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(54) **Title:** SURFACE TREATMENT METHODS AND COMPOSITIONS THEREFOR

(57) **Abstract:** The disclosure provides methods and compositions therefor for treating a surface wherein a surface treatment layer is formed on the surface, thereby minimizing or preventing pattern collapse as the surface is subjected to typical cleaning steps in the semiconductor manufacturing process.

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SURFACE TREATMENT METHODS AND COMPOSITIONS THEREFOR

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional Application Serial No. 62/617,688, filed on January 16, 2018 and U.S. Provisional Application Serial No. 62/476,182, filed on March 24, 2017, both of which are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

The disclosure relates generally to liquid treatment of surfaces and more particularly to liquid treatment of surfaces where formation of a hydrophobic layer is desired.

BACKGROUND

At sub-20 nm critical dimensions, pattern collapse of FinFET's and dielectric stacks during wet clean and dry has become a major problem in semiconductor manufacturing processes. The conventional theory of pattern collapse implicates high capillary forces during rinse and dry as major contributors leading to the collapse phenomenon. However, other chemical and substrate properties may play an important role as well, namely, liquid surface tension and viscosity, substrate mechanical strength, pattern density and aspect ratio, and cleaner chemistry damage to substrate surfaces.

SUMMARY

It has been found that low surface tension modifying fluids that impart the surfaces of a semiconductor substrate (e.g., a silicon or copper wafer) with a hydrophobic layer (e.g., a hydrophobic monolayer) can minimize the capillary forces that drive pattern collapse during a cleaning or drying process. Without wishing to be bound by theory, it is believed that the Laplace pressure is minimized when the contact angle, i.e., the angle a liquid (e.g., water) creates when in contact with a substrate surface, is at or near 90 degrees. This in combination with the presence of a low surface tension fluid can greatly reduce the forces that cause pattern collapse.

In general, this disclosure provides methods and compositions for treating a patterned surface of a semiconductor substrate (e.g., a patterned wafer) where a hydrophobic layer is formed on the surface, thereby minimizing or preventing pattern collapse as the surface is subjected to typical cleaning and drying steps in a semiconductor manufacturing process. The methods disclosed herein employ compositions that form a hydrophobic layer on the surface such that the treated surface has a water contact angle of at least about 50 degrees.

In some embodiments, this disclosure features surface treatment methods. Such methods can be performed, for example, by contacting a surface of a substrate (e.g., a semiconductor substrate) with a surface treatment composition including (e.g., consisting of or consisting essentially of) at least one aprotic solvent and at least one surface treatment agent, wherein the surface treatment agent includes a Si-containing compound, and the surface treatment composition forms a surface treatment layer (e.g., a hydrophobic monolayer) on the surface such that the surface has a water contact angle of at least about 50 degrees.

In some embodiments, this disclosure features methods for treating a semiconductor substrate having a pattern disposed on a surface of the substrate. The method can include contacting the surface with a surface treatment composition, in which the surface treatment composition includes (e.g., consists of or consists essentially of) at least one aprotic solvent and at least one surface treatment agent, the at least one surface treatment agent includes a Si-containing compound, and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees. The pattern includes a feature having a dimension of at most about 20 nm.

In some embodiments, this disclosure features methods for cleaning a wafer having a pattern disposed on a surface of the wafer. Such methods can be performed, for example, by a) contacting the surface with an aqueous cleaner; b) optionally, contacting the surface with a first rinsing solution; c) contacting the surface with a surface treatment composition, wherein the surface treatment composition includes (e.g., consists of or consists essentially of) at least one aprotic solvent and at least one surface treatment agent, the at least one surface treatment agent includes a Si-containing compound, and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees; d) contacting the surface with a second rinsing solution; e) drying the surface; and f) removing the surface treatment layer. In some embodiments, the pattern includes a feature having a dimension of at most about 20 nm.

In some embodiment, this disclosure features surface treatment compositions including (e.g., consisting of or consisting essentially of) at least one aprotic solvent, and at least one surface treatment agent, in which the surface treatment agent is a Si-containing compound containing a trimethylsilyl group, an aminosilyl group, or a disilazane group, and the surface treatment composition forms a surface treatment layer on a surface such that the surface has a water contact angle of at least about 50 degrees. In some embodiments, when the Si-containing compound includes a disilazane group, the disilazane group includes no Si-H bond.

In some embodiment, this disclosure features surface treatment compositions including (e.g., consisting of or consisting essentially of) (a) from about 90 wt% to about 99.5 wt% at least one aprotic solvent selected from the group consisting of lactones, ketones, aromatic hydrocarbons, siloxanes, glycol dialkyl ethers, glycol alkyl ether acetates, esters, ureas, lactams, dimethyl sulfoxide, and N-methyl pyrrolidone, and (b) from about 0.5 wt% to about 10 wt% at least one surface treatment agent, in which the surface treatment agent is a Si-containing compound containing a trimethylsilyl group, an aminosilyl group, or a disilazane group. In some embodiments, when the Si-containing compound includes a disilazane group, provided that the disilazane group includes no Si-H bond.

In some embodiment, this disclosure features surface treatment compositions consisting of propylene carbonate, hexamethyldisilazane, and optionally, at least one co-solvent.

DETAILED DESCRIPTION

In some embodiments, this disclosure relates to surface treatment methods. Such methods can be performed, for example, by contacting a surface (e.g., a surface that has patterns) of a substrate (e.g., a semiconductor substrate) with a surface treatment composition including at least one (e.g., two, three, or four) aprotic solvent and at least one (e.g., two, three, or four) surface treatment agent. The surface treatment agent can be a Si-containing compound. In general, the surface treatment composition forms a surface treatment layer (e.g., a hydrophobic monolayer) on the surface such that the surface has a water contact angle of at least about 50 degrees.

