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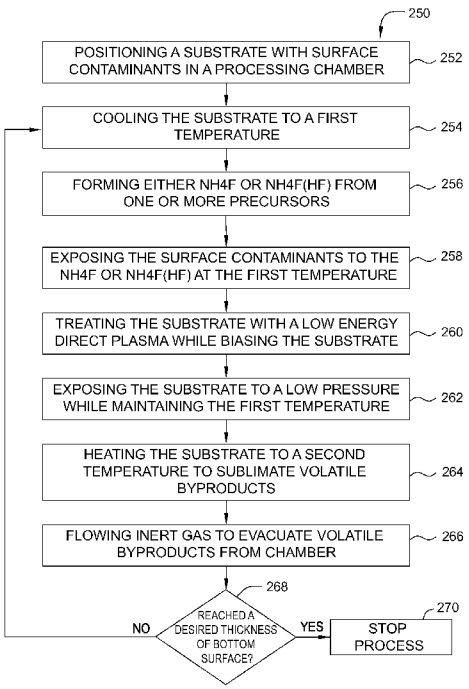


FIG. 2

(57) Abstract: Methods for processing a substrate are described herein. Methods can include positioning a substrate comprising silicon in a processing chamber, delivering a plasma to the surface of the substrate while biasing the substrate, exposing the surface of the substrate to ammonium fluoride (NH_4F), and annealing the substrate to a first temperature to sublimate one or more volatile byproducts.

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DIRECTIONAL SIO2 ETCH USING LOW-TEMPERATURE ETCHANT DEPOSITION AND PLASMA POST-TREATMENT

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Technology described herein relates to directional etching of native oxides. Specifically, technology described herein relates to post-treatment of an oxide surface to selectively etch the oxide surfaces.

[0002] Description With the increase in transistor density and subsequent decrease in the cross-sectional dimensions of device nodes, which can be less than 22 nm, pre-clean of native oxides is of particular importance. Pre-clean can include pre-contact clean or pre-silicide clean which requires removal of oxides from the bottom of vias or trenches of narrowing cross-sectional dimensions. As critical dimension of semiconductor devices decreases, distances between neighboring features formed on a semiconductor substrate are also shortened. Thus, it is important to control etching between vias and trenches during precleaning to prevent damaging nearby features.

of the Related Art

[0003] Current precleaning techniques generally includes a conformal etch of the substrate to remove the native oxides, such as SiO_2, prior to deposition of silicides or other contacts. However, a standard conformal etch can lead to excessive cross-sectional enlargement of vias and trenches thus creating possible leakage and ultimate device failure. Other precleaning techniques such as sputter etching remove native oxides from trench or contact bottom surfaces. However, the sputtering process can also lead to redeposition of field oxides at the via or trench opening. The redeposited oxides create an overhang at vias and trenches openings leading to poor subsequent contact fill.

[0004] Thus, methods are needed to preferentially etch from the bottom surfaces of features to prevent damage to features during precleaning.

SUMMARY OF THE INVENTION

[0005] Embodiments described herein generally relate to selective etching of native silicon oxides. In one embodiment, a method can include positioning a substrate comprising silicon in a processing chamber; delivering a plasma to the surface of the substrate while biasing the substrate; and exposing the surface of the substrate to ammonium fluoride (NH_4F).

[0006] In another embodiment, a method can include positioning a substrate comprising silicon in a processing chamber; delivering a plasma to the surface of the substrate while biasing the substrate; and exposing the surface of the substrate to ammonium fluoride (NH_4F) or ammonium hydrogen fluoride ($NH_4F(HF)$).

[0007] In another embodiment, a method can include positioning a silicon-containing substrate in a processing chamber, the silicon-containing substrate can include an exposed surface with one or more features formed in the exposed surface; and a native oxide layer formed on the exposed surface; cooling the substrate to a first temperature; exposing the surface of the substrate to ammonium fluoride (NH_4F) at the first temperature; biasing the substrate; exposing the substrate to a low energy inert plasma to selectively form one or more volatile products on the top and bottom surfaces of the features; exposing the substrate to low pressure at a second temperature to sublimate the non-reacted NH_4F from the surface of the substrate; and heating the substrate to a third temperature, which is higher than the first and second temperature, to sublimate the one or more volatile products.

[0008] In another embodiment, a method can include positioning a silicon-containing substrate in a processing chamber, the silicon-containing substrate comprising an exposed surface with one or more features formed in the exposed surface; and a native oxide layer formed on the exposed surface; cooling the substrate to a first temperature at a first pressure; exposing the surface of the substrate to ammonium fluoride (NH_4F) at the first temperature; biasing the substrate; exposing the substrate to a direct plasma to selectively form one or more volatile products on the top and bottom surfaces of the features; exposing the

substrate to a second pressure at a second temperature to sublimate the non-reacted NH_4F from the surface of the substrate; and heating the substrate to a third temperature, which is higher than the first temperature, to sublimate the one or more volatile products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings.

[0010] It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0011] Figure 1 is a schematic top-view diagram of an illustrative multi-chamber processing system useable with embodiments described herein.

[0012] Figure 2 is a diagram of a method for directional etching according to one embodiment.

[0013] Figures 3A-3D are graphical representations of a substrate etched according to one embodiment.

[0014] Figure 4 depicts etch rate of the silicon oxide and silicon nitride as a function of pedestal temperature according to one embodiment.

[0015] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements disclosed in one embodiment may be beneficially utilized on other embodiments without specific recitation.

