

STRIPPING AND CLEANING COMPOSITIONS FOR MICROELECTRONICS

FIELD OF THE INVENTION

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[0001] This invention relates to methods and alkaline-containing photoresist stripping and cleaning compositions for cleaning microelectronics substrates, and particularly such compositions useful with and compatible with metal electrode stacks used in the flat panel display (FPD) markets. The compositions of this invention provide enhanced protection of metal, i.e., inhibition of corrosion, when
10 such microelectronic substrates are subjected to an aqueous rinse.

BACKGROUND TO THE INVENTION

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[0002] Many photoresist strippers and residue removers have been proposed for use in the microelectronics field as downstream or back end of the manufacturing line cleaners. In the manufacturing process a thin film of photoresist is deposited on a substrate material, and then circuit design is imaged on the thin film. Following baking, the exposed resist is removed with a photoresist developer. The resulting
20 image is then transferred to the underlying material, which is generally a dielectric or metal, by way of plasma etch gases or chemical etchant solutions. The etchant gases or chemical etchant solutions selectively attack the photoresist-unprotected area of the substrate. As a result of the plasma etching process, photoresist and etched material by-products are deposited as residues around or on the sidewall of the etched
25 openings on the substrate and the photoresist.

[0003] Additionally, following the termination of the etching step, the resist mask must be removed from the protected area of the substrate so that the next process operation can take place. This can be accomplished in a plasma ashing
30 step by the use of suitable plasma ashing gases or wet chemical strippers. Finding

a suitable cleaning composition for removal of this resist mask material without adversely affecting, e.g., corroding, etching or dulling, the metal circuitry has also proven problematic.

5 [0004] As microelectronic fabrication integration levels have increased and patterned microelectronic device dimensions have decreased, it has become increasing difficult to provide suitable photoresist stripping and cleaning compositions that provide suitable stripping and cleaning properties without producing other detrimental effects. In the area of flat panel display (FPD)
10 applications, particularly with the use of select metals and alloys, the problem of metal corrosion during photoresist stripping and the water rinse is a severe drawback.

[0005] Due to issues with electrical performance and reliability in mass
15 production, a variety of metal stacks are utilized for forming gate lines in FPD technology. Multiple metal layers such as Mo/AlNd/Mo, and especially double layers such as Mo/AlNd, AlNd/Ti, and AlNd/Cr are common for gate line metal stacks in current manufacturing of FPD technologies. However, in stacks where the AlNd alloy is located beneath another metal, aluminum corrosion during the rinse step can
20 be a critical problem for electrical performance. This corrosion is commonly known as overhang and can create voids that weaken the metal structure. Loss of aluminum to corrosion during the chemical cleaning or water rinse steps can also create notching in the metal lines, which is the most common defect at FPD technology. The composition of the cleaning solution and its behavior in water plays
25 a key role in causing corrosion. A typical photoresist remover for FPD applications might include polar organic solvents blended with organic amines and other solvating agents. Amines have been shown to increase the effectiveness of photoresist removal in solvent blends. However, the water rinse following this type of remover can create a strongly alkaline aqueous solution and that can lead to
30 considerable loss of metal from the patterned lines. This necessitates an

intermediate rinse between the cleaning/stripping step and the aqueous rinse. Such an intermediate rinse, typically with isopropyl alcohol, adds undesirable time, safety concerns, environmental consequences, and cost to the manufacturing process.

- 5 [0006] There is therefore a need for an alkaline-containing stripping and cleaning compositions for photoresists that enable one to completely remove photoresists and etch and/or ash residue from the microelectronic substrate yet not produce any significant metal corrosion during a subsequent aqueous rinse step, especially for FPD microelectronic elements.