Semiconductor substrates that can be treated by the surface treatment compositions described herein typically are constructed of silicon, silicon germanium, silicon nitride, copper, Group III-V compounds such as GaAs, or any combination thereof. In some embodiments, the semiconductor substrate can be a silicon wafer, a copper wafer, a silicon dioxide wafer, a silicon nitride wafer, a silicon oxynitride wafer, a carbon doped silicon oxide wafer, a SiGe wafer, or a GaAs wafer. The semiconductor substrates may additionally contain exposed integrated circuit structures such as interconnect features (e.g., metal lines and dielectric materials). Metals and metal alloys used for interconnect features include, but are not limited to, aluminum, aluminum alloyed with copper, copper, titanium, tantalum, cobalt, nickel, silicon, polysilicon titanium nitride, tantalum nitride, tin, tungsten, SnAg, SnAg/Ni, CuNiSn, CuCoCu, and CoSn. The semiconductor substrate may also contain layers of interlayer dielectrics, silicon oxide, silicon nitride, titanium nitride, silicon carbide, silicon oxide carbide, silicon oxide nitride, titanium oxide, and carbon doped silicon oxides.

In some embodiments, the semiconductor substrate surface to be treated by the surface treatment compositions described herein includes features containing SiO_2, SiN, TiN, SiOC, SiON, Si, SiGe, Ge, or W. In some embodiments, the substrate semiconductor surface includes features containing SiO_2 and/or SiN.

In general, the semiconductor substrate surface to be treated by the surface treatment compositions described herein includes patterns formed by a prior semiconductor manufacturing process (e.g., a lithographic process including applying a photoresist layer, exposing the photoresist layer to an actinic radiation, developing the photoresist layer, etching the semiconductor substrate beneath the photoresist layer, and/or removing the photoresist layer). In some embodiments, the patterns can include features having at least one (e.g., two or three) dimension (e.g., a length, a width, and/or a depth) of at most about 20 nm (e.g., at most about 15 nm, at most about 10 nm, or at most about 5 nm) and/or at least about 1 nm (e.g., at least about 2 nm or at least about 5 nm).

In general, the surface treatment compositions described herein include at least one (two, three, or four) aprotic solvent and at least one (e.g., two, three, or four) surface treatment agent. As used herein, the phrase “aprotic solvent” refers to a solvent that lacks a hydrogen atom bounded to an oxygen (e.g., as in a hydroxyl group) or a nitrogen (e.g., as in an amine group). In some embodiments, the aprotic solvent can be a polar aprotic solvent having a relatively high dipole moment (e.g., at least 2.7). In some embodiments, the aprotic solvent is selected from the group consisting of carbonate solvents (e.g., propylene carbonate or dimethyl carbonate), lactones (e.g., gamma-butyrolactone), ketones (e.g., cyclohexanone), aromatic hydrocarbons (e.g., toluene, xylene, or mesitylene), siloxanes (e.g., hexamethyldisiloxane), glycol dialkyl ethers (e.g., dipropylene glycol dimethyl ether or propylene glycol dimethyl ether), glycol alkyl ether acetates (e.g., propylene glycol methyl ether acetate (PGMEA)), esters (e.g., ethyl lactate), ureas (e.g., 1,3-dimethyl-2-imidizolidinone or 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone), lactams, dimethyl sulfoxide, and N-methyl pyrrolidone.

In some embodiments, the aprotic solvent is selected from the group consisting of carbonate solvents (such as propylene carbonate). In some embodiments, the aprotic solvent is selected from the group consisting of lactones (such as gamma-butyrolactone).

In some embodiments, the at least one aprotic solvent is from at least about 90 wt% (e.g., at least about 91 wt%, at least about 92 wt%, at least about 93 wt%, at least about 94 wt%, at least about 95 wt%, at least about 96 wt%, at least about 97 wt%, or at least about 98 wt%) to at most about 99.9 wt% (e.g., at most about 99.5 wt%, at most about 99 wt%, at most about 98 wt%, or at most about 97 wt%) of the surface treatment compositions described herein.

In general, the surface treatment agents contemplated for use in the compositions and methods of the disclosure are Si-containing compounds. In some embodiments, the surface treatment agents can be disilazanes. For example, the surface treatment agent can be hexamethyldisilazane, heptamethyldisilazane, N-methyl hexamethyldisilazane, 1,3-diphenyltetramethyldisilazane, or 1,1,3,3-tetraphenyl-1,3-dimethyldisilazane.

In some embodiments, the surface treatment agents contemplated for use in the compositions and methods of the disclosure are selected from the group consisting of compounds including a trimethylsilyl group. For example, the surface treatment agent can be N-(trimethylsilyl)dimethylamine, N-(trimethylsilyl)diethylamine, 4-trimethylsilyloxy-3-penten-2-one, bis(trimethylsilyl)sulfate, methoxytrimethylsilane, N-allyl-N,N-bis(trimethylsilyl)amine, N-(trimethylsilyl)diethylamine, N, N-bis(trimethylsilyl) urea, or tris(trimethylsilyl)phosphite.

In some embodiments, the surface treatment agents contemplated for use in the compositions and methods of the disclosure are selected from the group consisting of aminosilanes. For example, the aminosilane can be bis(dimethylamino)dimethylsilane or phenethyldimethyl(dimethylamino)silane.

In some embodiments, the at least one surface treatment agent is from at least about 0.5 wt% (e.g., at least about 1 wt%, at least about 2 wt%, at least about 3 wt%, at least about 4 wt%, at least about 5 wt%, at least about 6 wt%, at least about 7 wt%, or at least about 8 wt%) to at most about 10 wt% (e.g., at most about 9.5 wt%, at most about 9 wt%, at most about 8 wt%, or at most about 7 wt%) of the surface treatment compositions described herein.

Without wishing to be bound by theory, it is believed that the surface treatment compositions described herein can form a surface treatment layer (e.g., a hydrophobic layer such as a hydrophobic monolayer) on a patterned surface of a semiconductor substrate such that the patterned surface has a water contact angle of at least about 50 degrees (e.g., at least about 55 degrees, at least about 60 degrees, at least about 65 degrees, at least about 70 degrees, at least about 75 degrees, at least about 80 degrees, at least about 85 degrees, at least about 89 degrees, at least about 90 degrees, at least about 95 degrees, or at least about 100 degrees). Without wishing to be bound by theory, it is believed that such a surface treatment layer can prevent or minimize the collapse of the patterned features on the semiconductor substrate during a cleaning or drying step typically used in the semiconductor manufacturing process. In some embodiments, upon treatment with the surface treatment compositions described herein, at least about 70% (e.g., at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, at least about 98%, or at least about 99%) of the features (e.g., pillars) on a patterned wafer can remain uncollapsed after a cleaning or drying step.