DETAILED DESCRIPTION

[0016] Methods for removing native oxides are described herein. Precleaning of surfaces in vias and trenches can lead to etching of sidewalls and subsequent reduction of cross sectional dimensions. This reduction of cross-sectional dimensions can lead to device failure. The embodiments described herein allow for etching of surfaces to remove native oxides from bottoms of vias and trenches while preserving the cross-sectional dimensions of the via or trench. By treatment with an etchant at low temperatures, biasing the substrate and activation of the etchant by plasma treatment, the etchant on the bottom surfaces of trenches and vias will be etched preferentially over sidewall surfaces.

[0017] By employing a directional post-treatment of the native oxide surface after to conformal exposure to an etchant at low temperatures, the etchant on the affected surface is activated for etching while the non-activated surface is nominally etched due to desorption of the etchant before annealing. The invention is more fully explained with reference to the figures below.

[0018] Figure 1 is a schematic top-view diagram of an illustrative multi-chamber processing system 200 that can be adapted to perform processes as disclosed herein having one or more processing chambers coupled thereto, such as processing chamber 100. The system 200 can include one or more load lock chambers 202, 204 for transferring substrates into and out of the system 200. Typically, since the system 200 is under vacuum, the load lock chambers 202, 204 can “pump down” the substrates introduced into the system 200. A first robot 210 can transfer the substrates between the load lock chambers 202, 204, and a first set of one or more substrate processing chambers 212, 214, 216, 100 (four are shown). Processing chambers 100 and 216 can be degas chambers used to pre-heat and drive moisture out of incoming substrates. Processing chambers 212 and 214 can be preclean chambers. The positions of the processing chamber 212 and 214 utilized to perform the preclean process relative to the other chambers is for illustration, and the position of the processing chamber 212 and 214 may be optionally be switched with any one of the processing chambers 212, 214, 216 or

100, if desired. Further, one or more of the chambers can be positioned at empty position 248, if desired.

[0019] The first robot 210 can also transfer substrates to/from one or more transfer chambers 222, 224. The transfer chambers 222, 224 can be used to maintain ultrahigh vacuum conditions while allowing substrates to be transferred within the system 200. A second robot 230 can transfer the substrates between the transfer chambers 222, 224 and a second set of one or more processing chambers 232, 234, 236, 238. Similar to processing chambers 212, 214, 216, 100, the processing chambers 232, 234, 236, 238 can be outfitted to perform a variety of substrate processing operations.

[0020] The processing chamber 212 or 214 may be configured to remove native oxides or other contaminants from a substrate surface prior to forming a pre-contact layer or metal silicide layer on the substrate, such as native oxides from the bottoms of features disposed on a substrate. The processing chamber 212 or 214 can be particularly useful for performing the plasma assisted dry etch process (i.e. the "preclean process"). The processing chamber 212 or 214 may be a Preclean PCII, PCXT or etch chambers which are available from Applied Materials, Inc., located in Santa Clara, California. It is noted that other chambers available from other manufactures may also be utilized to practice the present invention.

[0021] After the preclean process is performed in the processing chamber 212 or 214, the substrate may further be transferred to any of the processing chambers 100, 212, 214, 216, 232, 234, 236, 238 disposed in the system 200 to perform the second step of the process, such as a SiConi chamber or etch chamber from Applied Materials, Inc located in Santa Clara, CA.

[0022] Figure 2 is a diagram of a method for directional etching according to one embodiment. The method 250 can include positioning a substrate with a native oxide layer in the processing chamber, as in 252. The processing chamber can be a processing chamber as described with reference to Figure 1 or it can be a different processing chamber. The processing chamber should be capable of at least

maintaining the substrate at a specific temperature, biasing the substrate and forming NH_4F (*e.g.* creating NH_4F remotely in a plasma). The substrate can be a silicon substrate with features formed on the surface. The features can include one or more of vias and trenches of varying cross-sectional dimensions, such as less than 27 nm. The substrate can have a surface contaminant formed on at least one surface. The surface contaminant, such as native oxides, may be formed on one or more of the surfaces of the substrate, such as a silicon dioxide formed on all exposed surfaces. The surface contaminants may also be of varying thickness dependant on the circumstances of formation, such as exposure to the atmosphere. Other layers or features may be formed under the silicon oxide, such as a layer of silicon nitride or metal silicides.

[0023] The method 250 can further include cooling the substrate to a first temperature, as in 254. An NH_4F etching is a dry etch process for removing one or more silicon oxides using an ammonia (NH_3) and nitrogen trifluoride (NF_3) gas mixture performed within a processing chamber. The substrate is generally cooled to a temperature which allows deposition of NH_4F but below the reaction temperature. This temperature will be dependent on process conditions such as processing chamber pressure. In one or more embodiments, the substrate can be cooled to a temperature below 15°C, such as between 15°C and 0°C, using a cooling apparatus formed within the support member. In one embodiment, the substrate is maintained at 10°C. In another embodiment, the substrate is maintained at a temperature of between 10ºC and 0ºC.

[0024] The method 250 can further include forming ammonium fluoride (NH_4F) or ammonium hydrogen fluoride ($NH_4F(HF)$) to deposit the etchant, as in 256. An NH_4F etching is a dry etch process for removing one or more silicon oxides using an ammonia (NH_3) and nitrogen trifluoride (NF_3) gas mixture performed within a processing chamber. The substrate can be cooled to a temperature below the reaction temperature of NH_4F or $NH_4F(HF)$.

[0025] The method 250 can further include exposing the substrate to NH_4F or $NH_4F(HF)$ introduced to the chamber to remove surface contaminants on a surface of the substrate, as in 258. In one embodiment, ammonia and nitrogen trifluoride gases are then introduced into the plasma chamber to form the etching gas mixture. The amount of each gas introduced into the plasma chamber is variable and may be adjusted to accommodate, for example, the thickness of the oxide layer to be removed, the geometry of the substrate being cleaned, the volume capacity of the plasma, the volume capacity of the chamber, as well as the capabilities of the vacuum system coupled to the chamber. The ratio of the etching gas mixture may be predetermined to remove various oxides on the substrate surface. The ratio of gas mixture in the etching gas mixture may be adjusted to preferentially remove the post-treated oxides, such as native oxides formed on the top and bottom surfaces of the features. In one embodiment, molar ratio of ammonia to nitrogen trifluoride in the etching gas mixture may be set to uniformly remove silicon oxides.