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SUMMARY OF THE INVENTION

- [0007] The invention provides alkaline-containing cleaning compositions for
15 cleaning microelectronic substrates, particularly FPD microelectronic substrates, that are able to essentially completely clean such substrates and produce essentially no metal corrosion of the metal elements of such substrates. The invention also provides method of using such alkaline-containing cleaning compositions to clean microelectronic substrates, particularly FPD microelectronic substrates, without
20 producing any significant metal corrosion of the metal elements of the microelectronic substrate. The alkaline-containing cleaning compositions of this invention comprise (a) a nucleophilic amine, (b) a moderate to weak acid having a strength expressed as a "pKa" for the dissociation constant in aqueous solution of from about 1.2 to about 8, preferably from about 1.3 to about 6, and more preferably
25 from about 2.0 to about 6, and most preferably of from about 2 to about 5 (c) a compound selected from an aliphatic alcohol, diol, polyol or aliphatic glycol ether, and (d) an organic co-solvent preferably having a solubility parameter of from about 8 to about 15, obtained by taking the square root off the three Hansen solubility parameters (dispersive, polar and hydrogen bonding). The cleaning compositions of
30 this invention will have an amount of weak acid such that the equivalent mole ratio of

acid groups to amine groups is greater than .75 and may range up to and beyond a ratio of 1, such as for example a ratio of 1.02 or more. The pH of the alkaline-containing cleaning compositions of this invention will be from about pH 4.5 to 9.5, preferably from about pH 6.5 to 9.5 and most preferably from about pH 8.5 to 9.5.

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[0008] The cleaning compositions of this invention can be used to clean any suitable microelectronic substrate, and are especially useful to clean FPD microelectronic substrate elements and are able to do so without causing any significant metal corrosion in a subsequent aqueous wash step of the microelectronic substrate. The cleaning compositions of this invention are particularly suitable for cleaning FPD microelectronic substrates containing aluminum, and especially those containing aluminum/neodymium components without causing any significant metal corrosion in a subsequent aqueous wash step of the microelectronic substrate.

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DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

[0009] The alkaline-containing cleaning compositions of this invention contain a nucleophilic amine. Any suitable nucleophilic amine can be employed in the compositions of this invention. Examples of suitable nucleophilic amines include, but are not limited to, 1-amino-2-propanol, 2-(2-aminoethoxy)ethanol, 2-aminoethanol, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethylamino)ethylamine, diethanolamine, triethanolamine, and the like. The nucleophilicity of the amine component should be high. The amount of the nucleophilic amine component employed in the cleaning composition of this invention will generally be from about 1% to about 50%, preferably from about 10% to about 45%, and especially from about 12% to about 25%, based on the total weight of the cleaning composition.

30 [0010] The alkaline-containing cleaning compositions of this invention contain

an aliphatic alcohol, diol, polyol or aliphatic glycol ether component. The aliphatic component of the is preferably an alkyl or alkylene moiety containing from about 2 to about 20 carbon atoms, preferably from about 2 to about 10 carbon atoms, and most preferably from about 2 to about 6 carbon atoms. Any suitable aliphatic alcohol, diol, polyol or aliphatic glycol ether can be employed in the compositions of this invention. Examples of such suitable compounds include, but are not limited to, isopropanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, butanediols and butenediols, such as 2-butene-1,4-diol, pentanediols such as 2-methyl-2,4-pentanediol, hexanediols, glycerol, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, propylene glycol dimethyl ether, 2-(2-butoxyethoxy)-ethanol and the like. Particularly preferred are alkane diols of from 2 to 6 carbon atoms and especially ethylene glycol and propylene glycol. The amount of aliphatic alcohol, diol, polyol or aliphatic glycol ether component in the cleaning compositions of this invention will generally be from about 10% to about 80%, preferably from about 20% to about 60%, and especially from about 25% to about 40%, based on the total weight of the cleaning composition.

[0011] The alkaline-containing cleaning compositions of this invention will have present any suitable organic co-solvent component, preferably an organic co-solvent having a solubility parameter of from about 8 to about 15. The co-solvent may be any one or more suitable co-solvents. Such suitable co-solvents include, but are not limited to, 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, 1-ethyl-2-pyrrolidinone, 1-propyl-2-pyrrolidinone, 1-hydroxyethyl-2-pyrrolidinone, sulfur oxides such as dialkyl sulfones, dimethyl sulfoxide, tetrahydrothiophene-1,1-dioxide compounds such as sulfolane, methyl sulfolane, ethylsulfolane, dimethylacetamide and dimethylformamide and the like. The amount of co-solvent component in the cleaning compositions of this invention will generally be from about 20% to about 80%, preferably from about 25% to about 70%, and especially from about 30% to

about 45%, based on the total weight of the cleaning composition.