In some embodiments, the surface treatment compositions described herein can further include at least one catalyst. Exemplary catalysts include, but are not limited to, triazoles (e.g., benzotriazole), anhydrides (e.g., phthalic anhydride or acetic anhydride), organic acids (e.g., sulfonic acids such as methanesulfonic acid or trifluoromethanesulfonic acid), inorganic acids (e.g., sulfuric acid).

In some embodiments, the at least one catalyst is from at least about 0.1 wt% (e.g., at least about 0.2 wt%, at least about 0.3 wt%, at least about 0.4 wt%, at least about 0.5 wt%, at least about 0.6 wt%, at least about 0.7 wt%, or at least about 0.8 wt%) to at most about 1 wt% (e.g., at most about 0.95 wt%, at most about 0.9 wt%, at most about 0.8 wt%, at most about 0.7 wt%, at most about 0.6 wt%, or at most about 0.5 wt%) of the surface treatment compositions described herein. Without wishing to be bound by theory, it is believed that the catalyst can facilitate the formation of the surface treatment layer by the surface treatment agent on a patterned surface of a semiconductor substrate (e.g., through facilitating a reaction between the surface treatment agent and the patterned surface).

In some embodiments, the surface treatment compositions described herein can further include water. In some embodiments, the water is at most about 2 wt% (e.g., at most about 1.5 wt%, at most about 1 wt%, at most about 0.8 wt%, at most about 0.6 wt%, at most about 0.5 wt%, at most about 0.4 wt%, at most about 0.2 wt%, or at most about 0.1 wt%) of the surface treatment compositions described herein. In some embodiments, the surface treatment compositions described herein are substantially free of water (except for the trace amount of water in the solvent). In such embodiments, the surface treatment compositions described herein can include at most about 1000 ppm (e.g., at most about 100 ppm, at most about 10 ppm, or at most about 1 ppm) water.

In some embodiments, the surface treatment compositions described herein can specifically exclude one or more of the additive components, in any combination, if more than one. Such components are selected from the group consisting of non-aromatic hydrocarbons, cyclic silazanes (e.g., heterocyclic silazanes), protic solvents (e.g., alcohols or amides), lactones (e.g., those with 5- or 6-membered rings), certain Si-containing compounds (e.g., those having a Si-H group or an aminosilyl group), polymers, oxygen scavengers, quaternary ammonium salts including quaternary ammonium hydroxides, amines, bases (such as alkaline bases (e.g., NaOH, KOH, LiOH, $Mg(OH)_2$, and $Ca(OH)_2$)), surfactants, defoamers, fluoride-containing compounds (e.g., HF, H_2SiF_6, H_2PF_6, HBF_4, NH_4F, and tetraalkylammonium fluoride), oxidizing agents (e.g., peroxides, hydrogen peroxide, ferric nitrate, potassium iodate, potassium permanganate, nitric acid, ammonium chlorite, ammonium chlorate, ammonium iodate, ammonium perborate, ammonium perchlorate, ammonium periodate, ammonium persulfate, tetramethylammonium chlorite, tetramethylammonium chlorate, tetramethylammonium iodate, tetramethylammonium perborate, tetramethylammonium perchlorate, tetramethylammonium periodate, tetramethylammonium persulfate, urea hydrogen peroxide, and peracetic acid), abrasives, silicates, hydroxycarboxylic acids, carboxylic and polycarboxylic acids lacking amino groups, silanes (e.g., alkoxysilanes), cyclic compounds (e.g., cyclic compounds containing at least two rings, such as substituted or unsubstituted naphthalenes, or substituted or unsubstituted biphenylethers) other than the cyclosiloxanes described herein, chelating agents (e.g., azoles, diazoles, triazoles, or tetrazoles), corrosion inhibitors (such as azole or non-azole corrosion inhibitors), buffering agents, guanidine, guanidine salts, pyrrolidone, polyvinyl pyrrolidone, metal halides, and metal-containing catalysts.

In some embodiments, the surface treatment methods described herein can further include contacting the surface of a substrate with at least one aqueous cleaning solution before contacting the surface with a surface treatment composition. In such embodiments, the at least one aqueous cleaning solution can include water, an alcohol, aqueous ammonium hydroxide, aqueous hydrochloric acid, aqueous hydrogen peroxide, an organic solvent, or a combination thereof.

In some embodiments, the surface treatment methods described herein can further include contacting the surface of a substrate with a first rinsing solution (e.g., water, an organic solvent such as isopropanol, or a combination thereof) after contacting the surface with the at least one aqueous cleaning solution but before contacting the surface with the surface treatment composition. In some embodiments, the surface treatment methods described herein can further include contacting the surface with a second rinsing solution (e.g., water, an organic solvent such as isopropanol, or a combination thereof) after contacting the surface with the surface treatment composition. In some embodiments, the surface treatment methods described herein can further include drying the surface (e.g., after contacting the surface with first rinsing solution, the surface treatment composition, or the second rinsing solution). In some embodiments, the surface treatment methods described herein can further include removing the surface treatment layer from the surface.

In some embodiments, this disclosure provides methods for cleaning a semiconductor substrate (e.g., a wafer) having a pattern disposed on a surface of the substrate. Such methods can be performed, for example, by:

a) optionally, contacting the surface with an aqueous cleaner;

b) optionally, contacting the surface with a first rinsing solution;

c) contacting the surface with a surface treatment composition, wherein the surface treatment composition includes at least one aprotic solvent and at least one surface treatment agent, in which the at least one surface treatment agent includes a Si-containing compound, and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees;

d) optionally, contacting the surface with a second rinsing solution;

e) drying the surface; and

f) optionally, removing the surface treatment layer to form a cleaned, patterned surface.

In such embodiments, the pattern can include a feature having a dimension of at most about 20 nm.

