

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 July 2003 (24.07.2003)

PCT

(10) International Publication Number
WO 03/060045 A1

- (51) International Patent Classification⁷: C11D 1/62, C23G 1/00, 1/02, C03C 23/00, B08B 3/00, 3/12, 6/00
- (21) International Application Number: PCT/US03/00291
- (22) International Filing Date: 6 January 2003 (06.01.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/042,612 9 January 2002 (09.01.2002) US
- (71) Applicant: ASHLAND INC. [US/US]; P.O. Box 2219, Columbus, OH 43216 (US).
- (72) Inventors: EGBE, Matthew, I.; 122 Flannery Drive, West Norriton, PA 19403 (US). PETERS, Darryl, W.; 111 Kennedy Mill Road, Stewartsville, NJ 08886 (US).
- (74) Agents: CONNAUGHTON, Martin; Ashland Inc., P.O. Box 219, Columbus, OH 43216 et al. (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 03/060045 A1

(54) Title: AQUEOUS STRIPPING AND CLEANING COMPOSITION

(57) Abstract: The present invention relates to aqueous compositions used to remove post etch organic and inorganic residue as well polymeric residues and contaminants from semiconductor substrates. The compositions are comprised of a water soluble organic solvent, a sulfonic acid and water.

Aqueous Stripping And Cleaning Composition

Cross-reference to related applications: not applicable

- 5 Statement regarding federally funded sponsored research or development: not applicable

Background of the invention

10 In the manufacture of semiconductors or semiconductor microcircuits it is necessary to remove materials from the surface of the substrate of the semiconductor device. In some instances the materials to be removed are polymeric compositions referred to as photoresists. In other instances the materials to be removed are residues of etching or ashing processes or simply
15 contaminants. The purpose of stripping and/or cleaning compositions is to remove unwanted materials from a semiconductor substrate without corroding, dissolving or dulling the exposed surface of the substrate.

The art contains numerous references to compositions of different types for use in stripping photoresist and/or cleaning etch residue, ash or other contaminants
20 from semiconductor substrates. For example a series of patents issued to Allied Signal disclose nonaqueous organic stripping compositions comprising one or more organic sulfonic acids in conjunction with organic solvents and various improvements. The first patent in the series U.S. 4,165,295 discloses a composition for removing polymeric organic substances such as photoresist
25 comprising one or more organic, sulfonic acids one or more organic solvents, optionally a phenol and from about 5 to 250 ppm of a fluoride ion. The second patent U.S. 4,215,005 provides an improvement in the composition where in the fluoride is present in conjunction with a complexing agent having a nitrogen with an available unshared electron pair. The third patent in the series U.S.
30 4,221,674 provides another improvement in the composition where between 0.01 to 5 weight % of a nitrile compound is added to the composition. The fourth patent in the series U.S. 4,242,218 comprises a phenol free stripping composition comprising a sulfonic acid in admixture with chlorinated aryl

compounds, alkylaryl compounds having 1-14 alkyl carbon atoms an isoparaffinic hydrocarbon or mixtures thereof.

U.S. 5,308,745 discloses alkaline containing photoresist stripping compositions having reduced metal corrosion containing non-nitrogen containing weak acids having a pK in an aqueous solution of 2.0 or higher and an equivalent weight of less than about 140. The weak acids are employed in an amount that will neutralize from 19% to 75% of the amine present in the composition. U.S. 5,972,862 discloses a cleaning liquid for semiconductor devices comprising a fluoride containing compound, a water soluble organic solvent, inorganic or organic acids and optionally a quaternary ammonium salt or carboxylic acid ammonium salt and/or organic carboxylic acid amine salt. U.S. 6,231,677 discloses the use of one or more carboxylic acids in stripping compositions. WO 00/02238 discloses a cleaning chemistry based on a choline compound such as choline hydroxide. The compositions are comprised of a choline compound, water and an organic solvent. The compositions may in addition contain hydroxyl amine and a corrosion inhibitor.