[0026] In one embodiment, etching rate of the etching gas mixture may be adjusted by adjusting a flow rate of nitrogen trifluoride while maintaining a molar ratio of ammonia and nitrogen trifluoride above a predetermined value. In one embodiment, etching rate may be increased or decreased by increasing or decreasing the flow rate of nitrogen trifluoride while the ratio of ammonia and nitrogen trifluoride remains above about 3:1. In another embodiment, ratio of ammonia and nitrogen trifluoride can be about 1:1.

[0027] The ammonia and nitrogen trifluoride gases can be dissociated into reactive species in a remote plasma chamber. The dissociated species can combine to form a highly reactive ammonia fluoride (NH_4F) compound and/or ammonium hydrogen fluoride ($NH_4F{\cdot}HF$) in the gas phase. These molecules react with the substrate surface to be processed. In one embodiment, the carrier gas is first introduced into the chamber, a plasma of the carrier gas is generated, and then the reactive gases, ammonia and nitrogen trifluoride, are added to the plasma.

[0028] Not wishing to be bound by theory, it is believed that the etchant gas, NH_4F and/or $NH_4F{\cdot}HF$, reacts with the silicon oxide surface to form ammonium hexafluorosilicate $(NH_4)_2SiF_6$, NH_3, and H_2O products. The NH_3 and H_2O are vapors at processing conditions and removed from the chamber by a vacuum pump. A thin film of $(NH_4)_2SiF_6$ is left behind on the substrate surface. This reaction mechanism can be summarized as follows:

$$NF_3 + 3NH_3 \rightarrow NH_4F + NH_4F{\cdot}HF + N_2$$

$$6NH_4F + SiO_2 + \text{heat} \rightarrow (NH_4)_2SiF_6 + 2H_2O + 4\,NH_3$$

$$(NH_4)_2SiF_6 + \text{heat} \rightarrow 2NH_3 + 2HF + SiF_4$$

[0029] The reaction as shown above requires temperature to both form $(NH_4)_2SiF_6$ and to sublimate the $(NH_4)_2SiF_6$ to NH_3, HF, SiF_4. By cooling the substrate below an activation, the NH_4F is present on the surface but nominally reacting with the silicon oxide.

[0030] The method 250 can further include treating the substrate with a low energy direct plasma while biasing the substrate, as in 260. The direct plasma can comprise any inert gas. Inert gases include noble gases, such as helium or argon. The direct plasma is formed into a plasma of sufficiently low energy so as to not sputter the substrate. Stated another way, the direct plasma is a primarily ionized species so that the directionality is random at least to some degree. The direct plasma may be either formed remotely in a plasma chamber and delivered to the chamber or formed inside the chamber itself.

[0031] The direct plasma is flowed toward the substrate which is simultaneously biased. The bias on the substrate can be of any power level which will not promote sputtering, such as between 25W and 250W. The bias can be delivered at varying frequencies, such as a bias from 200kHz to 60 MHz, with specific examples including 350 kHz, 13.56 MHz, 60 MHz or combinations thereof. As previously disclosed, the direct plasma is a low energy plasma which is largely ionized, thus having a approximately random directional movement when no other forces are

applied. The bias applied to the substrate attracts the ionized gas in the plasma toward the substrate, where the ionized gas strikes surfaces which are perpendicular to the direction of ionized gas movement, such as the bottom of a via or trench on a substrate. The ionized gas provides activation energy for the formation of $(NH_4)_2SiF_6$ from NH_4F as previously disposed on the surface and SiO_2 as present in the native silicon oxide layer.

[0032] The method 250 can further include exposing the substrate to a low pressure while maintaining the first temperature, as in 262. After the NH_4F and SiO_2 are reacted, the non-reacted NH_4F, which is primarily on the sidewalls of the vias and trenches, can be low pressure sublimated at a low temperature. Low pressures can include any pressures which will allow for desorption of non-reacted NH_4F, such as a pressure of 20 mTorr. The low pressure allows for desorption of the non-reacted NH_4F. Further, by keeping the temperature low, the non-reacted NH_4F will not react with the remaining SiO_2 to create $(NH_4)_2SiF_6$ on undesired areas, such as on the sidewalls of trenches and vias. Non-reacted precursors are then removed from the chamber so as to not affect further processing.

[0033] The method 250 can further include removing the $(NH_4)_2SiF_6$ by heating the substrate to a second temperature to sublimate volatile byproducts, as in 264. After the thin film is formed on the substrate surface, the support member may be elevated to an anneal position in close proximity to a heated gas distribution plate. The heat radiated from the gas distribution plate may dissociate or sublimate the thin film of $(NH_4)_2SiF_6$ into volatile SiF_4, NH_3, and HF products. These volatile products are then removed from the chamber by the vacuum pump as described above. Typically, a temperature of 75°C or more is used to effectively sublimate and remove the thin film from the substrate. Preferably, a temperature of 100°C or more is used, such as between about 115°C and about 250°C.

