

PATENT SPECIFICATION

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(54) STRIPPING SOLUTION

(71) We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be prepared, to be particularly described in and by the following statement:—

The invention relates to stripping solutions for removing organic films and deposits, such as the polymeric etch resists employed in the manufacture of semiconductors from silicon bodies or silicon dioxide coated silicon bodies.

In the chemical arts the removal of organic deposits, layers or films from silicon and silicon dioxide surfaces has been a much considered problem. While various chromium-containing acidic mixtures have been employed, there has remained room for improvement in effectiveness both as to speed and temperature of removal. While cleaning of industrial and laboratory glassware may be cited as one field of use for such compositions, there has in recent years developed a more challenging use in the manufacture of semiconductors for electronic purposes. In the manufacture of semiconductors, it is common practice in certain operations to develop desired circuit geometries or patterns onto the silicon body or a silicon dioxide layer thereon during the many processing steps. These geometries are commonly etched into the silicon body or the silicon dioxide layer by selective etching using an etch resist patterned to the desired geometry. This is commonly done by coating the semiconductor with a polymeric photoresist of either the positive or negative acting type, and exposing this coating through a pattern mask to visible or ultra-violet light or other energy source such as an electron beam. The exposed portion of the photoresist film in the case of positive acting

resists, or the unexposed portion in the case of negative acting resists, is dissolved and removed by a developer solvent. The residual photoresist film is usually dried and baked, leaving the desired pattern of polymeric etch resist that will not be attacked by the chemicals doing the desired etching or other operation on the semiconductor surfaces not protected by the polymeric resist. After the desired operation is performed, it becomes necessary to remove the remaining polymeric etch resist. Sulphuric acid and sulphuric acid solutions or slurries containing chromic acid have been found effective for this purpose at 90°—100°C. or higher temperatures, as also have various organic solutions containing solvents and phenolic materials.

In one aspect this invention consists in stripping solutions comprising sulphuric acid, at least 0.3% by weight of chromium trioxide, 0.5 to 80% by weight of nitric acid and 2 to 20% by weight of water, the sulphuric acid and nitric acid constituting at least 75% of the solution, and the solution being free from active amounts of fluorine, chlorine and alkali and alkaline earth metals.

In another aspect the invention consists in a method of stripping organic deposits from an inorganic surface, especially a silicon or silicon dioxide surface, which comprises washing the surface with a stripping solution as defined above. It has been found that washing with the above stripping solutions does not mean etching, peeling or other visible degradation of silicon bodies or silicon dioxide film on silicon bodies even after five or ten cycles of coating and removal of etch resist, and does not affect the electrical resistivity of the silicon bodies. The solutions are effective also for removing other polymeric and like organic deposits from other inorganic surfaces such as silica, glass and the like and from organic surfaces such as polyethylene, polytetrafluoroethylene and acrylonitrile-butadiene-styrene terpolymers. One effect of

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the nitric acid is substantially to increase the solubility of chromium trioxide in the sulphuric acid/nitric acid mixture, so increasing the maximum in saturation concentration thereof in the solution obtainable at 30°C. The proportion of water in the solution is preferably from 2% to 16%; proportions substantially above 20% result in considerably lower stripping efficiency.

- 5 The stripping capacity of the solutions of the invention increases with their CrO_3 content, and the preferred solutions are those containing relatively high proportions of CrO_3 .
 10 Solutions containing more than 2% CrO_3 are much more efficient than prior art stripping solutions of sulphuric acid and CrO_3 only, while even solutions containing less than 2% of the trioxide can effectively strip at room temperature (10°—40°C.) coatings that could
 15 be effectively stripped by prior art stripping agents only at temperatures of 90°—100°C. or above.

- The CrO_3 may be supplied to the stripping system in any convenient form, e.g. as the
 25 anhydride of chromic acid sold in commerce in the crystalline state, or in the form of salts such as chromates, e.g. $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, K_2CrO_4 and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, and dichromates, e.g. $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ and
 30 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

- The solubility of CrO_3 in the sulphuric acid/nitric acid mixtures is highest at equivalent sulphuric acid concentrations of about 85%, and the preferred compositions of high
 35 CrO_3 content (2 to 4%) and water content 2—16% have an equivalent sulphuric acid concentration of at least 75% when the nitric acid content is below 40%, or at least 67% when the nitric acid content is 40% or above.
 40 Equivalent sulphuric acid concentrations is given by

$$\% \text{H}_2\text{SO}_4 \times 100 / (\% \text{H}_2\text{SO}_4 + \text{H}_2\text{O})$$

(All percentages are by weight).