Brief summary of the invention

The invention relates to aqueous compositions used to remove photoresist, etch and ash residue and contaminants from semiconductor substrates. The aqueous compositions have a low surface tension, low viscosity and are compatible with various substrates including Al/Cu, Cu, Ti, W, Ta, TiN, W, TaN, low-k materials such as methylsilsesquioxane (MSQ), black diamond, SiLK and high-k materials such as Pt/BST/oxide. BST is barium-strontium-tantate. The compositions contain a water soluble organic solvent, a sulfonic acid, water and optionally corrosion inhibitors. The compositions of the invention are free of fluoride containing compounds and inorganic amines.

Brief description of the several views of the drawings: not applicable

Detailed description of the invention

The invention relates to aqueous compositions used to remove photoresist, etch and ash residue and contaminants from semiconductor substrates. The compositions are comprised of a water soluble organic solvent that is soluble in water, a sulfonic acid or its corresponding salt, water and optionally a corrosion inhibitor.

The water soluble organic solvent includes organic amines, amides, sulfoxides, sulfones, lactams, imidazolidinones, lactones, polyhydric alcohols and the like. Examples of organic amines include monoethanolamine, N-methylethanolamine, ethylenediamine, 2-(2-aminoethylamino)ethanol, diethanolamine, dipropylamine, 2-ethylaminoethanol, dimethylaminoethanol, cyclohexylamine, benzylamine, pyrrole, pyrrolidine, pyridine, morpholine, piperidine, oxazole and the like. Examples of amides includes N,N-dimethylformamide, dimethylacetamide, diethylacetamide and the like. Examples of sulfoxides include dimethyl sulfoxide. Examples of sulfones include dimethyl sulfone and diethyl sulfone. Examples of lactams includes N-methyl-2-pyrrolidone and imidazolidinone. Examples of lactones includes butyrolactone and valerolactone. Examples of polyhydric alcohols includes ethylene glycol, propylene glycol, ethylene glycol monomethyl ether acetate, etc. Examples of preferred water soluble organic solvents includes monoethanolamine, N-methylethanolamine, dimethylsulfoxide and dimethylacetamide. The water soluble organic solvent can be present as a single compound or mixture of compounds. The water soluble organic solvent is present in the composition in amounts of from 30 to 90 weight %, preferably from 40 to 85 weight %, most preferably from 45 to 80 weight % based on the total weight of the composition.

In addition to the water soluble organic solvent, the compositions also contain a sulfonic acid or its corresponding salts. Examples of suitable sulfonic acids include p-toluenesulfonic acid, 1,5-naphthalenedisulfonic acid, 4-ethylbenzenesulfonic acid, dodecylbenzenesulfonic acid, cumensulfonic acid, methylethylbenzenesulfonic acid, isomers of xylenesulfonic acid and the corresponding salts of the sulfonic acids listed above. Examples of salts of sulfonic acids includes ethanolammonium p-toluenesulfonate and triethanolammonium p-toluenesulfonate. The sulfonic acid or its corresponding

salts can be present in the compositions as a single acid or salt, or mixture of sulfonic acids or corresponding salts. The sulfonic acid or corresponding salt is present in amounts of from 1 to 20 wt%, preferably from 1.5 to 15 wt%, most preferably 3 to 10 wt% based on the total weight of the composition.

5 Water is a necessary component of the stripping and cleaning compositions of the present invention. Water is present in amounts from 5 to 50 wt%, preferably 5 to 35 wt%, most preferably from 10 to 30 wt% based on the total weight of the composition.

Optionally, the stripping and cleaning compositions contain a corrosion
10 inhibitor. A single corrosion inhibitor compound or mixture of corrosion inhibitors can be used in the stripping and cleaning compositions. Examples of corrosion inhibitors includes benzotriazole, benzoic acid, malonic acid, gallic acid, catechol, ammonium malonate, and the like. The corrosion inhibitor is present in the stripping and cleaning compositions in amounts up to 20 wt%,
15 preferrably from 0.1 to 15 wt%, based on the total weight of the stripping and cleaning composition.

Other commonly known components such as dyes, biocides etc. can be included in the stripper and cleaner compositions in amounts up to a total of 5 wt% based on the total weight of the composition.