In step a) of the above described method, the substrate (e.g., a wafer) bearing a patterned surface is treated with one or more aqueous cleaning solutions. When the patterned surface is treated with two or more aqueous cleaning solutions, the cleaning solutions can be applied sequentially. The aqueous cleaning solutions can be water alone or can be solutions containing water, a solute, and optionally an organic solvent. In some embodiments, the aqueous cleaning solutions can include water, an alcohol (e.g., a water soluble alcohol such as isopropanol), an aqueous ammonium hydroxide solution, an aqueous hydrochloric acid solution, an aqueous hydrogen peroxide solution, an organic solvent (e.g., a water soluble organic solvent), or a combination thereof.

In step b), the cleaning solution from step a) can be optionally rinsed away using a first rinsing solution. The first rinsing solution can include water, an organic solvent (e.g., isopropanol), or an aqueous solution containing an organic solvent. In some embodiments, the first rinsing solution is at least partially miscible with the cleaning solution used in step a). In some embodiments, step b) can be omitted when the cleaning solution used in step a) is not moisture sensitive or does not contain any appreciable amount of water.

In step c), the substrate surface can be treated with a surface treatment composition of the disclosure described above to form a modified surface having a surface treatment layer (e.g., a hydrophobic layer). The modified surface thus formed can be hydrophobic and can have a water contact angle of at least about 50 degrees. In some embodiments, this step can be performed at a temperature of about 20-35°C for a process time ranging from about 10 seconds to about 300 seconds.

In step d), after the substrate surface is treated with a surface treatment composition, the surface can optionally be rinsed with a second rinsing solution. The second rinsing solution can include water, an organic solvent (e.g., isopropanol), or an aqueous solution containing an organic solvent. In some embodiments, this step can be performed at a temperature of about 20-70°C.

In step e), the substrate surface can be dried (e.g., by using a pressurized gas). Without wishing to be bound by theory, it is believed that, after the substrate surface is treated with a surface treatment composition described herein, the collapse of patterns on the surface during this drying step is minimized.

In step f), after the drying step, the surface treatment layer (e.g., a hydrophobic layer) can optionally be removed. In general, the surface treatment layer can be removed by a number of methods depending on the chemical characteristics of the modified surface. Suitable methods for removing the surface treatment layer include plasma sputtering; plasma ashing; thermal treatment at atmospheric or sub atmospheric pressure; treatment with an acid, base, oxidizing agent or solvent containing condensed fluid (e.g., supercritical fluids such as supercritical CO_2); vapor or liquid treatment; UV irradiation; or combinations thereof.

The semiconductor substrate having a cleaned, patterned surface prepared by the method described above can be further processed to form one or more circuits on the substrate or can be processed to form into a semiconductor device (e.g., an integrated circuit device such as a semiconductor chip) by, for example, assembling (e.g., dicing and bonding) and packaging (e.g., chip sealing).

In some embodiments, this disclosure features articles (e.g., an intermediate semiconductor article found during the manufacturing of a semiconductor device) that includes a semiconductor substrate, and a surface treatment composition described herein supported by the semiconductor substrate. The surface treatment composition can include at least one aprotic solvent and at least one Si-containing compound, such as those described above.

The present disclosure is illustrated in more detail with reference to the following examples, which are for illustrative purposes and should not be construed as limiting the scope of the present disclosure.

Example 1

Surface treatment solutions (i.e., formulations 1-101) were prepared by mixing the components at room temperature. The compositions of formulations 1-101 are summarized in Table 1 below. All percentages listed in Table 1 are weight percentages, unless indicated otherwise.

The Coupons containing SiO_2 or SiN thin films on Si substrates were cut into 1x1 inch squares. The coupons were immersed vertically into 100 mL of stirred (50 RPM) Surface Treatment Solutions and were kept at the corresponding temperatures indicated in Table 1. The coupons were processed for the corresponding times indicated in Table 1. The coupons were then rinsed with isopropanol at 50ºC and dried by using pressurized nitrogen gas.

The coupons were placed on the AST VCA 3000 Contact Angle Tool and the following procedure was followed to measure the contact angles:

1. Place the SiO_2 or SiN coupon onto the stage.
2. Raise the stage upward by rotating Vertical Knob clockwise until the specimen is just below the needle.
3. Dispense a drop of De-ionized water, lightly touching the specimen surface, then lower the specimen until the droplet separates from the needle tip.
4. Center the drop across the field-of-view using transverse knob for stage adjustment.
5. Focus the drop in field-of-view to get a sharp image by moving the stage along guide rails.
6. Click the “AutoFAST” button to freeze the image and calculate. Two numbers will be displayed; these are the left and right contact angles.
7. To calculate manually, use the mouse to place five markers around the droplet.
8. Select the droplet icon from the Main Menu to calculate the contact angle.

9. This will create a curve fit and tangent lines on the image. Two numbers will be displayed in the left-hand-corner of the screen; these are the left and right contact angles.

10. Repeat above procedure at 3 substrate sites and average the resulting contact angles and report the average result in Table 1.

Table 1

Form. #	Solvent[1]	Co-solvent	Silane	Catalyst	T (ºC)	Process time (s)	SiO_2 CA[2]	SiN CA[2]
0	No Treatment						< 15	< 15
1	Propylene Carbonate	--	3% HMDS[3]	--	25	180	90	87
2	Propylene Carbonate	0.2% H_2O	3% HMDS	--	25	180	88	89
3	Propylene Carbonate	0.4% H_2O	3% HMDS	--	25	180	88	88
4	Propylene Carbonate	0.6% H_2O	3% HMDS	--	25	180	89	89
5	Propylene Carbonate	1% H_2O	3% HMDS	--	25	180	85	88
6	Propylene Carbonate	1.5% H_2O	3% HMDS	--	25	180	84	83
7	Propylene Carbonate	2% H_2O	3% HMDS	--	25	180	63	48
8	Propylene Carbonate	--	0.1% HMDS	--	25	180	39	36
9	Propylene Carbonate	--	0.5% HMDS	--	25	180	54	59
10	Propylene Carbonate	--	1% HMDS	--	25	180	68	66
11	Propylene Carbonate	--	2% HMDS	--	25	180	81	79
12	Propylene Carbonate	--	5% HMDS	--	25	180	92	90
13	Propylene Carbonate	--	10% HMDS	--	25	180	90	90
14	Propylene Carbonate	--	3% HMDS	--	25	10	88	89
15	Propylene Carbonate	--	3% HMDS	--	25	30	91	88
16	Propylene Carbonate	--	3% HMDS	--	25	60	90	88
17	Propylene Carbonate	--	3% HMDS	--	25	300	92	90