- The stripping solutions may contain minor
 45 quantities of other ingredients, for example thickeners such as colloidal silica, so long as they do not interfere with the intended use. Fluorine, chlorine, alkali metals or alkaline earth metals, borates, phosphates or other
 50 materials which might affect the silicon bodies or silicon dioxide film must not be present in active concentrations, though for certain applications and with certain specific concentrations of CrO_3 in the stripping solutions,
 55 alkali metal or other cations introduced in the form of salts may be tolerated if not present in an active concentration. (The concentration at which a given cation or cations become active may be readily determined by routine
 60 experiment). In such cases it may be desirable for reasons of economy or convenience to add the CrO_3 in the form of a sodium salt of

chromic acid up to the point of tolerance, any make-up CrO_3 that may be required then being added in the form of the acid anhydride or a salt whose cation is not objectionable, for example the ammonium salt. Hydrogen (H^+) is not, of course, an objectionable cation. For some purposes, it is preferred to have the solutions substantially completely free of cations such as Na^+ , K^+ and NH_4^+ , in which case the CrO_3 is provided in a form other than a salt. By "substantially completely free", it is not intended to exclude such trace amounts of cation impurities as may be introduced with the sulphuric and nitric acids, for example amounts of about 10 ppm and less.

It is to be understood that the weight percentage of CrO_3 referred to in the specification and claims refers to the CrO_3 radical, and not the compound which is the source of the chromate ions. Thus, one part by weight of a dichromate having two chromium atoms has a higher CrO_3 equivalence than one part of a chromate having only one chromium atom.

In the manufacture of semiconductors from silicon dioxide-coated silicon bodies, metallic aluminium films are frequently associated with the silicon dioxide films, and in such circumstances strippers harmless to the aluminium must be used. See, for example, U.S. Patent No. 3,426,422. The strippers of the invention have been found to be the equal of or superior to prior art strippers in this respect, when both are used at the appropriate stripping temperatures.

The stripping solutions of the invention can be produced in various ways. Thus water and then sulphuric acid may be added to nitric acid with agitation and cooling, and then the CrO_3 may be added with additional agitation and cooling. A part or all of the water may be present as a constituent of one or both of the acids used, or a nitric acid containing more than the desired amount of water may be employed and oleum used in place of all or part of the sulphuric acid.

The stripping operation may be carried out in conventional ways. Thus the article to be cleaned may be washed by immersion, by a flowing stream or in a stirred body of the solution, or by a spray directed against it. The solutions can be used effectively both at ordinary room temperatures, and at elevated temperatures, at which the rate of cleaning is increased. Thus their use at temperatures of 100°C. or so effects exceedingly rapid removal of etch resists such as Kodak Metal Etch Resist, usually designated "KMBR", a product of Eastman Kodak Company.

The following Examples illustrate the invention. Parts are by weight.

Examples 1—16

Nitric acid of concentration 70.54% was introduced into a round bottom glass flask

fitted with cooling bath, agitator, thermometer, and drying tube, followed by the gradual addition first of distilled water and then 95.56% sulphuric acid with agitation and cooling, the temperature being maintained at 20°—30°C. When all the sulphuric acid had been added the temperature was reduced to 0°—5°C., at which CrO_3 is more soluble in the acid mixtures; and the CrO_3 was added as crystals of chromic acid anhydride. The amounts of sulphuric and nitric acids, CrO_3 and water are shown in the Table below. In order to evaluate the various solutions for use in the manufacture of semi-conductors, the following test procedure was employed. Silicon wafers, commercially coated with a silicon dioxide film according to practices regularly employed in the semiconductor industry (8000 Angstrom steam-grown films), were employed as test specimens. An etch resist solution sold commercially for this purpose was applied to the film uniformly by the technique known as spin casting. (The composition used, referred to above as KMER, is a xylene solution of a prepolymer of the polyisoprene type and a photo-activated sensitizer or developer for promoting hardening and insolubilizing.) The coated wafers were heated to a temperature

of about 100°C. for about 30 minutes to evaporate off the solvent. They were then masked with an opaque stencil to shield portion of the coating and were exposed to light rays from a 600 watt Westinghouse "Oxy Movie Flood" lamp at a distance of about 9 inches for about one-half minute to harden the coating and render it insoluble. The wafers were then immersed in and washed with xylene to remove the uncured portions of the coating. The wafers were then baked at 160°C. (or at 200°C. where indicated in the Table) for 30 minutes to further harden the polymer. Each wafer now possessed on one surface a silicon dioxide film which was partially exposed and partially protected by cured organic polymer.

