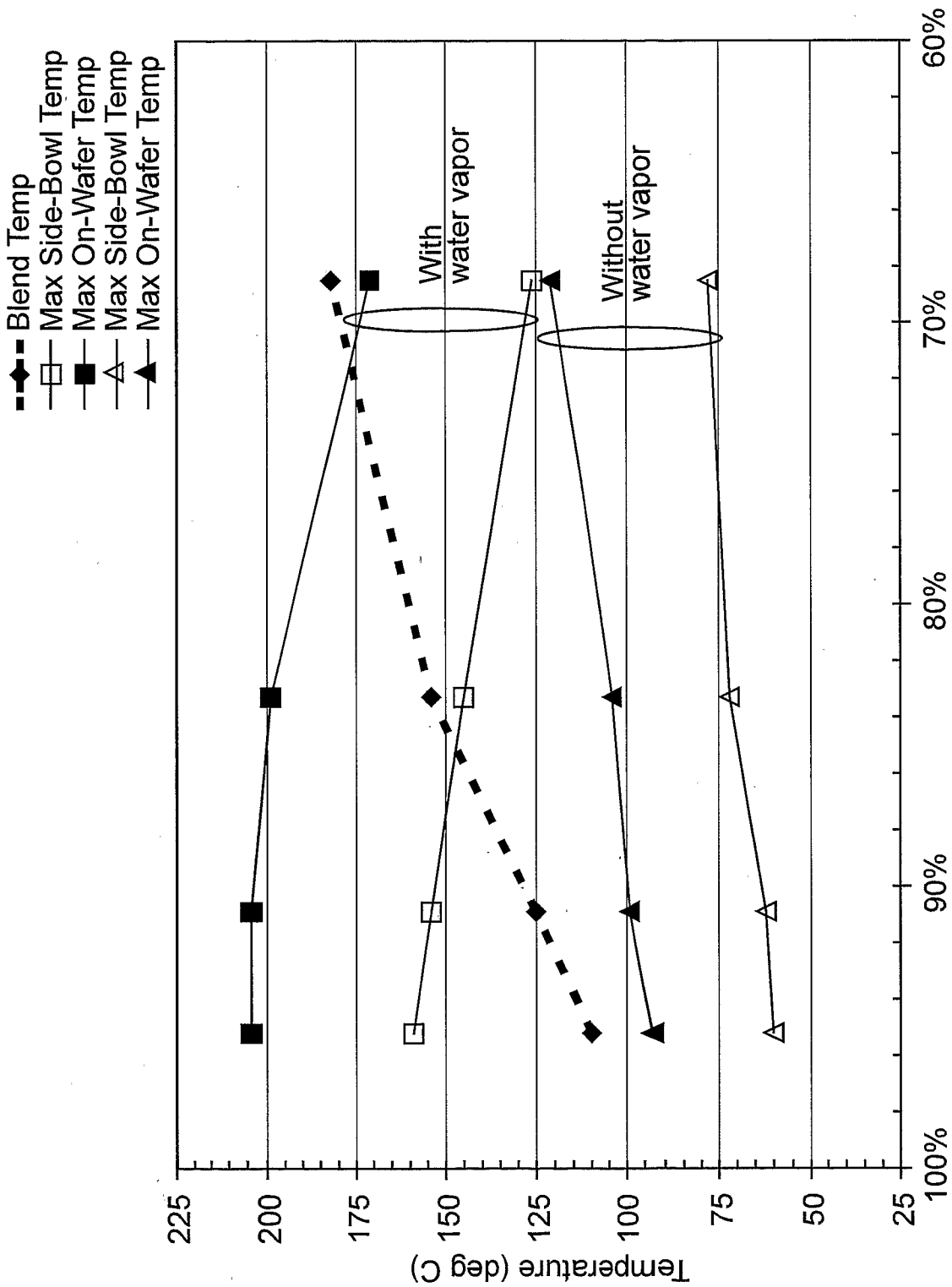

Blend Temp
Max Side-Bowl Temp
Max On-Wafer Temp
Max Side-Bowl Temp
Max On-Wafer Temp
With water vapor
Without water vapor
Temperature (deg C)
225
200
175
150
125
100
75
50
25
100%
90%
80%
70%
60%
Vol% H2SO4 (%)