[0012] The alkaline-containing cleaning compositions of this invention have present a component comprising any suitable moderately strong to weak acid having
5 a strength expressed as a "pKa" for the dissociation constant in aqueous solution of from about 1.2 to about 8, preferably from about 1.3 to about 6, and more preferably from about 2.0 to about 5. Such acids can be organic or inorganic acids. Example of such suitable weak acids include, but are not limited to, carboxylic acids such as acetic acid, propanoic acid, malonic acid, phthalic acid, phenoxyacetic acid,
10 mercaptobenzoic acid, 2-mercatpptoethanol and the like, and inorganic acids such as carbonic acid, hydrofluoric acid, hypophosphorus acid and the like. The amount of weak acid employed in the composition will generally be in an amount such that the equivalent mole ratio of acid moieties to amine moieties is greater than 0.75, preferably from greater than 0.75 to about 1.6 and most preferably from about 0.76
15 to about 1.0. When present in the foregoing amounts the acid component will generally comprise from about 1% to about 50%, preferably from about 10% to about 35%, and most preferably from about 12% to about 25%, by weight of the total components in the composition.

20 [0013] The alkaline-containing cleaning compositions of this invention can also optionally contain other components, including but not limited to, corrosion inhibitors, non-corrosive surfactants and similar non-corrosive components employed in alkaline-containing microelectronic cleaner compositions.

25 [0014] The compositions on this invention, their use to clean microelectronic substrates, especially FPD microelectronic substrates and their non-metal corroding properties is illustrated by, but not limited to, the following examples.

[0015] The following test procedure was employed in the following examples.
30 Test samples consisted of a glass substrate and a metal electrode composed of a

molybdenum layer on an aluminum/neodymium (Al/Nd) (~97% Al) layer. Both layers were applied by sputtering and patterned by photolithography as follows: 1) 1.5 μ m of a positive photoresist was applied by spin coating, 2) the coated resist was soft baked at about 80° C, 3) then the photoresist coated substrate was exposed for patterning, 4) the exposed, patterned substrate was then developed for 60 seconds, followed by 5) hard baking at over 140° C for three minutes. The metals are then etched in a multi-step process such that there is no overhang of the molybdenum layer.

- 10 **[0016]** Samples were prepared by cleaving the glass substrate sheet into pieces about 1-2 cm². These samples were cleaned by suspension in a test solution at conditions described hereinafter in a small stirred bath. For tests of cleaning efficiency, samples were next rinsed in flowing deionized water for one minute. To better simulate corrosion in rinse water, samples cleaned at 70° C for three minutes, were placed directly in a 5 % solution of the same cleaning material composition in deionized water at 30° C for 5 minutes. No formulations tested cause corrosion of the molybdenum layer, so only corrosion of Al/Nd is indicated. The water rinse pH was also determined from a 5% solution concentration of the cleaning compositions. Drying with N₂ immediately followed either rinse step. Sample cleanliness and corrosion were determined by scanning electron microscope analysis.

[0017]. In the examples below, the following terms are used:

For "cleaning": "Clean" represents complete removal of all resist and "Incomplete" indicates any amount of bulk resist not removed from the metals.

For "Corrosion": "None" indicates no loss of Al/Nd line material, "Slight" indicated loss of fine edges of Al/Nd lines at the substrate interface, and "Some" indicates limited corrosion of the bulk Al/Nd line.

"Molecular weight ratio" means the ratio of the molecular weight of the acid component to the amine component multiplied by the ratio of number of acid

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groups in the acid component to the number of amine groups in the amine component.

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EXAMPLES

[0018] Example 1: An initial solution comprised of N-methylpyrrolidinone (about 44%), ethylene glycol (about 33%), and monoethanolamine (about 22%) was prepared. To this solution was added glacial acetic acid to produce the test
10 solutions indicated below.