Form. #	Solvent[1]	Co-solvent	Silane	Catalyst	T (ºC)	Process time (s)	SiO_2 CA[2]	SiN CA[2]
18	Propylene Carbonate	--	3% 4-Trimethylsilyloxy-3-penten-2-one	--	25	180	83	65
19	Propylene Carbonate	--	5% 4-Trimethylsilyloxy-3-penten-2-one	--	25	180	80	57
20	Propylene Carbonate	--	3 % Bis(dimethylamino)-dimethylsilane	--	25	180	93	94
21	Propylene Carbonate	--	3% Bis-(trimethylsilyl)sulfate	--	25	180	88	74
22	Dimethyl Carbonate	--	3% HMDS	--	25	180	69	69
23	Diethyl Carbonate	--	3% HMDS	--	25	180	67	66
24	γ-Butyrolactone	--	3% HMDS	--	25	180	82	84
25	γ-Butyrolactone	--	3 % Bis(dimethylamino)-dimethylsilane	--	25	180	95	90
26	γ-Butyrolactone	--	3% Bis-(trimethylsilyl)sulfate	--	25	180	65	--
27	γ-Butyrolactone	--	3% Bis-(trimethylsilyl)sulfate	0.5% BTA	25	180	61	57
28	γ-Butyrolactone	--	3% Bis-(trimethylsilyl)sulfate	0.5% Phthalic Anhydride	25	180	67	66
29	γ-Butyrolactone	--	3% Bis-(trimethylsilyl)sulfate	0.5% BTA	50	180	86	76
30	γ-Butyrolactone	--	3% HMDS	--	25	300	86	82
31	γ-Butyrolactone	--	3% HMDS	0.5% Phthalic anhydride	25	300	90	90
32	γ-Butyrolactone	--	3% Methoxytrimethyl-silane	--	25	300	<10	<10
33	γ-Butyrolactone	--	3% Methoxytrimethyl-silane	0.5% Phthalic anhydride	25	300	80	11
34	γ-Butyrolactone	--	3% N-Allyl-N,N-bis(trimethylsilyl)amine	--	25	300	77	--
35	γ-Butyrolactone	--	3% 1,1,3,3-Tetraphenyl-1,3-dimethyl-disilazane	--	25	300	58	--
36	γ-Butyrolactone	--	3% N-(Trimethylsilyl)-diethylamine	--	25	300	85	--
37	γ-Butyrolactone	--	3% N-methyl hexa-methyldisilazane	--	25	300	91	--
38	γ-Butyrolactone	--	3% 1,3-Diphenyltetra-methyldisilazane	--	25	300	63	--
39	γ-Butyrolactone	--	3% Bis(trimethylsilyl)	--	25	300	65	--

Form. #	Solvent[1]	Co-solvent	Silane	Catalyst	T (ºC)	Process time (s)	SiO_2 CA[2]	SiN CA[2]
			sulfate					
40	DMSO	--	3% Phenethyldimethyl-(dimethylamino)silane	0.5% Phthalic Anhydride	25	180	42	48
41	DMSO	--	3% N,N,-Bis(trimethyl silyl) urea	0.5% Phthalic Anhydride	25	180	33	43
42	DMSO	--	3 % N,N,-Bis(trimethyl silyl) urea	--	25	180	17	21
43	DMSO	--	3 % Bis(dimethylamino)-dimethylsilane	--	25	180	85	86
44	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% BTA	25	180	83	74
45	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% Phthalic Anhydride	25	180	83	74
46	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% BTA	50	180	85	75
47	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% of 96 % H_2SO_4	25	180	67	59
48	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% of MSA	25	180	76	64
49	DMSO	--	3 % HMDS	--	25	300	69	64
50	DMSO	--	3 % HMDS	0.5% Acetic Anhydride	25	300	89	87
51	DMSO	--	3 % HMDS	0.5% Phthalic anhydride	25	300	87	86
52	DMSO	--	3% N-methyl hexa-methyldisilazane	0.5% Phthalic	25	300	92	92
53	DMSO	--	1.5% Bis-(trimethylsilyl)sulfate	0.5% BTA	25	60	80	80
54	DMSO	--	3% Bis-(trimethylsilyl)sulfate	0.5% BTA	25	60	88	85
55	DMSO	--	4.5% Bis-(trimethylsilyl)sulfate	0.5% BTA	25	60	90	91
56	NMP	--	3 % HMDS	--	25	300	66	61
57	NMP	--	3 % HMDS	0.5% Acetic Anhydride	25	300	87	89
58	NMP	--	3 % HMDS	--	25	300	66	61
59	NMP	--	3 % HMDS	0.5% Phthalic anhydride	25	300	88	88
60	NMP	--	3% N-methyl hexa-methyldisilazane	0.5% BTA	25	300	89	91

