Title of the Invention: Chemical-Mechanical Abrasive Composition and Method

Field of the Invention

The invention pertains to a chemical-mechanical abrasive composition and method. The chemical-mechanical abrasive composition is useful in polishing the surface of a semiconductor wafer.

Background and Object of the Invention

Chemical-mechanical polishing (CMP) is a planarization technique which was developed to address the problem associated with the difficulty in focusing during a photolithography process for producing integrated circuits due to the difference in the thickness of deposited films. The chemical-mechanical polishing technique was first applied to the production of the elements with a size in the order of 0.5 microns. With the reduction in the size of elements, the chemical-mechanical polishing technique was applicable to an increased number of layers. Until the elements were developed to be in the order of 0.25 microns, the chemical-mechanical polishing became an important and essential planarization technique. In general, the polishing method for producing a wire circuit comprises mounting a semiconductor wafer on a spinning platen equipped with an abrasive head and applying an abrasive slurry comprising abrasive particles and chemical additives to the surface of the wafer to enhance the abrasion performance. In fact, the CMP technique is the one which first modifies the surface to be polished by

changing the chemical properties of the surface and then removes the modified surface in a mechanically abrasive manner.

During polishing methods, different chemical-mechanical abrasive slurries should be used with reference to different designs and production processes for various IC patterns. With respect to the polishing of a dielectric layer, commonly known or commercialized abrasive slurries are normally adjusted to be in the basic pH range, i.e. from 10 to 11.5, so as to enhance the removal rate of the dielectric layer. Alternatively, using CeO_2 or Si_3N_4 particles to enhance the abrasion rate was previously taught. For example, EP 0 786 504 A2 discloses a polishing composition having a high selectivity for polishing silicon dioxide relative to silicon nitride, said composition comprising silicon nitride particles, water and an acid. U.S. Patent No. 5,759,917 discloses a chemical-mechanical polishing composition and method for polishing silicon dioxide and silicon nitride in the production of semiconductors and integrated circuits. The composition of U. S. Patent No. 5,759,917 has a high selectivity for polishing silicon dioxide relative to silicon nitride and comprises a salt, a soluble cerium, and a carboxylic acid, and has a pH ranging from 3 to 11. U.S. Patent No. 5,861,054 discloses a polishing composition for use in polishing silicon dioxide and silicon nitride with a high selectivity for silicon dioxide relative to silicon nitride, which composition comprises an acidic solvent and silicon nitride with a primary particle size in the range of from 0.01 to 1000 nm. U.S. Patent No. 5,891,205 discloses a chemical-mechanical polishing composition for polishing semiconductor devices, which composition comprises an alkaline aqueous dispersion that contains mixed particles of

cerium oxide and silicon dioxide. In yet another alternative, it has been previously taught to use harder Al_2O_3 abrasive particles to enhance the abrasion rate. For example, U.S. Pat. No. 5,084,071 discloses a method for polishing an electronic component substrate using of a chemical-mechanical polishing slurry, which polishing slurry comprises no more than 1 weight percent of alumina, abrasive particles (e.g. SiO_2, CeO_2, SiC, Si_3N_4, or Fe_2O_3 particles), a transition metal chelated salt (e.g. ammonium iron EDTA) for use as a polishing accelerator, and a solvent for said salt. U.S. Pat. No. 5,336,542 discloses a polishing composition comprising alumina abrasive particles and a chelating agent selected from the group consisting of polyaminocarboxylic acid (e.g. EDTA) and the sodium and potassium salts thereof. The composition of U.S. Pat. No. 5,336,542 may further comprise boehmite or an aluminum salt.

One object of the present invention is to provide a chemical-mechanical abrasive composition which can effectively enhance the removal rate of a dielectric layer in either an acidic or a basic medium. The materials which can be used as dielectrics include silicon dioxide, silicon nitride, borophosphosilicate glass (BPSG), and those having a low dielectric constant (low-k), and the composites thereof. It has been discovered that the chemical-mechanical abrasive composition of the present invention is also effective in polishing polysilicon.