20 The stripper and cleaner compositions of the present invention are typically prepared by mixing the components together in a vessel at room temperature until all solids have dissolved. Examples of the aqueous stripper and cleaner compositions of the present invention are set forth in Table I.

Table I

Compound/ Formulation #	1	2	3	4	5	6	7	8	9	10	11	12	13
MEA	70.0	71.0	70.0	-	70.0	70.0	70.0	72.0	-	-	71.0	73.5	72.0
NMEA	-	-	-	70.0	-	-	-	-	-	-	-	-	-
DMSO	-	-	-	-	-	-	-	-	71.0	-	-	-	-
DMAc	-	-	-	-	-	-	-	-	-	71.0	-	-	-
ToSA	7.0	7.0	7.0	-	7.0	7.0	7.0	7.0	7.0	7.0	-	7.0	-
NDSA	-	-	-	5.0	-	-	-	-	-	-	-	-	-
EBSA	-	-	-	-	-	-	-	-	-	-	7.0	-	-
DBSA	-	-	-	-	-	-	-	-	-	-	-	-	5.0
Deionized Water	20.5	19.5	19.5	23.0	22.0	21.5	21.0	19.0	19.5	19.5	19.5	19.5	20.5
Gallic Acid	1.5	1.5	1.5	1.0	-	0.5	1.0	1.0	1.5	1.5	1.5	-	1.5
Benzo- triazole	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	-	1.0

MEA = monoethanolamine
 NMEA = N-methylethanolamine
 DMSO = dimethylsulfoxide
 DMAc = dimethylacetamide
 ToSA = p-toluene sulfonic acid
 NDSA = 1,5-Naphthalenedisulfonic acid
 EBSA = 4-ethylbenzene sulfonic acid
 DBSA = Dodecylbenzene sulfonic acid

5

The aqueous stripping and cleaning compositions are used to remove post etch and ash, organic and inorganic residues as well as polymeric residues from semiconductor substrates at low temperatures with low corrosion. In general, the stripping and cleaning processes using the compositions of the invention are carried out by immersing a substrate in the stripper/cleaner composition at a temperature of from 25°C to 85°C for a period of from 3 minutes to 1 hour. However, the compositions of the present invention can be used in any method known in the art that utilizes a liquid for removal of photoresist, ash or etch residues and/or contaminants.

Following are nonlimiting examples of the uses of the compositions of the invention.

Example 1

A positive photoresist was spin-coated on to a substrate of chemical-vapor-deposited Al-Cu film on silicon wafer. The positive photoresist consisted of diazonaphthoquinone and novolak resin. The photoresist coating was baked at 90 °C for 90 seconds. A pattern was defined on the photoresist by exposure, through a patterned mask, to i-line (365 nm) rays followed by development. The patterned wafer was plasma etched with Cl₂/BCl₃ etch gas mixture for 168 seconds at 5 torr of pressure and 20 °C. The etched pattern was subjected to oxygen plasma ash for 55 seconds at 0.3 torr pressure and 65 °C. The patterned and ashed wafer was treated by immersing the wafer in a bath containing formulation 3 from table 1 for 30 minutes at 65 °C. Analysis of the cleaned wafer was done by inspection of SEM pictures of the wafers. The SEM photographs showed that the wafer was clean and free of residue and there was no evidence of corrosion.

Example 2

A TEOS (tetraethoxysilicate) was coated on a TiN antireflective coating (ARC) layer which in turn was coated on Al-Cu layer which was chemically deposited on a silicon wafer. A positive photoresist layer was spin-coated on the TEOS layer. The photoresist coated was baked at 90 °C for 90 seconds. A pattern was defined on the photoresist by exposure to i-line rays through a patterned

mask followed by development. A two step plasma process was used to transfer the pattern from the resist to the substrate. The first step involved the subjecting the wafer to CO/CF₄/Ar/CHF₃ plasma etch gas mixture for the TEOS layer and in-situ followed immediately by Ar/CF₄/O₂ for the TiN ARC layer. The etched pattern was ashed with oxygen plasma for 150 seconds at 0.3 torr pressure and 60 °C. The etched and ashed wafer was treated by immersing the wafer in a bath containing formulation 3 for 30 minutes at 65 °C. Analysis of the cleaned wafer was done by inspecting a SEM picture of the wafer. The SEM showed that the wafer was clean and free of residue and there was no evidence of corrosion.