[0034] The method 250 can further include flowing inert gas to evacuate the volatile byproducts from the chamber, as in 266. The thermal energy to dissociate the thin film of $(NH_4)_2SiF_6$ into its volatile components is transferred by the gas

distribution plate through convection or radiation. In one aspect, the distribution plate is heated to a temperature of between 100ºC and 150ºC, such as about 120ºC. Further embodiments use a low energy plasma, such as a plasma as described with reference to the post-treatment process, to enhance the sublimation of volatile byproducts. The plasma is delivered to the surface of the substrate uniformly and at an energy level which will not sputter the oxides form the substrate. By using a low energy plasma while simultaneously heating the substrate, it is believed that the activation energy for sublimation can be reduced. For example, a layer of $(NH_4)_2SiF_6$ may be of a certain thickness which requires a temperature of 120ºC over a certain time period to sublimate. By using a low energy plasma, the layer of $(NH_4)_2SiF_6$ can be sublimated at 100ºC over the same time period or at 120ºC over a shorter time period.

[0035] The method can further include making a determination of whether a desired thickness of the bottom surface has been reached, as in 268. If a desired etch rate has not been achieved, the substrate can be cooled to the first temperature and the process can begin again. Based on the selectivity and the directionality, the process can be repeated numerous times to achieve desired results, such as repeating the process 10 times. Further, though the general steps are repeated in each cycle, the individual steps can be any disclosed embodiment, without regard to the previous embodiment chosen at that step. For example, if a helium plasma was delivered to a substrate with a bias of 100W in the first cycle, the second cycle could be an argon plasma delivered to the substrate with a 50W bias.

[0036] If a desired etch rate has been achieved, the process can be ended, as in 270. The processing chamber is purged and evacuated. The processed substrate is then removed from the chamber by lowering the substrate member to the transfer position, de-chucking the substrate, and transferring the substrate through a slit valve opening.

[0037] Without intending to be bound by theory, it is believed that at low temperatures, the chemical etch rate is practically zero because the NH_4F etchant

deposits but does not form $(NH_4)_2SiF_6$. During a standard NH_4F etch process, the substrate will be maintained at a temperature less than 40ºC, such as a temperature between 25ºC and 40ºC. In this temperature range, the reaction between the NH_4F and the oxide layer on the substrate is believed to be reaction limited, such that higher levels of reactant will lead to increased and uniform etching of the oxide layer. When the temperature is raised below the reaction temperature, the deposition rate no longer reflects the formation of $(NH_4)_2SiF_6$. Therefore, the areas of silicon oxide have the reactants present but do not have the energy required to make the product. The areas which have been post-treated with the inert plasma, however, form $(NH_4)_2SiF_6$.due to directional energy provided by the inert plasma. As such, at temperatures below 15ºC, the silicon oxide is not etched in areas not targeted by inert plasma (*e.g.* side walls of vias and trenches) and it is etched in targeted areas (*e.g.* upper surface of the substrate and bottoms of trenches).

[0038] Important to note is that the etching process is further selective for etching of silicon oxide over other layers which may be disposed on the substrate. NH_4F etchant will etch silicon oxide without substantial etching of layers such as silicon nitride or metal silicides. The experimentally determined selectivity between SiO_2 and SiN is greater than 7:1 and in some examples greater than 9:1. Selectivity of SiO_2 to Si is at least greater than 5:1. Thus, the above method provides for both selectivity and directionality in etching of native oxides.

[0039] Figures 3A-3D are graphical representations of a substrate 300 etched according to one or more embodiments. Figure 3A depicts a substrate 300 with a native oxide layer 303 according to one embodiment. The substrate 300 can be a silicon-containing substrate, such as a crystalline silicon substrate. The substrate 300 has an upper surface 302. The upper surface 302 has a surface contaminant, such as a native oxide layer 303, formed thereon. In one embodiment, the native oxide layer is a silicon oxide layer formed on a silicon-containing substrate. The native oxide layer 303 can be a result of transfer between chambers (*i.e.*, exposure to atmosphere). The substrate 300 can further have vias and trenches formed therein, such as a via 308. The native oxide layer 303 can be deposited on sidewall

surfaces 306 of features and bottom surfaces 304 of features. The substrate 300 can be positioned in a processing chamber as described above.

[0040] Figure 3B depicts a substrate during low temperature treatment with an NH_4F etchant 307 according to one embodiment. Though described for clarity as an NH_4F etchant, it is understood that the etchant includes all components formed from the ammonia and nitrogen trifluoride gases in the plasma, such as $NH_4F(HF)$ as described with reference to Figure 2. The NH_4F etchant 307 can be conformally deposited on the native oxide surface 303. When this step is performed at temperatures lower than 15ºC, such as 10ºC, the NH_4F etchant will not react with the native oxide layer 303 to form $(NH_4)_2SiF_6$. In one embodiment, the NH_4F etchant 307 should be present on the surface of the substrate for as short a time as possible to prevent spontaneous formation of $(NH_4)_2SiF_6$.

[0041] Figure 3C depicts a substrate 300 during plasma treatment according to one embodiment. The substrate 300 is treated with a low energy direct plasma 310, as described with reference to the embodiments above. The plasma 310 can activate the NH_4F etchant 307 on the top and bottom surfaces 304 to form the etchant layer 312. The etchant layer comprises both $(NH_4)_2SiF_6$ from the activation with plasma, as well as unreacted NH_4F etchant. The substrate should be maintained at a temperature below 15ºC, such as 10ºC, to prevent activity of the NH_4F etchant 307 on the sidewalls. The NH_4F etchant 307 deposited on sidewall surfaces 306 is largely unaffected by the plasma 310. The bias in the substrate 300 provides directionality to the plasma 310 to prevent the plasma 310 from targeting the sidewall surfaces 306. The bias delivered to the substrate can be between 25W and 200W.