In the polishing method for semiconductor devices, as shown in Figure 1, a chemical-mechanical polishing slurry should be used to planarize the silicon dioxide layer and stop at the silicon nitride layer. The removal rate of silicon

dioxide to silicon nitride should be at least greater than 3. Accordingly, another object of the present invention is to provide a chemical-mechanical abrasive composition for use in the polishing of semiconductor devices, which composition is able to provide a ratio of greater than 3 of the removal rate of silicon dioxide to that of silicon nitride.

As for the polishing of metals, for example, in the copper processes for producing semiconductors, the polishing method should involve several steps. In the first step, as shown in Figure 2(a), an abrasive slurry is used to polish the copper film of a semiconductor and stops at the tantalum nitride (TaN) layer, wherein the ratio of the removal rate of the copper film to that of the tantalum nitride layer should be at least greater than 3. In the second step, as shown in Figure 2(b), another abrasive slurry is used to polish the tantalum nitride layer and the copper film of the semiconductor and stops at a dielectric layer, wherein the ratio of the removal rate of the tantalum nitride layer to that of the copper film should be at least greater than 1. Since in the first and second steps, the copper film may be subjected to a dishing phenomenon, a third step of over-polishing, as shown in Figure 2(c), may be needed. The third abrasive slurry used in the third step should achieve a removal rate of the dielectric layer that is greater than or the same as that of the copper film and tantalum nitride layer. The polishing technology for metals has been disclosed in prior patents. For example, U.S. Pat. No. 5,114,437 discloses a polishing composition for an aluminum substrate, said composition comprising an alumina polishing agent having an average particle size of 0.2 to 5 μm, and a polishing accelerator selected from the group consisting of chromium(III)

nitrate, lanthanum nitrate, ammonium cerium(III) nitrate, and neodymium nitrate. U.S. Pat. No. 5,209,816 discloses a method for polishing an Al- or Ti-containing metal layer with a chemical-mechanical abrasive slurry. The abrasive slurry contains, in addition to a solid abrasive material, about 0.1-20% by volume of H_3PO_4 and about 1-30% by volume of H_2O_2. U.S. Pat. No. 5,225,034 discloses a chemical-mechanical abrasive slurry, which comprises $AgNO_3$, solid abrasive particles, and an oxidant selected from H_2O_2, HOCl, KOCl, $KMgO_4$, or CH_3COOOH. The slurry is used for polishing the copper layer on a semiconductor wafer so as to produce copper wires on the wafer. U.S. Pat. No. 5,340,370 discloses a chemical-mechanical polishing slurry for tungsten or tungsten nitride film, which comprises an oxidizing agent such as potassium ferricyanide, an abrasive, and water, and has a pH range between 2 and 4. U.S. Pat. No. 5,516,346 discloses a slurry for chemical mechanically polishing a titanium film, said slurry comprising potassium fluoride in a concentration sufficient to complex with said titanium film, and an abrasive such as silica, and having a pH level less than 8.

Yet another object of the present invention is to provide a chemical-mechanical abrasive composition which can effectively improve the removal rate of metals. Depending on different IC pattern designs and different semiconductor processes, the chemical-mechanical composition of the invention can provide the same or different abrasion selectivities to the metal wires and dielectric layers in integrated circuits.

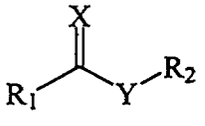
Brief Description of Drawings

Figure 1 schematically shows the planarization of SiO_2 in a semiconductor process.

Figure 2 schematically shows the polishing steps used in a copper process for producing semiconductors.

Summary of the Invention

The invention provides a chemical-mechanical abrasive composition for use in semiconductor processing, which comprises an aqueous medium, an abrasive, and an abrasion accelerator. The abrasion accelerator mainly functions to enhance the removal rate of the substances to be removed, and is selected from the compounds of the following formula, the acid-addition salts thereof, or mixtures of two or more of the foregoing compounds and salts:



wherein X and Y are independently lone-pair electrons containing atoms or atomic groups; and R_1 and R_2 are independently H, alkyl, amino, aminoalkyl, or alkoxy. The chemical-mechanical abrasive composition of the invention may optionally comprise an acidic component and/or the salt thereof, so as to further enhance the abrasion rate.

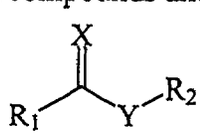
The invention further provides a method of using the above chemical-mechanical abrasive composition for polishing the surface of a semiconductor wafer.