Form. #	Solvent[1]	Co-solvent	Silane	Catalyst	T (°C)	Process time (s)	SiO_2 CA[2]	SiN CA[2]
61	NMP	--	3% N-methyl hexamethyldisilazane	0.5% Phthalic	25	300	93	89
62	Dipropylene glycol dimethyl ether	--	3% Tris-(trimethylsilyl)-phosphite	0.5 % Phthalic Anhydride	25	180	58	50
63	Dipropylene glycol dimethyl ether	--	3% Tris(trimethylsilyl)phosphite	--	25	180	24	20
64	Dipropylene glycol dimethyl ether	--	3 % Bis(dimethylamino)-dimethylsilane	--	25	180	79	81
65	Dipropylene glycol dimethyl ether	--	3% N-methyl hexamethyldisilazane	0.5% BTA	25	300	81	59
66	PGMEA[4]	--	3% HMDS	--	25	180	78	87
67	PGMEA	--	10 % HMDS	--	25	180	88	91
68	PGMEA	--	6 % HMDS	--	25	180	81	79
69	PGMEA	--	6 % HMDS	0.5% BTA	25	180	85	85
70	PGMEA	--	3 % Bis(dimethylamino)-dimethylsilane	0.5% BTA	25	60	89	86
71	PGME[5]	--	3 % HMDS	--	25	300	27	30
72	PGME	--	3 % HMDS	0.5% Phthalic anhydride	25	300	75	24
73	Isopropanol	--	3 % HMDS	--	25	300	48	41
74	Isopropanol	--	3 % HMDS	0.5% Phthalic anhydride	25	300	80	44
75	Glacial Acetic Acid	--	3 % Bis(dimethylamino)-dimethylsilane	--	25	180	72	72
76	Toluene	--	3 % HMDS	--	25	300	65	64
77	Toluene	--	3 % HMDS	0.5% Phthalic anhydride	25	300	83	69
78	Cyclohexanone	--	6 % HMDS	--	25	180	84	84
79	Cyclohexanone	--	6 % HMDS	0.5% BTA	25	180	80	84
80	Cyclohexanone	--	3 % Bis(dimethylamino)-dimethylsilane	0.5% BTA	25	60	81	54
81	Ethyl Lactate	--	6 % HMDS	--	25	180	81	77
82	Ethyl Lactate	--	6 % HMDS	0.5% BTA	25	180	75	72
83	Ethyl lactate	--	3 % Bis(dimethylamino)-dimethylsilane	0.5% BTA	25	60	61	65
84	1,3-dimethyl-2-imidizolidinone	--	3 % HMDS	--	25	180	57	72

Form. #	Solvent[1]	Co-solvent	Silane	Catalyst	T (ºC)	Process time (s)	SiO_2 CA[2]	SiN CA[2]
85	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone	--	3 % HMDS	--	25	180	50	50
86	Propylene carbonate	6% HMDSO[6]	3% HMDS	--	25	30	80.6	--
87	Xylene	6% HMDSO	3% HMDS	--	25	30	65.9	--
88	PGMEA	6% HMDSO	3% HMDS	--	25	30	57.2	--
89	Dimethyl carbonate	6% HMDSO	3% HMDS	--	25	30	57.0	--
90	Cyclohexanone	6% HMDSO	3% HMDS	--	25	30	71.0	--
91	Propylene carbonate	6% HMDSO	3.3% HMDSA[7]	--	25	30	78.8	--
92	Propylene carbonate	6% HMDSO	4.3% TMSDMA[8]	--	25	30	96.1	--
93	Propylene carbonate	6% HMDSO	5.4% BDADMS[9]	--	25	30	91.6	--
94	Xylene	6% HMDSO	0.6% TMSDMA	--	25	30	89.1	--
95	Xylene	6% HMDSO	2.2% TMSDMA	--	25	30	88.2	--
96	Propylene carbonate	10% Xylene	8% HMDS	--	25	30	95.4	--
97	Propylene carbonate	10% Mesitylene	8% HMDS	--	25	30	95.9	--
98	Xylene	6% Propylene carbonate	2% TMSDMA	--	25	30	91.3	--
99	Mesithylene	6% PGMEA	2% TMSDMA	--	25	30	90.9	--
100	HMDSO	10% Propylene carbonate	2% TMSDMA	--	25	30	93.8	--
101	HMDSO	10% PGMEA	2% TMSDMA	--	25	30	92.5	--

1 Solvent makes up the remainder of the formulation
2 “CA” refers to contact angle (degrees)
3 “HMDS” refers to hexamethyldisilazane
4 “PGMEA” refers to propylene glycol methyl ether acetate
5 “PGME” refers to propylene glycol methyl ether
6 “HMDSO” refers to hexamethyldisiloxane
7 “HMDSA” refers to heptamethyldisilazane
8 “TMSDMA” refers to N-(trimethylsilyl)dimethylamine
9 “BDADMS” refers to bis(dimethylamino)dimethylsilane

As shown in Table 1, a majority of formulas 1-101 containing an aprotic solvent and a Si-containing compound exhibited a contact angle close to 90º on a SiO_2 or SiN surface.

Example 2

Surface treatment solutions (i.e., formulations 102-115) were prepared by mixing the components at room temperature. The compositions of formulations 102-115 are summarized in Table 2 below. All percentages listed in Table 2 are weight percentages, unless indicated otherwise.

Patterned wafers were treated with formulations 102-115. High aspect ratio Si pillar patterned wafers were diced into 0.5 inch by 0.5 inch coupons. The coupons were then immersed into stirred 25°C surface treatment solutions for 30-180 seconds. The coupons were removed from the surface treatment solutions and rinsed in a beaker containing stirred 50°C isopropyl alcohol for 60 seconds. The coupons were then removed from the Isopropyl alcohol rinse and dried with a N_2 gas dispense gun oriented perpendicularly to the coupon at a working distance of 1 inch with gas pressure of 45 psi. The coupons were then analyzed by scanning electron microscopy over three randomly selected sites at a magnification of 50000x and the number of uncollapsed silicon pillars were tabulated. The average of uncollapsed Si-pillars at the three sites are reported in Table 2 as a percentage of the total Si pillars observed.

Table 2

Form. #	Solvent[1]	Co-solvent	Silane	T (°C)	Process time (s)	Uncollapsed Si Pillars
102	PGMEA	3% HMDSO	2.2% TMSDMA	25	30	94.6%
103	PGMEA	5% HMDSO	2.2% TMSDMA	25	30	99.6%
104	PGMEA	10% HMDSO	2.2% TMSDMA	25	30	99.5%
105	Dimethyl Carbonate	3% HMDSO	2.2% TMSDMA	25	30	96.8%
106	Dimethyl Carbonate	5% HMDSO	2.2% TMSDMA	25	30	98.8%
107	Dimethyl Carbonate	10% HMDSO	2.2% TMSDMA	25	30	98.4%
108	PGMEA	1.5% HMDSO	2.2% TMSDMA	25	30	97.8%
109	PGMEA	0.8% HMDSO	2.2% TMSDMA	25	30	76.8%
110	Xylene	1.5% HMDSO	2.2% TMSDMA	25	30	98.2%

Form. #	Solvent[1]	Co-solvent	Silane	T (ºC)	Process time (s)	Uncollapsed Si Pillars
111	Methyl ethyl ketone	1.5% HMDSO	2.2% TMSDMA	25	30	98.6%
112	N-butyl lactate	1.5% HMDSO	2.2% TMSDMA	25	30	97.5%
113	Acetone	47.8% HMDSO	2.2% TMSDMA	25	180	91.7%
114	Propylene Carbonate	10% Xylene	8% HMDS	25	30	99.5%
115	Propylene Carbonate	10% Mesithylene	8% HMDS	25	30	97.5%

1 Solvent makes up the remainder of the formulation

As shown in Table 2, upon treatment with formulations 102-115, a substantial portion of silicon pillars on patterned silicon wafers remained after a cleaning or drying process.