Fig. 5

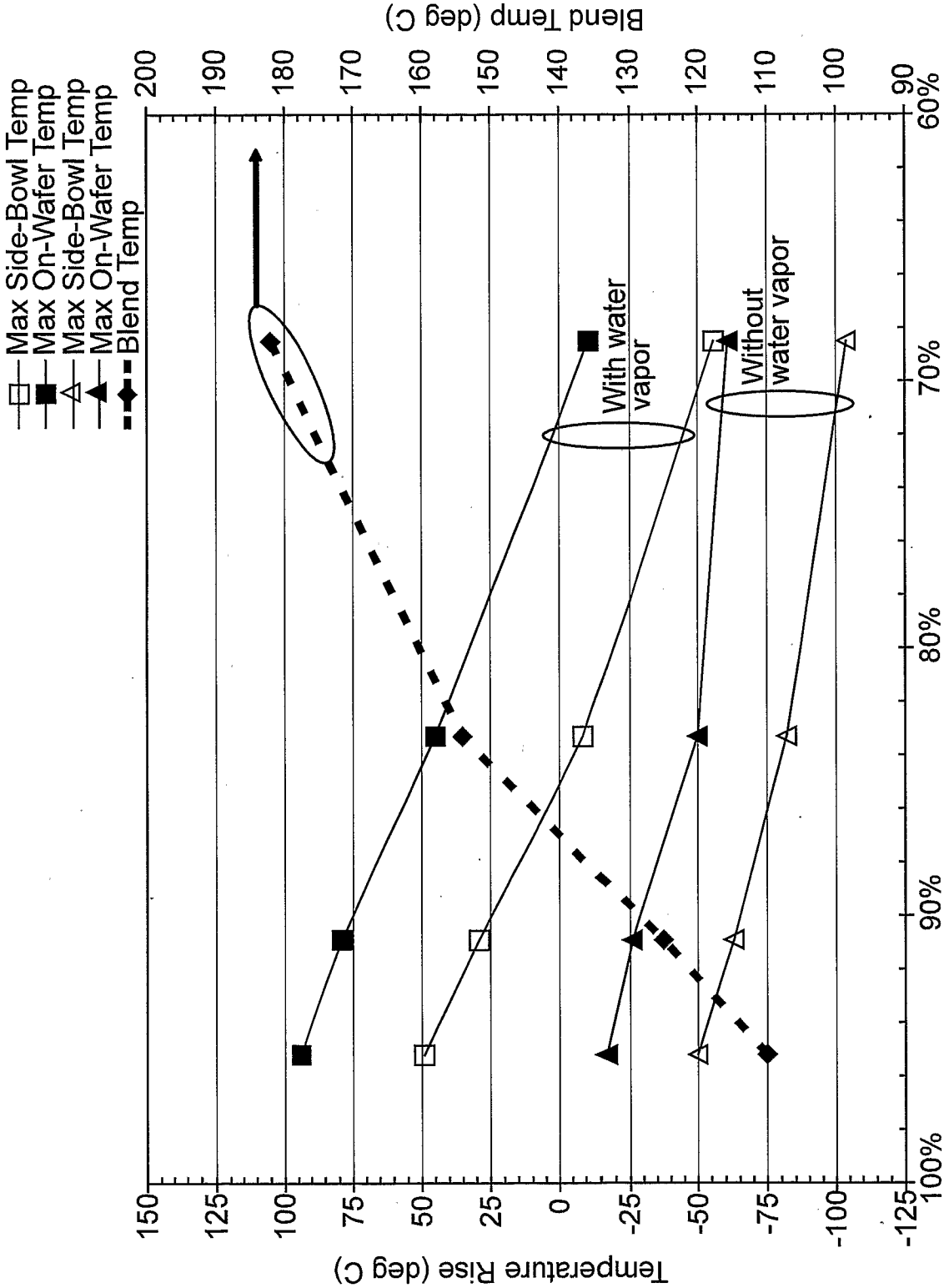

Max Side-Bowl Temp
Max On-Wafer Temp
Max Side-Bowl Temp
Max On-Wafer Temp
Blend Temp
Blend Temp (deg C)
Temperature Rise (deg C)
Vol% H2SO4 (%)
With water vapor
Without water vapor
200
190
180
170
160
150
140
130
120
110
100
90
150
125
100
75
50
25
0
-25
-50
-75
-100
-125
60%
70%
80%
90%
100%