[0042] Figure 3D depicts the substrate 300 after etching with the NH_4F etchant, according to one embodiment. After the $(NH_4)_2SiF_6$ film 312 is formed on and from the top and bottom surfaces 304, the remaining NH_4F etchant 307 is desorbed from the surface by low pressure while maintaining the temperature below 15ºC, or preferably below 10ºC. Further embodiments can include altering pressure or

temperature to optimize the desorption of the NH_4F etchant 307 from the sidewall surface 306. In another embodiment, the temperature is increased to a temperature above the dew point of the NH_4F etchant 307, such as above 70ºC. In this way, the desorption rate is increased while preventing adsorption of the NH_4F etchant 307 on the sidewall surfaces 306 of the substrate 300.

[0043] Next, the substrate is annealed to sublimate the $(NH_4)_2SiF_6$ film thus exposing the cleaned surfaces 314. The substrate 300 is heated to a second temperature, such as a temperature higher than about 75ºC. In one embodiment, the second temperature can be greater than about 100ºC. The thickness and composition of sidewall surfaces 306 are substantially unchanged.

[0044] Figure 4 depicts etch rate of the silicon oxide and silicon nitride as a function of pedestal temperature according to one embodiment. Etch rates were measured and plotted as shown in the graph with the oxide etch rate in Å/sec. over temperature in degrees C. The silicon nitride showed no substantial etching at any temperature in comparison to the silicon oxide. Silicon oxide etching increases linearly in the presence of NH_4F in temperatures between 15ºC and 30ºC. From 30ºC to about 70ºC, the silicon oxide surface decreases until it reaches the etch rate of silicon nitride. The decline in etch rate for silicon oxide after 30ºC is believed to be related to an increase in desorption of the NH_4F from the surface of the substrate prior to the formation of $(NH_4)_2SiF_6$. At temperatures higher than 70ºC, the etch rate on the untreated surface is substantially lower than either the prior temperature untreated surface etch rate or the treated surface etch rate. It is believed that, at this temperature or above, the adsorption rate and the desorption rate are equal. Thus, a minimal amount of $(NH_4)_2SiF_6$ is formed on the silicon oxide. Thus, by maintaining the temperature of the deposited NH_4F either below 15ºC or above 70ºC, the formation of $(NH_4)_2SiF_6$ in the presence of NH_4F on silicon oxide can be controlled for directional etching.

Conclusion

[0045] Embodiments described herein relate to methods of directional removal of native oxides form a surface. Above embodiments show preferential etching of post-treated surfaces over untreated surfaces. SiO_2 is formed natively on silicon surfaces and must be removed for proper deposition in vias and trenches. However, it is important to avoid changing the cross-sectional dimensions of the modern day vias and trenches, which can lead to device failure. A deposition of NH_4F at a low temperature will be effective for depositing the NH_4F conformally with limited formation of $(NH_4)_2SiF_6$ on the silicon oxide. Subsequently, by treating a biased substrate with a low energy inert plasma, the $(NH_4)_2SiF_6$ layer will form preferentially on the bottom and top horizontal surfaces over the sidewall surfaces. Subsequent annealing will be effective for removing the plasma-treated SiO_2 without affecting the untreated SiO_2 on the side walls of the vias or trenches.

[0046] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A method, comprising:

positioning a substrate comprising silicon in a processing chamber;

delivering a plasma to the surface of the substrate while biasing the substrate; and

exposing the surface of the substrate to ammonium fluoride (NH_4F) or ammonium hydrogen fluoride ($NH_4F(HF)$).

2. The method of claim 1, further comprising cooling the surface of the substrate to a temperature at or below 15ºC while exposing the surface of the substrate to NH_4F.

3. The method of claim 1, wherein the delivery of the plasma and the exposure to NH_4F is repeated a plurality of times before annealing the substrate.

4. The method of claim 1, further comprising maintaining the substrate at temperatures at or below 15ºC while delivering the plasma.

5. The method of claim 1, further comprising annealing the substrate to a temperature above 100ºC.

6 The method of claim 1, wherein the NH_4F or the $NH_4F(HF)$ are formed by remote plasma.

7. The method of claim 1, wherein the NH_4F or the $NH_4F(HF)$ are formed using a gas mixture comprising a 3:1 ratio of ammonia (NH_3) and nitrogen trifluoride (NF_3) respectively.

8. A method, comprising:

positioning a silicon-containing substrate in a processing chamber, the silicon-containing substrate comprising:

an exposed surface with one or more features formed in the exposed surface; and

a native oxide layer formed on the exposed surface;

cooling the substrate to a first temperature at a first pressure;

exposing the surface of the substrate to ammonium fluoride (NH_4F) at the first temperature;

biasing the substrate;

exposing the substrate to a direct plasma to selectively form one or more volatile products on the top and bottom surfaces of the features;

exposing the substrate to a second pressure at a second temperature to sublimate the non-reacted NH_4F from the surface of the substrate; and

heating the substrate to a third temperature, which is higher than the first temperature, to sublimate the one or more volatile products.

9. The method of claim 8, wherein the first temperature is less than 15ºC.

10. The method of claim 8, wherein the second temperature is greater than 70ºC.

11. The method of claim 8, wherein the third temperature is a temperature of greater than 100ºC.

12. The method of claim 8, further comprising exposing the substrate to low pressure and low temperatures while delivering the low energy remote plasma.

13. The method of claim 8, wherein the NH_4F is formed from a gas mixture comprising ammonia (NH_3) and nitrogen trifluoride (NF_3).

14. The method of claim 13, wherein the gas mixture is a 3:1 ratio of ammonia (NH_3) and nitrogen trifluoride (NF_3) respectively.