Composition (amount of acid)	Equivalent mole ratio acid/amine	pH 5% sol.	Cleaning (3 min. 70° C)	Al/Nd corrosion (5% sol. 30° C)
14.3% acetic acid	0.765	9.4	Clean	None
15.1% acetic acid	0.82	9.29	Clean	None
16.1% acetic acid	0.88	9.06	Clean	None
17.1% acetic acid	0.94	8.65	Clean	None
17.9% acetic acid	1	6.63	Clean	None
18.1% acetic acid	1.02	6.34	Clean	None

[0019] Example 2: An initial solution comprised of N-methylpyrrolidinone
15 (about 44%), ethylene glycol (about 33%), and monoethanolamine (about 22%) was prepared. To this solution was added the acids indicated below.

Composition-added acid	Equivalent mole ratio acid/amine	pH 5% sol.	Cleaning (3 min. 70° C)	Al/Nd corrosion (5% sol. 30° C)
13.8% hypophosphorous acid	0.8	9.21	Clean	None
22.5% malonic acid	0.8	4.77	Clean	Some

[0020] Example 3: Solutions were prepared with compositions of N-
20 methylpyrrolidinone (37%), monoethanolamine (19%), glacial acetic acid (15%), and the remaining component (29%) as indicated below.

Added component	Equivalent mole ratio acid/amine	pH 5% sol.	Cleaning (3 min. 70° C)	Al/Nd corrosion (5% sol. 30° C)
propylene glycol	0.8	9.39	Clean	Some
2-methyl-2,4-pentanediol	0.8	9.37	Clean	None
glycerol	0.8	9.38	Clean	None
2-butene-1,4-diol	0.8	9.37	Clean	Slight
Isopropanol	0.8	8.9	Clean	None
2-(2-butoxyethoxy)-ethanol	0.8	9.12	Clean	None

- 5 **[0021]** Example 4: Solutions were prepared with compositions of monoethanolamine (19%), glacial acetic acid (14.3%), and the remaining percentage comprising N-methylpyrrolidinone (NMP) and ethylene glycol (EG) indicated.

Composition %NMP/%EG	Equivalent mole ratio acid/amine	pH 5% sol.	Cleaning (3 min. 70° C)	Cleaning (30 sec. 70° C)	Al/Nd corrosion (5% sol. 30° C)
100%/0%	0.765	9.24	Clean	Redeposit	None
57%/43%	0.765	9.4	Clean	Clean	None
43%/53%	0.765	9.41	Clean	Clean	Slight
0%/100%	0.765	9.43	Clean	Redeposit	Some

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- [0022]** Comparative Example A: A solution comprising N-methylpyrrolidinone (47%), ethylene glycol (35.3%), and glacial acetic acid (17.7%) was prepared.

Composition	Equivalent mole ratio acid/amine	pH 5% sol.	Cleaning (3 min. 70° C)	Al/Nd corrosion (5% sol. 30° C)
No Amine	N/A	2.48	Incomplete	None

- 15 **[0023]** Comparative Example B: This example was conducted by the same procedure as Example 1, except a solution comprising N-methylpyrrolidinone (30%), monoethanolamine (10%), and 2-(2-Butoxyethoxy)ethanol (17%) was prepared.

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The exposure temperature was 70° C and the exposure time was three minutes. These conditions yielded a complete clean. A five-minute, 5% solution rinse showed complete corrosion of the visible Al/Nd layer such that the molybdenum overlayer was undercut considerably.

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[0024] While the invention has been described herein with reference to the specific embodiments thereof, it will be appreciated that changes, modification and variations can be made without departing from the spirit and scope of the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes,
10 modification and variations that fall with the spirit and scope of the appended claims.

I claim:

1. A composition for cleaning microelectronic substrates comprising the following components:

5 (a) a nucleophilic amine,

(b) a moderate to weak acid having a strength expressed as a "pKa " for the dissociation constant in aqueous solution of from about 1.2 to about 8,

10 (c) a compound selected from the group consisting of an aliphatic alcohol, diol, polyol or glycol ether, and

(d) an organic co-solvent,

and the weak acid component (b) is present in the composition in an amount such that the equivalent mole ratio of acid/amine is greater than .75 and the pH of the composition is from about pH 4.5 to 9.5.