Detailed Description of the Invention

The invention relates to a chemical-mechanical abrasive composition for effectively polishing the surface of a semiconductor wafer, said composition comprising an aqueous medium, an abrasive, and an abrasion accelerator. The abrasive composition of the invention may comprise from 0.1 to 30% by weight, and preferably from 3 to 25% by weight of the abrasive, and from 0.01 to 5 % by weight, and preferably 0.03 to 2% by weight of the abrasion accelerator.

In IC processing, the entire planarization of a wafer surface is accomplished by chemical-mechanical abrasion. During the chemical-mechanical abrasion, the substances removed from the wafer surface may re-bond to the wafer surface and be deposited on the wafer surface. This will not only reduce the abrasion rate and the planarization extent, but also cause defects to form on the wafer surface. Consequently, there is a need for compounds with a chelation ability to facilitate the removal of the substances to be removed from the wafer surface, so as to avoid the re-bonding of these substances to the wafer surface. The present invention provides an abrasion accelerator with a better chelation property.

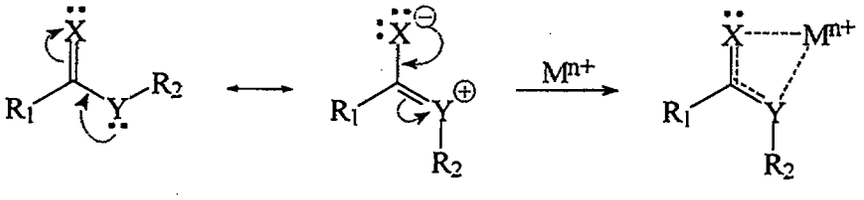
The abrasion accelerator of the invention is selected from the compounds of the following formula, the acid-addition salts thereof, and mixtures of two or more of the foregoing compounds and salts:



wherein X and Y are independently lone-pair electrons containing atoms or atomic groups, such as oxygen atoms, sulfur atoms, or the NH groups; and R_1

and R_2 are independently H, C_1-C_6alkyl, amino, aminoC_1-C_6alkyl, or C_1-C_6alkoxy.

The mechanism involved by the abrasion accelerator compounds of the invention to chelate the atoms or atomic groups of substances, thereby removing said substances, is believed to be as follows:



wherein M is an atom or atomic group of the substances to be removed, and n is the valence charge of M.

It was surprisingly found that the abrasive composition of the invention can enhance the abrasion rate no matter whether the abrasion is conducted in an acidic, neutral, or basic condition.

The abrasive used in the abrasive composition of the invention can be any commercially available abrasive, such as SiO_2, Al_2O_3, ZrO_2, CeO_2, SiC, Fe_2O_3, TiO_2, Si_3N_4, or a mixture thereof. These abrasives normally have the advantages of high purity, high surface area, and narrow particle size distribution, and are thus suitable for use in abrasive compositions as abrasive particles.

When applied to different processes, the chemical-mechanical abrasive composition of the invention can be formulated to have a desired constitution by altering the species and concentration of the abrasion accelerator or the

amount of the abrasive particles. The abrasion accelerators which are suitable for use in the invention may include, for example, methyl glycinate, glycinamide, aminoguanidine, semicarbazide, guanidine, urea, formamidine, acetamidine, formamide, acetamide, formyl hydrazide, acethydrazide, ethyl glycinate, methyl carbazate, ethyl carbazate, methyl carbamate, or ethyl carbamate, or an acid-addition salt thereof, such as the hydrochloride, nitrate, carbonate, or sulfate salt thereof, or a derivative with a similar structure thereof, or a mixture of two or more of the foregoing compounds. Preferably, the abrasion accelerator is selected from the group consisting of methyl glycinate hydrochloride, glycinamide hydrochloride, aminoguanidine carbonate, semicarbazide hydrochloride, guanidine carbonate, and a mixture thereof.

The chemical-mechanical abrasive composition of the invention may optionally comprise from 0.001 to 2% by weight of an acidic component and/or the salt thereof to further enhance the abrasion rate. The acidic component, which may be used in the present invention, could be any commercially available acid, such as nitric acid, hydrogen chloride, carbonic acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, chloric acid, bromic acid, iodic acid, perchloric acid, perbromic acid, periodic acid, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, malonic acid, succinic acid, glutaric acid, dipic acid, glycolic acid, lactic acid, citric acid, malic acid, tartaric acid, oxalic acid, glycine, creatine, dimethylglycine, or alanine, or a mixture thereof. For example, the composition of the invention may comprise ammonium carbonate to further

enhance the abrasion rate.

