

PATENT SPECIFICATION

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- (21) Application No. 4135/75
- (22) Filed 30 Jan. 1975
- (31) Convention Application No. 438127
- (32) Filed 30 Jan. 1974 in
- (33) United States of America (US)
- (44) Complete Specification published 14 Sept. 1977
- (51) INT CL² G03C 11/00
- (52) Index at acceptance
G2X B5D



(54) POLYMERIC ETCH RESIST STRIPPERS

(71) We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the Laws of the State of New York, United States of America, of 1411 Broadway, New York, New York 10018, 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 performed, to be particularly described in and by the following statement:—

This invention relates to a stripping composition for the removal of organic films and deposits such as polymeric etch resists employed in the manufacture of semiconductors and microcircuits

During manufacture of semiconductors and semiconductor microcircuits, it is frequently necessary to coat the materials from which the semiconductors and microcircuits are manufactured with a polymeric organic substance which serves as a photoresist, i.e. a substance which forms an etch resist upon exposure to light. Subsequently, the polymeric organic substance must be removed. There is therefore a need for a stripping agent which will remove the organic substance from the coated material.

Prior art products for the removal of organic substances frequently contained a strong oxidizing agent such as chromic acid. Unless the concentration and exposure of the oxidizing agent to the coated material was strictly controlled the acid-containing stripping agent would attack the material to which the organic substance was applied. Organic strippers for removing polymeric organic substances from materials used in the manufacture of semiconductors and microcircuits are therefore preferred. Previously available organic stripping agents have formed insoluble precipitates upon exposure to air or did not strip the organic substance with the speed desired, or had undesirable colour, or contained a large number of components, or frequently corroded aluminium materials, or were not sufficiently compatible with both organic solvents and water for use in general application. Especially for use in automated process equipment,

therefore, previously organic stripping agents have been unsatisfactory.

A class of compositions useful for removing organic polymeric deposits from the surface of materials used in the manufacture of semiconductors and microcircuits has now been discovered. The compositions are suitable for the above described stripping operations without attacking or damaging the numerous inorganic materials which may be encountered in such stripping operations in the electrical and electronics industry. The stripping compositions of the invention do not cause etching, peeling or other visible degradation of these inorganic materials even after five or ten cycles of coating and removing polymeric organic substances, e.g. etch resists, and do not affect the electrical resistivity or conductivity of the materials. In addition, the compositions of this invention do not form insoluble precipitates upon standing in air, will strip photoresists in less time than was previously possible using prior art organic stripping compositions, have a less undesirable colour, contain fewer components than required in prior art organic stripping compositions, do not corrode aluminium materials, have improved miscibility in organic solvents and in water and are suitable for use in automated process equipment. The stripper of the invention is a composition which comprises:

- (a) 25 to 35% by weight of phenol, acetic acid or a mixture of phenol and acetic acid,
- (b) 10 to 30% by weight of at least one phenol sulphonic acid,
- (c) 15 to 30% by weight of at least one chlorinated hydrocarbon, and
- (d) 25 to 35% by weight of a surface active agent having an HLB number of 11.0 to 12.5.

HLB has its usual meaning of hydrophilelipophile balance.

Phenol sulphonic acid can be any of three isomers, and as commercially available is usually a mixture of the ortho and para isomers. In the examples below the commer-

cially available mixture was used, but in principle any isomer could be used alone or a different mixture could be used.

In the method of the present invention a material coated with a polymeric organic substance, e.g. a photoresist, is sprayed with or immersed in a solution of the above formulation. The polymeric organic substance then dissolves in the solution and is washed from the surface of the coated material with any suitable wash liquid such as water, perchloroethylene or trichloroethylene.

The surface active agent is preferably strongly anionic although it may be non-ionic provided there is a highly hydrophilic chain such as a polyol chain in the structure. Preferred surface active agents are alkyl or aryl sulphonates having an alkyl hydrophobic chain. The most preferred surface active agents are alkyl aryl sulphonates wherein the alkyl portion is a mixture of alkyl groups having an average chain length from 10 to 14 carbon atoms and the aryl group is benzene, toluene or xylene. In accordance with this invention linear dodecylbenzenesulphonic acid has been found to be the most preferred surface active agent.

The phenol or acetic acid in the stripper formulation appears to act in conjunction with the other components to dissolve and lift the polymeric organic substance from a substrate coated with the substance. The preferred compound for obtaining the best results seems to be phenol since a better dissolving and lifting action is obtained.