While the disclosure has been described in detail with reference to certain embodiments thereof, it is understood that modifications and variations are within the spirit and scope of that which is described and claimed.

WHAT IS CLAIMED IS:

1. A method for treating a semiconductor substrate having a pattern disposed on a surface of the substrate, comprising:

contacting the surface with a surface treatment composition, wherein the surface treatment composition comprises at least one aprotic solvent and at least one surface treatment agent, the at least one surface treatment agent comprises a Si-containing compound, and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees;

wherein the pattern comprises a feature having a dimension of at most about 20 nm.

2. The method of claim 1, wherein the surface comprises SiO_2, SiN, TiN, SiOC, SiON, Si, SiGe, Ge, or W.

3. The method of claim 1, wherein the at least one aprotic solvent is selected from the group consisting of carbonate solvents, lactones, ketones, aromatic hydrocarbons, siloxanes, glycol dialkyl ethers, glycol alkyl ether acetates, esters, ureas, lactams, dimethyl sulfoxide, and N-methyl pyrrolidone.

4. The method of claim 1, wherein the at least one aprotic solvent comprises a carbonate solvent.

5. The method of claim 4, wherein the carbonate solvent is propylene carbonate.

6. The method of claim 1, wherein the at least one aprotic solvent comprises a lactone.

7. The method of claim 6, wherein the lactone is gamma-butyrolactone.

8. The method of claim 1, wherein the at least one aprotic solvent Is from about 90 wt% to about 99.9 wt% of the surface treatment composition.

9. The method of claim 1, wherein the Si-containing compound is a disilazane.

10. The method of claim 9, wherein the disilazane is hexamethyldisilazane, heptamethyldisilazane, N-methyl hexamethyldisilazane, 1,3-diphenyltetramethyldisilazane, or 1,1,3,3-tetraphenyl-1,3-dimethyldisilazane.

11. The method of claim 1, wherein the Si-containing compound comprises a trimethylsilyl group.

12. The method of claim 11, wherein the Si-containing compound is N-(trimethylsilyl)dimethylamine, N-(trimethylsilyl)diethylamine, 4-trimethylsilyloxy-3-penten-2-one, bis-trimethylsilylsulfate, methoxytrimethylsilane, N-allyl-N,N-bis(trimethylsilyl)amine, N-(trimethylsilyl)diethylamine, N, N-bis-trimethylsilyl urea, or tris-trimethylsilylphosphite.

13. The method of claim 1, wherein the Si-containing compound is an aminosilane.

14. The method of claim 13, wherein the aminosilane is bis(dimethylamino)dimethylsilane or phenethyldimethyl(dimethylamino)silane.

15. The method of claim 1, wherein the at least one surface treatment agent Is from about 0.5 wt% to about 10 wt% of the surface treatment composition.

16. The method of claim 1, wherein the surface treatment composition further comprises a catalyst.

17. The method of claim 16, wherein the catalyst is benzotriazole, phthalic anhydride, acetic anhydride, methanesulfonic acid, sulfuric acid, or trifluoromethanesulfonic acid.

18. The method of claim 16, wherein the catalyst Is from about 0.1 wt% to about 1 wt% of the surface treatment composition.

19. The method of claim 1, wherein the surface treatment composition further comprises water, the water is at most about 2 wt% of the surface treatment composition.

20. The method of claim 1, wherein the surface treatment composition is substantially free of water.

21. The method of claim 1, wherein the surface treatment composition forms a surface treatment layer on a surface such that the surface has a water contact angle of at least about 65 degrees.

22. The method of claim 1, further comprising contacting the surface with at least one aqueous cleaning solution before contacting the surface with the surface treatment composition.

23. The method of claims 22, wherein the at least one aqueous cleaning solution comprise water, an alcohol, aqueous ammonium hydroxide, aqueous hydrochloric acid, aqueous hydrogen peroxide, an organic solvent, or a combination thereof.

24. The method of claim 22, further comprising contacting the surface with a first rinsing solution after contacting the surface with the at least one aqueous cleaning solution but before contacting the surface with the surface treatment composition.

25. The method of claim 1, further comprising contacting the surface with a second rinsing solution after contacting the surface with the surface treatment composition.

26. The method of claim 1, further comprising drying the surface.

27. The method of claim 1, further comprising removing the surface treatment layer.

28. A surface treatment composition, comprising:

at least one aprotic solvent, and

at least one surface treatment agent, the surface treatment agent being a Si-containing compound comprising a trimethylsilyl group, an aminosilyl group, or a disilazane group, provided that the disilazane group comprises no Si-H bond,

wherein the surface treatment composition forms a surface treatment layer on a surface such that the surface has a water contact angle of at least about 50 degrees.

29. The composition of claim 28, wherein the at least one aprotic solvent is selected from the group consisting of carbonate solvents, lactones, ketones, aromatic hydrocarbons, siloxanes, glycol dialkyl ethers, glycol alkyl ether acetates, esters, ureas, lactams, dimethyl sulfoxide, and N-methyl pyrrolidone.

30. The composition of claim 29, wherein the at least one aprotic solvent comprises a carbonate solvent.

31. The composition of claim 30, wherein the carbonate solvent is propylene carbonate.

32. The composition of claim 28, wherein the at least one aprotic solvent comprises a lactone.

33. The composition of claim 32, wherein the lactone is gamma-butyrolactone.

34. The composition of claim 28, wherein the at least one aprotic solvent is from about 90 wt% to about 99.9 wt% of the surface treatment composition.