The chemical-mechanical abrasive composition of the present invention may use water as a medium. In the preparation of the abrasive composition, water, and preferably conventional deionized water, may be used to make the abrasive composition to be in the form of a slurry.

The chemical mechanical abrasive composition of the present invention may further comprise other ingredients which are conventionally used in chemical mechanical abrasive compositions, only if they do not cause any adverse effect on the abrasive composition of the present invention. Therefore, the chemical-mechanical abrasive composition of the present invention may optionally comprise 0.1 to 10%, preferably 0.1 to 5% and more preferably 1 to 3% by weight of an oxidant conventionally used in the art, such as H_2O_2, $Fe(NO_3)_3$, KIO_3, CH_3COOOH, or $KMnO_4$.

The present invention will be further described by, but not limited to, the following examples. Any modifications or changes with reference to the present invention, which can be easily accomplished by persons skilled in the art, are to be encompassed in the scope of the present invention.

Examples

Abrasion Test

A. Species of wafer for abrasion test:

Species of film	Formation of film	Deposition thickness (Å)
TEOS	Chemical vapor deposition	8000

SiO_2	Thermal oxidation	8000
Si_3N_4	Chemical vapor deposition	3000
W	Chemical vapor deposition	8000
TaN	Chemical vapor deposition	5000
Cu	Chemical vapor deposition	8000
TiN	Chemical vapor deposition	5000

B. Abrasion platen: IPEC/Westech 472

C. Temperature: 25℃

D. Pad type: IC 1400 manufactured by Rodel Company

E. Flow rate of slurry: 150 ml/min

Abrasion Test Procedure

The thickness of a dielectric layer can be directly determined by an optical method. The present invention used Model SM 300, manufactured by KLA-Tencor Company, to determine the thickness of a dielectric layer. The thickness of a metal layer is determined by using Model RS 75, manufactured by KLA-Tencor Company.

Both before and after an abrasion test, the thickness of a film should be measured by a thickness measuring means. The sheet resistivity of a metal film is measured by a 4-point probe. The thickness of the film is determined by the following equation:

$$T \times R = \text{resistivity coefficient}$$

wherein T represents film thickness (Å), and R represents sheet resistivity

(Ω/cm^2). For various metal films, the resistivity coefficient will be a constant.

The abrasion rate is determined as follows:

A metal film thickness T_1 is first determined by the above apparatus of Model RS75. The film is polished by an exemplified slurry illustrated in the following examples for 1 minute. Thereafter, the wafer is cleaned by Evergreen Model 10X, commercially available from the Solid State Equipment Corporation. After spray-drying the wafer, a metal film thickness T_2 is measured by the apparatus of Model RS75. The abrasion rate of the metal film is represented by $T_1 - T_2$.

Example 1

Chemical-mechanical abrasive slurries respectively containing methyl glycinate hydrochloride, glycinamide hydrochloride, and aminoguanidine carbonate were prepared. The resultant slurries were used to polish TEOS film under the following conditions:

Pressure: 5 psi

Spindle speed: 60 rpm

Platen speed: 50 rpm

The results of the abrasion test for the resultant slurries are listed in Table 1.

Table 1

Run	Abrasive	Solid content (wt.%)	Abrasion accelerator /Amount (wt.%)	pH	TEOS removal rate (Å/min)
1	Silica gel	18	Methyl glycinate hydrochloride/0.2	2.5	2838
2	Silica gel	18	Methyl glycinate hydrochloride/0.2	7	2462
3	Silica gel	18	Glycinamide hydrochloride/0.2	4.5	2641
4	Silica gel	28	Aminoguanidine carbonate/0.2	10.8	3537
5	Silica gel	20	Aminoguanidine carbonate/0.2	10.5	2908
6	Silica gel	15	Aminoguanidine carbonate/0.2	10.4	2078

The above results reveal that the chemical-mechanical compositions of the present invention can enhance the abrasion rate in conditions with acidic to basic pH values

Example 2

Chemical-mechanical abrasive slurries respectively containing semicarbazide hydrochloride, aminoguanidine carbonate, and guanidine carbonate were prepared. The resultant slurries were used to polish SiO_2 film under the following conditions:

Pressure: 5 psi

Spindle speed: 70 rpm

Platen speed: 50 rpm

The results of the abrasion test for the resultant slurries are listed in Table 2.