The phenol sulphonic acid similarly seems to act to dissolve and lift the polymeric organic substance and it has been found that when from 15 to 25 percent by weight of stripper of phenol sulphonic acid is used, substantially faster stripping action occurs, more water can be tolerated in the stripper with less corrosion of aluminium substrates than was previously possible with prior art strippers and fewer undesirable precipitates result upon exposure of the stripper to air.

The chlorinated hydrocarbon assists in dissolving and diluting the organic substance and may for example be selected from metadichlorobenzene, orthodichlorobenzene, trichlorobenzene, chlorinated toluenes, perchloroethylene and mixture of any of these chlorinated hydrocarbons. A particularly effective chlorinated hydrocarbon has been found to be orthodichlorobenzene. The preferred chlorinated hydrocarbons boil between 120 and 210°C. and preferably between 150 to 190°C.

The polymeric organic substances which are to be removed by the strippers of this invention are usually photoresists which generally comprise polymers selected from low molecular weight polyisoprenes, polyvinyl cinnamates and phenol-formaldehyde resins. These photoresists are applied to a substrate,

e.g. aluminium, portions are masked and the entire portion is then exposed to light e.g. a 120 volt 640 watt quartz lamp for 1 to 15 seconds at a distance of 6 to 12 inches to further polymerize the exposed photoresists. The portion of the photoresist which is not exposed, i.e. masked from the light, is then removed by a mild solvent which does not dissolve the exposed photoresist thus leaving a pattern such as an electrical circuit pattern, on the exposed substrate. The remaining photoresist is then baked for further hardening and the portion of the substrate which is not covered by the photoresist is then etched or otherwise treated. The hardened photoresist must then be removed.

In using the stripper of this invention, the substrate covered by the photoresist is contacted with the stripper of this invention at a temperature of from 50 to 180°C. The preferred temperature is from 90 to 120°C. since a 90 degree temperature results in faster stripping time and since temperatures above 120°C. permit losses of stripper by evaporation at a rate which is not desirable. Times required for stripping of the photoresist are from 1 to 15 minutes at from 90°C to 120°C.

After stripping the substrate is rinsed in any suitable liquid. Examples of suitable rinsing liquids are: ethanol, isopropyl alcohol, trichloroethylene and mixtures of 1,1,2-trichlor 1,2,2-trifluoroethane with alcohols containing 1 to 3 carbon atoms.

The following examples serve to illustrate the stripper formulations and stripping method of this invention. In each example all parts and percentages are by weight. Three different stripper formulations are used in the following examples. Formulation A is a prior art organic stripper, Formulation B is a first embodiment of the stripper of this invention and Formulation C is a second embodiment of the stripper of this invention. The formulations are as follows:

Formulation A			110
Linear dodecylbenzenesulphonic acid	28%		
Phenol	28%		
Toluene sulphonic acid	18%		
Orthodichlorobenzene	18%		115
Perchloroethylene	8%		

Formulation B			120
Linear dodecylbenzenesulphonic acid	30%		
Phenol	30%		
Phenol sulphonic acid (mixture of isomers)	20%		
Orthodichlorobenzene	20%		

Formulation C			125
Linear dodecylbenzenesulphonic acid	28.0%		
Phenol	28.0%		

Phenolsulphonic acid (mixture of isomers)	18.5%
Orthodichlorobenzene	18.5%
Perchloroethylene	7.0%

Example 1

100 ml of formulations A, B and C are placed in separate 250 ml beakers open to the atmosphere at 20°C. and 80% relative humidity. After twenty-four hours formulation A becomes cloudy and contains undesirable precipitate whereas formulations B and C remain clear indicating that formulations B and C of the invention less readily form undesirable precipitates when contacted with air than prior art formulation A.

Example 2

Three silicon wafers are coated with polyisoprene photoresist. The photoresist coating is then exposed to a 120 volt 650 watt quartz lamp for 15 seconds at a distance of 12 inches. The photoresist coating is then baked at 240°C. for 2 hours. Each wafer is then immersed in one of formulations A, B and C at a temperature of 100°C. and the times required for stripping the photoresist from the wafer are measured. The results are set forth in Table I. The results indicate that formulations B and C of this invention permit faster stripping times than prior art formulation A.

TABLE I.

Formulation	Stripping Time
A	30 minutes
B	8 minutes
C	8 minutes

Example 3

After stripping, each of the wafers used in Example 2 is rinsed with a non-flammable mixture of 93 weight percent of 1,1,2-trichloro 1,2,2-trifluoroethanol and 7 weight percent isopropanol. Both of formulations B and C are removed by the rinse; whereas, formulation A is immiscible with the mixture and is not removed by the rinse. This example indicates that formulations B and C of this invention are more readily removed by rinsing liquids containing halogenated hydrocarbons than the prior art formulation.