We claim:

1. A composition, comprising;
 - A) a water soluble organic solvent,
 - 5 B) a sulfonic acid or its corresponding salt, and
 - C) water.
2. The composition as claimed in claim 1, further comprising a corrosion inhibitor.
3. The composition as claimed in claim 1, wherein the water soluble
10 organic solvent is monoethanolamine, N-methylethanolamine, dimethylsulfoxide, dimethylacetamide or mixtures thereof.
4. The composition as claimed in claim 1, wherein the sulfonic acid or its corresponding salt is p-toluene sulfonic acid, 1,5-naphthalene disulfonic acid, 4-ethylbenzene sulfonic acid, dodecylbenzene sulfonic acid or mixtures thereof.
- 15 5. The composition as claimed in claim 2, wherein the corrosion inhibitor is gallic acid, catechol, benzotriazole, benzoic acid, malonic acid, ammonium malonate or mixtures thereof.
6. A composition, comprising;
 - A) from 30 to 85 wt % of a water soluble organic solvent,
 - 20 B) from 1 to 20 wt % of a sulfonic acid or its corresponding salt,
 - C) from 5 to 50 wt % water.
7. The composition as claimed in claim 6, further comprising; from 0.1 to 15 wt % of a corrosion inhibitor.
8. A method of removing photoresist, etch and/or ash residue, or
25 contaminants from a semiconductor substrate, comprising; contacting the semiconductor substrate with a composition, comprising:
 - A) a water soluble organic solvent,
 - B) a sulfonic acid or its corresponding salt, and
 - C) water;
- 30 for a period of time sufficient to remove the photoresist, etch and/or ash residue, or contaminants.
9. The method as claimed in claim 8, wherein the composition further comprises a corrosion inhibitor.

10. The method as claimed in claim 8, wherein the water soluble organic solvent is monoethanolamine, N-methylethanolamine, dimethylsulfoxide, dimethylacetamide or mixtures thereof.
11. The method as claimed in claim 8, wherein the sulfonic acid or its
5 corresponding salt is p-toluene sulfonic acid, 1,5-naphthalene disulfonic acid, 4-ethylbenzene sulfonic acid, dodecylbenzene sulfonic acid or mixtures thereof.
12. The method as claimed in claim 9, wherein the corrosion inhibitor is gallic acid, catechol, benzotriazole, benzoic acid, malonic acid, ammonium malonate or mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/00291

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(7) : C11D 1/62; C23G 1/00, 1/02; C03C 23/00; B08B 3/00, 3/12, 6/00		
US CL : 510/493, 175, 489, 492, 495, 175, 499; 134/2, 3, 36, 41, 902		
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) U.S. : 510/493, 175, 489, 492, 495, 175, 499; 134/2, 3, 36, 41, 902		
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) East		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,321,166 A (McGRADY) 23 March 1982, col. 8, lines 3-5, 29-30, Example 1, col. 5, lines 62-65, col. 6, lines 9-10	1-5
X	US 5,972,862 A (TORII et al) 26 October 1999, col. 4, lines 65-68, col. 12, lines 15-18, col. 5, lines 1-7, col. 8, lines 1-2.	1-3, 5-10, 12
X	US 5,534,177 A (MAYHAN) 09 July 1996, Table 1, col. 3, lines 38-40.	1-5
X	US 4,199,483 A (JONES) 22 April 1980, col. 6, lines 1-55, col. 7, lines 40-45.	1-4, 6-7
Y	US 4,221,674 A (VANDER MEY) 09 September 1980, col. 2, lines 20-30.	4, 11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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	"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
"E" earlier application or patent published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search		Date of mailing of the international search report
07 March 2003 (07.03.2003)		19 MAR 2003
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230		Authorized officer <i>Randy P. Gulakowski</i> Randy P. Gulakowski Telephone No. 703-308-0661