Table 2

Run	Abrasive	Solid content (wt.%)	Abrasion accelerator/Amount (wt.%)	pH	TEOS removal rate (Å/min)
1	Fumed silica	10	Semicarbazide hydrochloride/0.2	10	1858
2	Fumed silica	10	Aminoguanidine carbonate/0.2	10	1523
3	Fumed silica	10	Guanidine carbonate/0.2	10	1405

Example 3

Chemical-mechanical abrasive slurries respectively containing aminoguanidine carbonate, semicarbazide hydrochloride, and guanidine carbonate were prepared. The resultant slurries were used to polish TEOS and silicon nitride films under the following conditions:

Pressure: 5 psi

Spindle speed: 70 rpm

Platen speed: 50 rpm

The results of the abrasion test for the resultant slurries are listed in Table 3.

Table 3

Run	Abrasive	Solid content (wt.%)	Abrasion accelerator/ Amount (wt.%)	pH	TEOS removal rate (Å/min)	Si_3N_4 removal rate (Å/min)	TEOS removal rate/Si_3N_4 removal rate
1	Fumed silica	15	Aminoguanidine carbonate/0.2	10	2548	785	3.2
2	Fumed silica	10	Aminoguanidine carbonate/0.5 Ammonium carbonate*/0.25	10	1811	513	3.5
3	Fumed silica	15	Semicarbazide hydrochloride/0.2	10	2801	732	3.8
4	Fumed silica	10	Semicarbazide hydrochloride/0.2	10	1858	557	3.3
5	Fumed silica	10	Semicarbazide hydrochloride/0.5 Ammonium carbonate/0.25	10	2220	518	4.3
6	Fumed silica	15	Guanidine carbonate/0.2	10	1405	432	3.3
7	Fumed silica	10	Guanidine carbonate0.2	10	2542	774	3.3

*Ammonium carbonate is added to further enhance the removal rate.

The above results show that the abrasive compositions of the present invention achieve desired removal rate of TEOS relative to that of silicon nitride, and thus achieve desired abrasion selectivities.

Example 4

Chemical-mechanical abrasive slurries respectively containing semicarbazide hydrochloride, aminoguanidine carbonate, and guanidine carbonate, and having a pH value ranging from 3.8 to 4.6 were prepared. The resultant slurries were used to polish copper, tantalum nitride, and TEOS films

under the following conditions:

Pressure: 4 psi

Back pressure: 0.5 psi

Spindle speed: 55 rpm

Platen speed: 50 rpm

The results of the abrasion test for the resultant slurries are listed in Table 4.

Table 4

Run	Abrasive	Solid content (wt.%)	Abrasion Accelerator/ Amount (wt.%)	Oxidant/ Amount (wt.%)	Cu removal rate (Å/min)	TaN removal rate (Å/min)	TEOS removal rate (Å/min)
1	Silica gel	15	Semicarbazide hydrochloride/0.2	H_2O_2/3	3729	802	1698
2	Silica gel	10	Semicarbazide hydrochloride/0.2	H_2O_2/3	4097	469	1278
3	Silica gel	15	Aminoguanidine carbonate/0.2	H_2O_2/3	416	1505	1495
4	Silica gel	10	Aminoguanidine carbonate/0.2	H_2O_2/3	289	807	1039
5	Silica gel	15	Guanidine carbonate/0.2	H_2O_2/3	266	1631	1597
6	Silica gel	10	Guanidine carbonate/0.2	H_2O_2/3	377	1413	1164

The abrasive compositions illustrated in Example 4 can be used in semiconductor abrasion processing to produce a pattern as shown in Figure 2. For example, the abrasive compositions of Run 1 and Run 2 can be used in the first step; the abrasive composition of Run 3 can be used in the second step; and the abrasive compositions of Run 4 to Run 6 can be used in the third step.