15. The method of claim 8, wherein second pressure is lower than the first pressure.

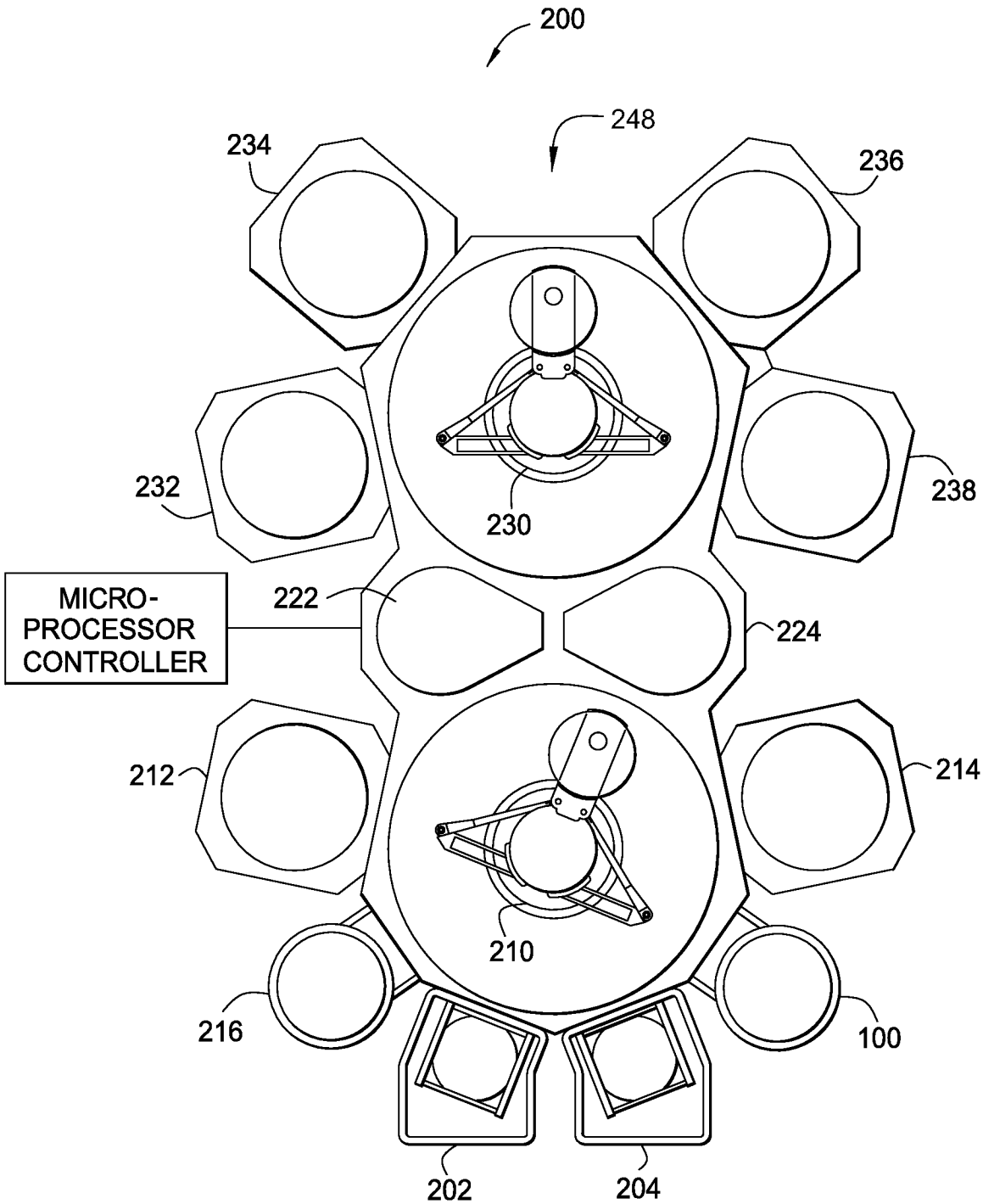

200
248
234
236
232
238
230
MICRO-
PROCESSOR
CONTROLLER
222
224
212
214
210
216
100
202
204

FIG. 1

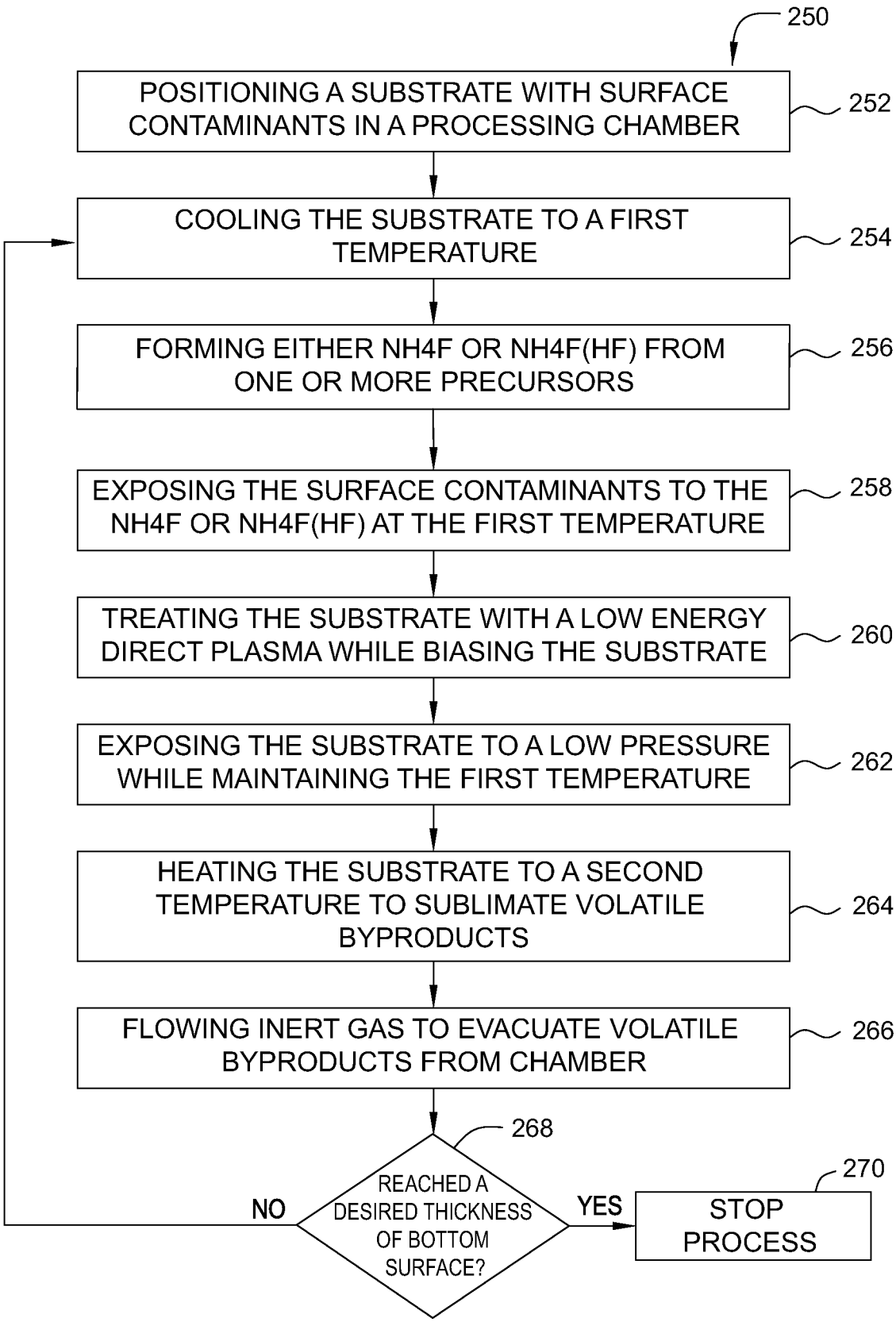

250
POSITIONING A SUBSTRATE WITH SURFACE CONTAMINANTS IN A PROCESSING CHAMBER
252
COOLING THE SUBSTRATE TO A FIRST TEMPERATURE
254
FORMING EITHER NH4F OR NH4F(HF) FROM ONE OR MORE PRECURSORS
256
EXPOSING THE SURFACE CONTAMINANTS TO THE NH4F OR NH4F(HF) AT THE FIRST TEMPERATURE
258
TREATING THE SUBSTRATE WITH A LOW ENERGY DIRECT PLASMA WHILE BIASING THE SUBSTRATE
260
EXPOSING THE SUBSTRATE TO A LOW PRESSURE WHILE MAINTAINING THE FIRST TEMPERATURE
262
HEATING THE SUBSTRATE TO A SECOND TEMPERATURE TO SUBLIMATE VOLATILE BYPRODUCTS
264
FLOWING INERT GAS TO EVACUATE VOLATILE BYPRODUCTS FROM CHAMBER
266
268
REACHED A DESIRED THICKNESS OF BOTTOM SURFACE?
NO
YES
270
STOP PROCESS