To test the stripping action of the various stripping solutions, a wafer was immersed in the stripping solution under test at 27°—28°C., except as otherwise indicated, and for the time indicated, in the Table. The wafer was then washed by dipping it in water, and then subjecting it to a stream of distilled water. The washed wafer was examined visually and microscopically (at 20X) to determine the extent of removal of the polymer and the condition of the silicon dioxide wafer.

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TABLE

Example	Equivalent H ₂ SO ₄ Percent	Concentration As Parts by Weight				Minutes for Stripping (2)
		H ₂ SO ₄	HNO ₃	H ₂ O	CrO ₃	
1	85.5	81.2	5.0	13.8	6.85	0.5 to 1.0
2 (1)	94.1	57.7	38.7	3.6	3.1	1.5—
3	73.5	44.1	40.0	15.9	0.93	1.5 to 4.0
4	73.5	44.1	40.0	15.9	0.5	1.5 to 4.0
5	79.5	47.7	40.0	12.3	3.33	1.0+; 1.5—
6 (1)	94.3	84.0	10.8	5.2	2.04	1.5—
7	85.5	84.6	1.0	14.4	6.42	1.5+; 4.0—
8	85.5	84.6	1.0	14.4	6.42	0.08 (3)
9	85.5	84.6	1.0	14.4	0.5	1.5 to 4.0
10	94.5	93.6	1.0	5.4	2.22	1.5+; 4.0—
11	71.5	20.0	72.0	8.0	2.83	1.5—
12	97.5	87.75	10.0	2.25	4.32	0.5
13	97.5	96.5	1.0	2.5	0.46	1.5—
14	85.5	85.1	0.5	14.4	5.61	1.5—
15	94.5	56.7	40.0	3.3	9.25	1.5—
16	79.5	71.5	10.0	18.5	1.86	4.0 to 10

Notes to Table:

- (1) Coating postbaked at 200°C. for 30 minutes.
- (2) The minus signs in this column indicate complete removal in less than the indicated time; the plus signs signify that all but a trace was removed in the indicated time.
- (3) Test at the usual 90°—100°C. stripping temperature.

No etching, peeling or other visible degradation of the silicon wafers was observed, and their electrical resistivity remained unaffected.

- 5 Compositions numbered 1, 6, 7, 10, 12 and 14, which contain at least 80% H₂SO₄, at least 2% CrO₃, at least 2% water, and at least 0.5% but not over 14% HNO₃ possess a valuable combination of properties rendering
- 10 them especially satisfactory stripping agents in semiconductor manufacture. They possess rapid stripping action, high stripping capacity, excellent freedom from fuming, and particu-

larly low corrosiveness towards aluminium metal.

Prior to the present invention compositions containing nitric, chromic and sulfuric acids have been disclosed for such purposes as metal finishing, but these compositions differ fundamentally from those of the present invention in having much higher water contents and, in general, an additional essential ingredient increasing the activity of the composition. Such compositions, containing hydrochloric acid, phosphoric acid, boric acid or hydrofluoric

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acid as an essential constituent, are disclosed in U. S. Patents 2,172,171, 2,497,905, 2,904,414 and 3,060,071. The compositions of these patents are wholly unsuitable for the purposes of the present invention.

WHAT WE CLAIM IS:—

1. A stripping solution comprising sulphuric acid, at least 0.3% by weight of chromium trioxide, 0.5 to 80% by weight of nitric acid and 2 to 20% by weight of water, the sulphuric acid and nitric acid constituting at least 75% by weight of the solution, and the solution being free from active amounts of fluorine, chlorine and alkali and alkaline earth metals.

2. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight and an equivalent sulphuric acid concentration (as hereinbefore defined) of at least 75% by weight.

3. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight, a nitric acid content of at least 40% by weight and an equivalent sulphuric acid concentration (as hereinbefore defined) of at least 67% by weight.

4. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight and a water content of 2 to 16% by weight, the equivalent sulphuric acid concentration (as hereinbefore defined) being at least 67% by weight when the nitric acid content is at least 40% by weight, and at least 75% by weight when the nitric acid content is less than 40% by weight.

5. A solution according to claim 1 having a chromium trioxide content of 2 to 4% by weight and a water content of 2 to 16% by weight, the equivalent sulphuric acid concentration (as hereinbefore defined) being at least 67% by weight when the nitric acid content is at least 40% by weight, and at least 75% by weight when the nitric acid content is less than 40% by weight.

6. A solution according to claim 1 which is an aqueous solution of chromic, sulphuric and nitric acids, having a chromium trioxide content of at least 2% by weight, a water content of at least 2% by weight, a sulphuric acid content of at least 80% by weight and a nitric acid content of 0.5 to 14% by weight.

7. A solution according to one of the preceding claims which is substantially completely free from cations other than hydrogen ions.

8. A solution according to claim 1 substantially as described in any one of the Examples.

9. A method of stripping organic deposits from an inorganic surface, comprising washing the surface with a stripping solution according to any one of claims 1 to 6 and 8.

10. A method according to claim 9 wherein the organic deposit is an organic etch resist polymer.

11. A method according to claim 9 or 10 wherein the inorganic surface is a silicon or silicon dioxide surface.

12. A method according to claim 11 wherein the surface is a silicon dioxide film carried by a silicon substrate.

13. A method according to claim 12 wherein the silicon substrate is suitable for production of a semiconductor.

14. A method according to any one of claims 9 to 13 wherein the washing is performed at 10° to 40°C.

15. A method according to any one of claims 9 to 14 wherein the surface is washed with a solution according to claim 7.

16. A method according to claim 9 substantially as described in any one of the Examples.

17. An inorganic surface stripped by a method according to any one of claims 9 to 14 and 16.

18. An inorganic surface stripped by a method according to claim 15.

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2. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight and an equivalent sulphuric acid concentration (as hereinbefore defined) of at least 75% by weight.

3. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight, a nitric acid content of at least 40% by weight and an equivalent sulphuric acid concentration (as hereinbefore defined) of at least 67% by weight.

4. A solution according to claim 1 having a chromium trioxide content of at least 2% by weight and a water content of 2 to 16% by weight, the equivalent sulphuric acid concentration (as hereinbefore defined) being at least 67% by weight when the nitric acid content is at least 40% by weight, and at least 75% by weight when the nitric acid content is less than 40% by weight.

5. A solution according to claim 1 having a chromium trioxide content of 2 to 4% by weight and a water content of 2 to 16% by weight, the equivalent sulphuric acid concentration (as hereinbefore defined) being at least 67% by weight when the nitric acid content is at least 40% by weight, and at least 75% by weight when the nitric acid content is less than 40% by weight.

6. A solution according to claim 1 which is an aqueous solution of chromic, sulphuric and nitric acids, having a chromium trioxide content of at least 2% by weight, a water content of at least 2% by weight, a sulphuric acid content of at least 80% by weight and a nitric acid content of 0.5 to 14% by weight.

7. A solution according to one of the preceding claims which is substantially completely free from cations other than hydrogen ions.

8. A solution according to claim 1 substantially as described in any one of the Examples.

9. A method of stripping organic deposits from an inorganic surface, comprising washing the surface with a stripping solution according to any one of claims 1 to 6 and 8.

10. A method according to claim 9 wherein the organic deposit is an organic etch resist polymer.

11. A method according to claim 9 or 10 wherein the inorganic surface is a silicon or silicon dioxide surface.

12. A method according to claim 11 wherein the surface is a silicon dioxide film carried by a silicon substrate.

13. A method according to claim 12 wherein the silicon substrate is suitable for production of a semiconductor.

14. A method according to any one of claims 9 to 13 wherein the washing is performed at 10° to 40°C.

15. A method according to any one of claims 9 to 14 wherein the surface is washed with a solution according to claim 7.

16. A method according to claim 9 substantially as described in any one of the Examples.

17. An inorganic surface stripped by a method according to any one of claims 9 to 14 and 16.

18. An inorganic surface stripped by a method according to claim 15.

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