Fig. 6

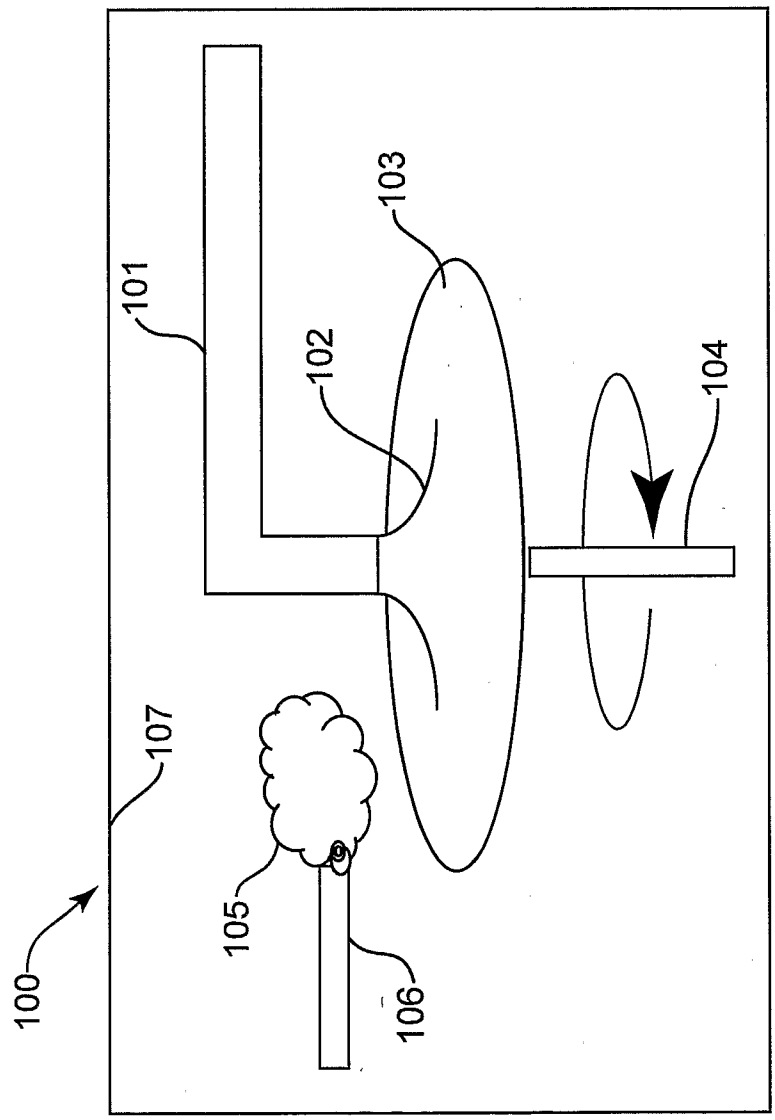


Fig. 7

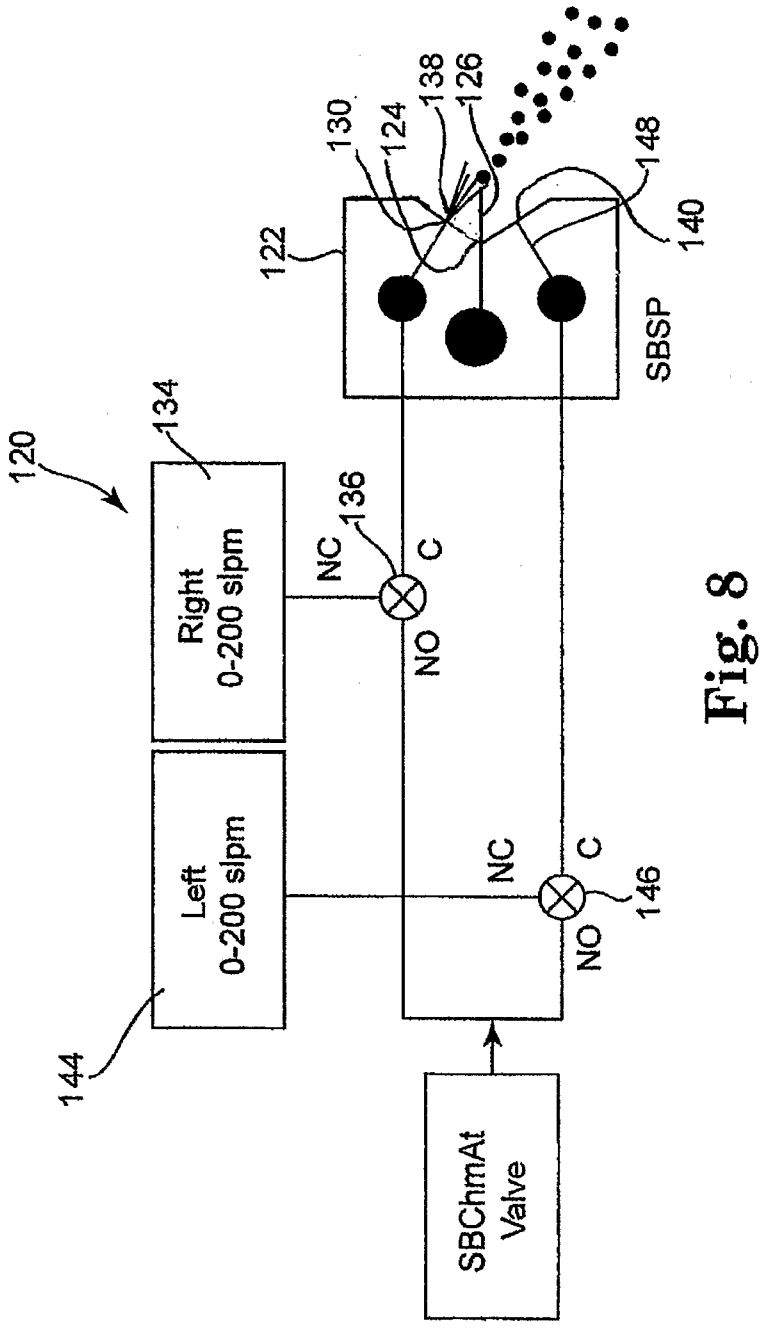

120
134
Right
0-200 slpm
Left
0-200 slpm
144
NC
C
NO
136
NC
C
NO
146
SBChmAt
Valve
122
130
124
138
126
148
140
SBSP

Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/045190

A. CLASSIFICATION OF SUBJECT MATTER
INV. B08B3/08 B08B7/00 G03F7/42

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B08B G03F H01L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/157686 A1 (KENNY ET AL) 31 October 2002 (2002-10-31) abstract paragraph [0012] - paragraph [0016] paragraph [0047] paragraph [0050] - paragraph [0057] paragraph [0092] paragraph [0129] - paragraph [0130] paragraph [0143] - paragraph [0145] claims figures	1-22

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 April 2007	07/05/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	van der Zee, Willem

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/045190

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 778 536 A (GREBINSKI) 18 October 1988 (1988-10-18) abstract column 1, line 10 - line 13 column 2, line 41 - column 5, line 31 claims figures	1,5,6, 10-12, 15,16, 18,19
A	US 6 274 506 B1 (CHRISTENSON ET AL) 14 August 2001 (2001-08-14) cited in the application abstract column 1, line 6 - line 13 column 5, line 34 - column 6, line 43 column 8, line 25 - line 34 column 9, line 16 - line 45 column 10, line 58 - column 11, line 46 column 12, line 59 - column 13, line 18 figures	1,15, 18-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/045190

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002157686 A1	31-10-2002	US 2003205240 A1 US 2004020513 A1	06-11-2003 05-02-2004
US 4778536 A	18-10-1988	NONE	
US 6274506 B1	14-08-2001	WO 0070656 A1	23-11-2000