35. The composition of claim 28, wherein the Si-containing compound is a disilazane.

36. The composition of claim 35, wherein the disilazane is hexamethyldisilazane, heptamethyldisilazane, N-methyl hexamethyldisilazane, 1,3-diphenyltetramethyldisilazane, or 1,1,3,3-tetraphenyl-1,3-dimethyldisilazane.

37. The composition of claim 28, wherein the Si-containing compound comprises a trimethylsilyl group.

38. The composition of claim 37, wherein the Si-containing compound is N-(trimethylsilyl)dimethylamine, N-(trimethylsilyl)diethylamine, 4-trimethylsilyloxy-3-penten-2-one, bis-trimethylsilylsulfate, methoxytrimethylsilane, N-allyl-N,N-bis(trimethylsilyl)amine, N-(trimethylsilyl)diethylamine, N, N-bis-trimethylsilyl urea, or tris-trimethylsilylphosphite.

39. The composition of claim 28, wherein the Si-containing compound is an aminosilane.

40. The composition of claim 39, wherein the aminosilane is bis-dimethylaminodimethylsilane or phenethyldimethyl(dimethylamino)silane.

41. The composition of claim 28, wherein the at least one surface treatment agent Is from about 0.5 wt% to about 10 wt% of the surface treatment composition.

42. The composition of claim 28, further comprising a catalyst.

43. The composition of claim 42, wherein the catalyst is benzotriazole, phthalic anhydride, acetic anhydride, methanesulfonic acid, sulfuric acid, or trifluoromethanesulfonic acid.

44. The composition of claim 42, wherein the catalyst Is from about 0.1 wt% to about 1 wt% of the surface treatment composition.

45. The composition of claim 28, wherein the surface treatment composition further comprises water, the water is at most about 2 wt% of the surface treatment composition.

46. The composition of claim 28, wherein the surface treatment composition is substantially free of water.

47. The composition of claim 28, wherein the surface treatment composition forms a surface treatment layer on a surface such that the surface has a water contact angle of at least about 65 degrees.

48. A surface treatment composition, comprising:

from about 90 wt% to about 99.5 wt% at least one aprotic solvent selected from the group consisting of lactones, ketones, aromatic hydrocarbons, siloxanes, glycol dialkyl ethers, glycol alkyl ether acetates, esters, ureas, lactams, dimethyl sulfoxide, and N-methyl pyrrolidone, and

from about 0.5 wt% to about 10 wt% at least one surface treatment agent, the surface treatment agent is a Si-containing compound comprising a trimethylsilyl group, an aminosilyl group, or a disilazane group, provided that the disilazane group comprises no Si-H bond.

49. The composition of claim 48, further comprising a catalyst or water.

50. A surface treatment composition, consisting of:
propylene carbonate,
hexamethyldisilazane, and
optionally, at least one co-solvent.

51. The composition of claim 50, wherein the hexamethyldisilazane is from about 0.5 wt% to about 10 wt% of the composition.

52. The composition of claim 50, wherein the at least one co-solvent comprises water, a siloxane, or an aromatic hydrocarbon.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/023697

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - G03F 7/42; C07C 311/48; C08L 83/14; G03F 7/075; G03F 7/40; H01L 21/3105 (2018.01)
CPC - G03F 7/422; C07C 311/48; C08L 83/14; G03F 7/0757; G03F 7/405; H01L 21/3105 (2018.05)

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)
See Search History document

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 practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2016/0291477 A1 (TOKYO OHKA KOGYO CO LTD) 06 October 2016 (06.10.2016) entire document	1-18, 20-27
Y	US 2014/0272706 A1 (FUJITSU LIMITED) 18 September 2014 (18.09.2014) entire document	1-18, 20-27
Y	US 2002/0037820 A1 (SMALL et al) 28 March 2002 (28.03.2002) entire document	5
Y	US 2008/0199977 A1 (WEIGEL et al) 21 August 2008 (21.08.2008) entire document	14
A	US 2010/0056409 A1 (WALKER et al) 04 March 2010 (04.03.2010) entire document	1-27

☐ 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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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 22 June 2018	Date of mailing of the international search report 06 JUL 2018
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/023697

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-27

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-27, are drawn to a method for treating a semiconductor.

Group II: claims 28-52, are drawn to a surface treatment composition.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, a method for treating a semiconductor, are not present in Group II; and the special technical features of Group II, a surface treatment composition, are not present in Group I.

The Groups I and II share the technical features of a surface treatment composition, comprising at least one aprotic solvent and at least one surface treatment agent, the at least one surface treatment agent comprises a Si-containing compound, and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees. However, these shared technical features do not represent a contribution over the prior art.

Specifically, US 2016/0291477 A1 Tokyo Ohka Kogyo Co Ltd teaches a surface treatment composition (Abstract, A surface treatment liquid), comprising at least one aprotic solvent and at least one surface treatment agent (Para. [0054] The surface treatment liquid of this embodiment preferably further contains a solvent. When the water repellent agent used is a silylating agent represented by the formula (s2), such as methoxytrimethylsilane, or a silylating agent represented by the formula (2), such as hexamethyldisilazane (HMDS); Para. [0058] Among these solvents, aprotonic solvents can satisfactorily maintain the activity of the water repellent agent), the at least one surface treatment agent comprises a Si-containing compound (Para. [0054] The surface treatment liquid of this embodiment preferably further contains a solvent. When the water repellent agent used is a silylating agent represented by the formula (s2), such as methoxytrimethylsilane, or a silylating agent represented by the formula (2), such as hexamethyldisilazane (HMDS)), and the surface treatment composition forms a surface treatment layer on the surface such that the surface has a water contact angle of at least about 50 degrees (Para. [0065] The time for the exposure of the substrate surface to the surface treatment liquid is preferably 1 to 60 seconds. The contact angle of water on the surface is preferably increased to 40° to 120°, more preferably to 60° to 100°, after the surface treatment).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.