WHAT WE CLAIM IS:—

1. A composition comprising:

- (a) 25 to 35% by weight of phenol, acetic acid or a mixture of phenol and acetic acid,
- (b) 10 to 30% by weight of at least one phenol sulphonic acid,
- (c) 15 to 30% by weight of at least one chlorinated hydrocarbon, and
- (d) 25 to 35% by weight of a surface active agent having an HLB number of 11.0 to 12.5.

2. A composition according to claim 1 wherein component a) comprises phenol.

3. A composition according to claim 1 or 2 wherein component d) comprises an anionic surface active agent.

4. A composition according to claim 3 wherein the surface active agent is an alkylarylsulphonate.

5. A composition according to claim 4 wherein the alkyl portion in the alkylarylsulphonate is a mixture of alkyl groups having an average chain length of 10 to 14 carbon atoms.

6. A composition according to claim 4 wherein the surface active agent is linear dodecylbenzenesulphonic acid.

7. A composition according to any one of the preceding claims wherein component c) comprises at least one chlorinated hydrocarbon having a boiling point of 120 to 210°C.

8. A composition according to any one of the preceding claims wherein component c) comprises at least one chlorinated hydrocarbon having a boiling point of 150 to 190°C.

9. A composition according to claim 8 wherein the chlorinated hydrocarbon is a dichlorobenzene.

10. A composition according to claim 9 wherein the chlorinated hydrocarbon is *ortho*-dichlorobenzene.

11. A composition according to claim 7 wherein component c) comprises a mixture of *ortho*-dichlorobenzene and perchloroethylene.

12. A composition according to claim 1 comprising 30% by weight of phenol, 20% by weight of at least one phenol sulphonic acid, 20% by weight of *ortho*-dichlorobenzene and 30% by weight of linear dodecylbenzenesulphonic acid.

13. A composition according to claim 1 comprising 28% by weight of phenol, 18.5% by weight of at least one phenol sulphonic acid, 18.5% by weight of *ortho*-dichlorobenzene, 7% by weight of perchloroethylene and 28% by weight of linear dodecylbenzenesulphonic acid.

14. A method of removing a polymeric organic substance from a substrate which method comprises contacting the polymeric organic substance on the substrate with a composition as claimed in any one of the preceding claims.

15. A method according to claim 14 wherein the polymeric organic substance is a photoresist which comprises polyisoprene, polyvinyl cinnamate or a phenolformaldehyde resin.

16. A method according to claim 14 or 15 which is carried out at a temperature of 50 to 180°C.

17. A method according to claim 16 which is carried out at a temperature of 90 to 120°C.

18. A method according to claim 14 substantially as hereinbefore described.



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Phenolsulphonic acid (mixture
of isomers) 18.5%
Orthodichlorobenzene 18.5%
Perchloroethylene 7.0%

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100 ml of formulations A, B and C are placed in separate 250 ml beakers open to the atmosphere at 20°C. and 80% relative humidity. After twenty-four hours formulation A becomes cloudy and contains undesirable precipitate whereas formulations B and C remain clear indicating that formulations B and C of the invention less readily form undesirable precipitates when contacted with air than prior art formulation A.

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4. A composition according to claim 3 wherein the surface active agent is an alkyl-arylsulphonate.

5. A composition according to claim 4 wherein the alkyl portion in the alkylarylsulphonate is a mixture of alkyl groups having an average chain length of 10 to 14 carbon atoms.

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12. A composition according to claim 1 comprising 30% by weight of phenol, 20% by weight of at least one phenol sulphonic acid, 20% by weight of *ortho*-dichlorobenzene and 30% by weight of linear dodecylbenzenesulphonic acid.

13. A composition according to claim 1 comprising 28% by weight of phenol, 18.5% by weight of at least one phenol sulphonic acid, 18.5% by weight of *ortho*-dichlorobenzene, 7% by weight of perchloroethylene and 28% by weight of linear dodecylbenzenesulphonic acid.

14. A method of removing a polymeric organic substance from a substrate which method comprises contacting the polymeric organic substance on the substrate with a composition as claimed in any one of the preceding claims.

15. A method according to claim 14 wherein the polymeric organic substance is a photoresist which comprises polyisoprene, polyvinyl cinnamate or a phenolformaldehyde resin.

16. A method according to claim 14 or 15 which is carried out at a temperature of 50 to 180°C.

17. A method according to claim 16 which is carried out at a temperature of 90 to 120°C.

18. A method according to claim 14 substantially as hereinbefore described.



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19. A substrate from which a polymeric organic substance has been removed by a method as claimed in any one of claims 14 to 18.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.