FIG. 2

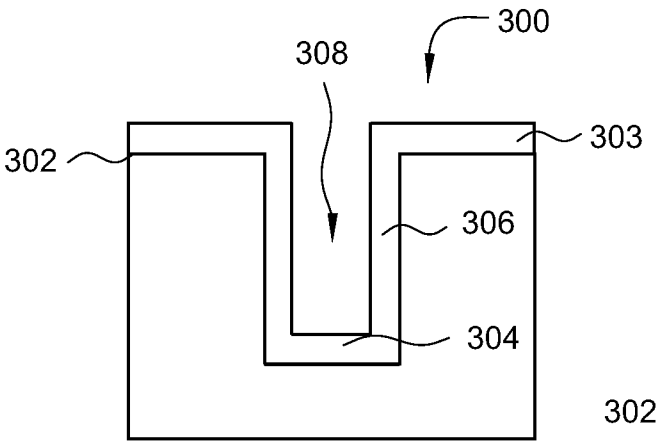


FIG. 3A

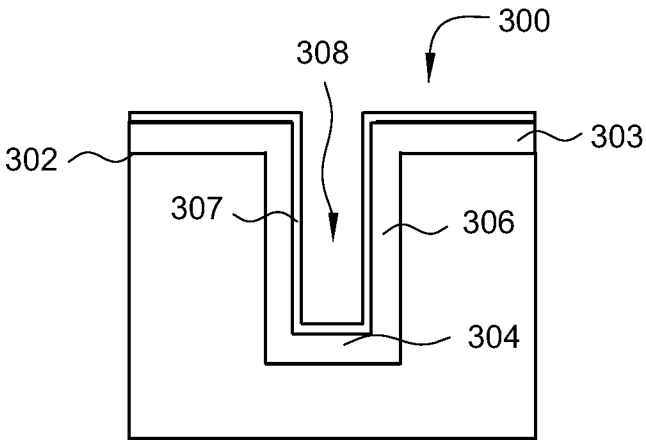


FIG. 3B

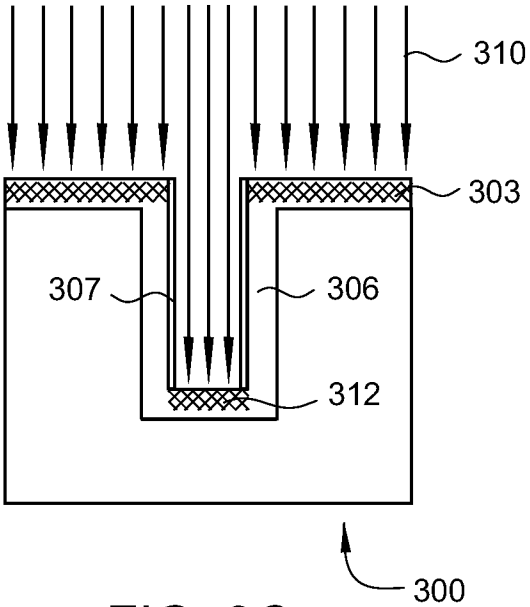


FIG. 3C

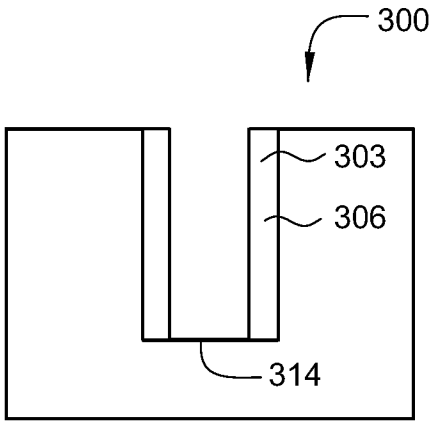


FIG. 3D

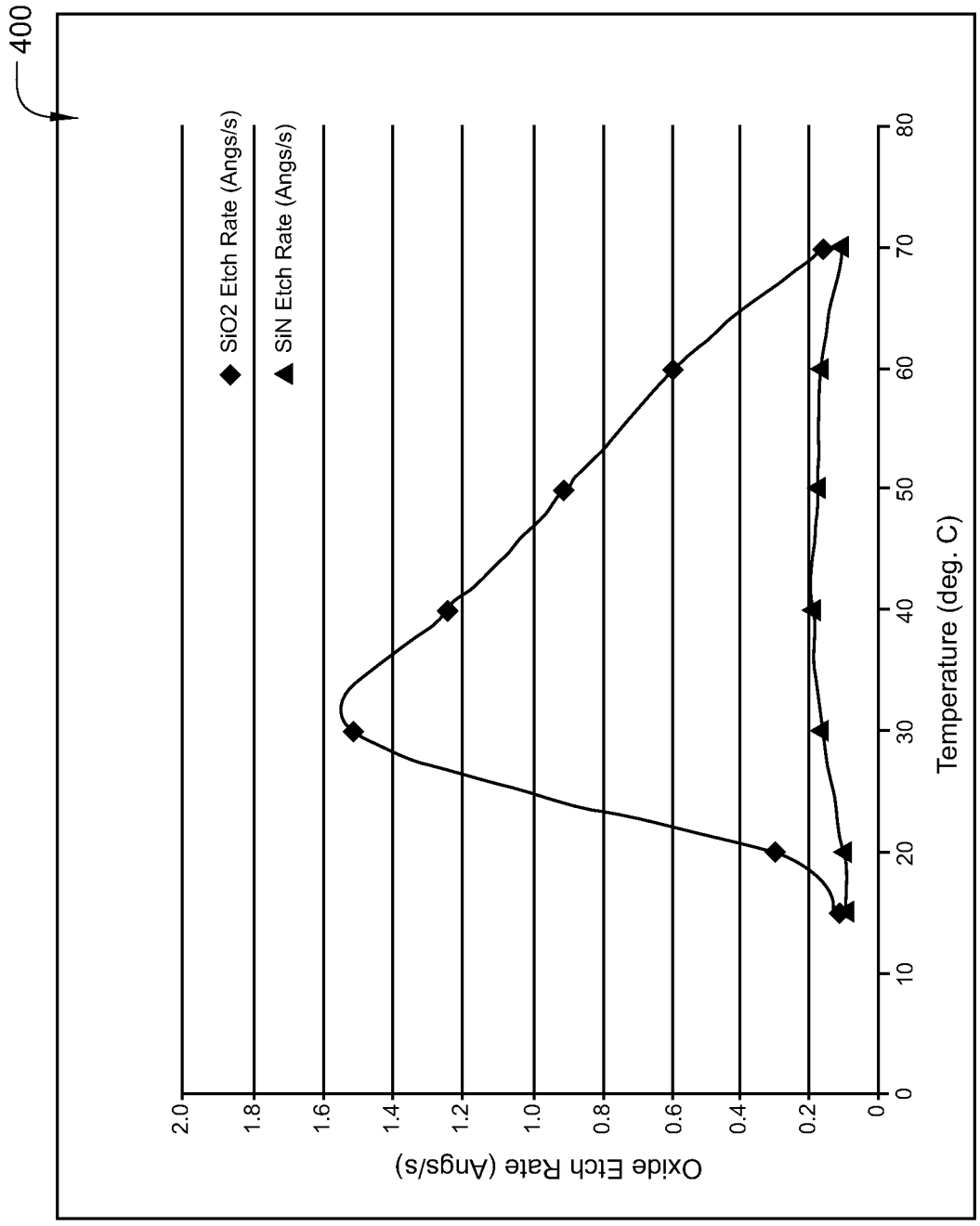

400
SiO2 Etch Rate (Angs/s)
SiN Etch Rate (Angs/s)
Oxide Etch Rate (Angs/s)
Temperature (deg. C)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
10
20
30
40
50
60
70
80

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/060198

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/3065(2006.01)i

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)
H01L 21/3065; H01L 21/302; H01L 21/304; H01L 21/20; H01L 21/28; H01L 21/461; H01L 21/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: substrate, plasma, bias, ammonium, fluoride and temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007-0123051 A1 (REZA ARGHAVANI et al.) 31 May 2007 See paragraphs [0035]-[0057], claims 1-10 and figure 3.	1-15
Y	US 6057247 A (SHINICHI IMAI et al.) 02 May 2000 See abstract, column 4, line 1 - column 8, line 22 and claim 1.	1-15
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
27 December 2013 (27.12.2013)	**27 December 2013 (27.12.2013)**

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INTERNATIONAL SEARCH REPORT

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PCT/US2013/060198

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PCT/US2013/060198

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