Example 5

Chemical-mechanical abrasive slurries respectively containing semicarbazide hydrochloride, aminoguanidine carbonate, and guanidine carbonate, and having a pH value ranging from 3.8 to 4.6 were prepared. The resultant slurries were used to polish tungsten, titanium nitride, and silicon dioxide films under the following conditions:

Pressure: 5 psi

Spindle speed: 70 rpm

Platen speed: 50 rpm

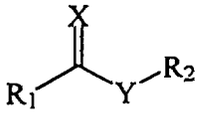
The results of the abrasion test for the resultant slurries are listed in Table 5.

Table 5

Run	Abrasive	Solid content (wt.%)	Abrasion accelerator/ Amount (wt.%)	Oxidant/ Amount (wt.%)	W metal removal rate (Å/min)	TiN removal rate (Å/min)	SiO_2 removal rate (Å/min)
1	Silica gel	10	Aminoguanidine carbonate/0.2	H_2O_2/3	2585	4402	1059
2	Silica gel	10	Guanidine carbonate/0.2	H_2O_2/3	1238	3913	1156
3	Silica gel	10	Guanidine carbonate/0.2	H_2O_2/1.5	542	5298	960
4	Silica gel	15	Guanidine carbonate/0.2	H_2O_2/0.5	472	3914	1861
5	Silica gel	10	Guanidine carbonate/0.2	H_2O_2/0.5	331	3956	1342
6	Silica gel	10	Semicarbazide hydrochloride/ 0.2	H_2O_2/1.5	457	5309	1042

We Claim:

1. A chemical-mechanical abrasive composition comprising an aqueous medium, an abrasive, and an abrasion accelerator, said abrasion accelerator being selected from the compounds of the following formula, the acid-addition salts thereof, or mixtures of two or more of the foregoing compounds and salts:



wherein X and Y are independently lone-pair electrons containing atoms or atomic groups; and R_1 and R_2 are independently H, C_1-C_6alkyl, amino, aminoC_1-C_6alkyl, or C_1-C_6alkoxy.

2. The composition according to Claim 1 wherein the X and Y are independently selected from O, S, and NH.

3. The composition according to Claim 1 wherein the abrasive is selected from SiO_2, Al_2O_3, ZrO_2, CeO_2, SiC, Fe_2O_3, TiO_2, Si_3N_4, or a mixture thereof.

4. The composition according to Claim 1 comprising 0.1-30% by weight of said abrasive.

5. The composition according to Claim 4 comprising 3-25% by weight of said abrasive.

6. The composition according to Claim 1 comprising 0.01-5% by weight of said abrasion accelerator.

7. The composition according to Claim 6 comprising 0.03-2% by weight of said abrasion accelerator.

8. The composition according to Claim 1 wherein said abrasion accelerator is selected from methyl glycinate, glycinamide, aminoguanidine, semicarbazide, guanidine, urea, formamidine, acetamidine, formamide, acetamide, formyl hydrazide, acethydrazide, ethyl glycinate, methyl carbazate, ethyl carbazate, methyl carbamate, or ethyl carbamate, or an acid-addition salt thereof, or a derivative with a similar structure thereof, or a mixture of two or more of the foregoing compounds.

9. The composition according to Claim 8 wherein said abrasion accelerator is selected from the group consisting of methyl glycinate hydrochloride, glycinamide hydrochloride, aminoguanidine carbonate, semicarbazide hydrochloride, guanidine carbonate, and a mixture thereof.

10. The composition according to Claim 1 further comprising an acidic component and/or a salt thereof.

11. The composition according to Claim 10, wherein said acidic component is selected from the group consisting of nitric acid, hydrogen chloride, carbonic acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, chloric acid, bromic acid, iodic acid, perchloric acid, perbromic acid, periodic acid, formic acid, acetic acid, propionic acid, butyric acid, valeric

acid, hexanoic acid, malonic acid, succinic acid, glutaric acid, dipic acid, glycolic acid, lactic acid, citric acid, malic acid, tartaric acid, oxalic acid, glycine, creatine, dimethylglycine, alanine, and a mixture thereof.

12. The composition according to Claim 10 wherein the salt is ammonium carbonate.

13. The composition according to Claim 1 further comprising an oxidant.

14. A method for polishing the surface of a semiconductor wafer comprising applying a chemical-mechanical abrasive composition as defined in any of Claims 1 to 13 to the surface of the semiconductor wafer.