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2. A composition according to claim 1 comprising from about 1% to about 50% component (a), from about 10% to about 80% of component (c), and from about 20% to about 80% component (d), the percentages being weight % based on the total weight of the composition.

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3. A composition according to claim 1 wherein the nucleophilic amine component is at least one amine selected from the group consisting of 1-amino-2-propanol, 2-(2-aminoethoxy)ethanol, 2-aminoethanol, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethylamino)ethylamine, diethanolamine and triethanolamine.
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4. A composition according to claim 1 wherein component (c) is at least one compound selected from the group consisting of isopropanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol,
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2-methyl-1,3-propanediol, 2-butene-1,4-diol, 2-methyl-2,4-pentanediol, hexanediol, glycerol, ethylene glycol monomethyl ether diethylene glycol monomethyl ether, propylene glycol dimethyl ether, and 2-(2-butoxyethoxy)-ethanol.

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5. A composition according to claim 1 wherein the organic co-solvent is a co-solvent having a solubility parameter of from about 8 to about 15.

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6. A composition according to claim 5 wherein the co-solvent is at least one compound selected from the group consisting of 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, 1-ethyl-2-pyrrolidinone, 1-propyl-2-pyrrolidinone, 1-hydroxyethyl-2-pyrrolidinone, a dialkyl sulfone, dimethyl sulfoxide, a tetrahydrothiophene-1,1-dioxide, dimethylacetamide and dimethylformamide.

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7. A composition according to Claim 6 wherein the solvent is selected from the group consisting of sulfolane and 1-methyl-2-pyrrolidinone, the nucleophilic amine is selected from the group consisting of monoethanolamine and 1-amino-2-propanol, component (c) is selected from the group consisting of ethylene glycol, propylene glycol, 2-methyl-2,4-pentanediol, glycerol, 2-butene-1,diol, isopropanol and 2-(2-butoxyethoxy)ethanol.

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8. A composition according to claim 1 wherein the acid component (b) is at least one acid having a pKa value of from 2 to 5.

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9. A composition according to claim 7 wherein the acid component (b) is at least one acid having a pKa value of from 2 to 5.

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10. A composition according to claim 1 wherein component (b) comprises at least one acid selected from the group consisting of acetic acid, propanoic acid, malonic acid, phenylacetic acid and hypophosphorus acid.

11. A composition according to claim 7 wherein component (b) comprises at least one acid selected from the group consisting of acetic acid, propanoic acid, malonic acid, phenylacetic acid and hypophosphorus acid.

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12. A composition according to claim 1 wherein the nucleophilic amine comprises monoethanolamine, the co-solvent comprises 1-methyl-2-pyrrolidinone, the compound of component (c) is ethylene glycol and the acid of component (b) is acetic acid.

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13. A process for cleaning a microelectronic substrate without producing any substantial metal corrosion, the substrate containing photoresist polymeric material and a metal, the process comprising contacting the substrate with a cleaning composition for a time sufficient to clean the substrate, wherein the cleaning composition comprises:

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(a) a nucleophilic amine,

(b) a moderate to weak acid having a strength expressed as a "pKa" for the dissociation constant in aqueous solution of from about 1.2 to about 8,

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(c) a compound selected from the group consisting of an aliphatic alcohol, diol, polyol or glycol ether, and

(d) an organic co-solvent,

and the weak acid component (b) is present in the cleaning composition in an amount such that the equivalent mole ratio of acid/amine is greater than .75 and the pH of the composition is from about pH 4.5 to 9.5.

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14. A process according to claim 13 wherein the cleaning composition comprises from about 1% to about 50% component (a), from about 10% to about 80% of component (c), and from about 20% to about 80% component (d), the percentages being weight % based on the total weight the composition.

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15. A process according to claim 13 wherein the nucleophilic amine component is at least one amine selected from the group consisting of 1-amino-2-propanol, 2-(2-aminoethoxy)ethanol, 2-aminoethanol, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethylamino)ethylamine, diethanolamine and triethanolamine.
16. A process according to claim 13 wherein component (c) is at least one compound selected from the group consisting of isopropanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 2-butene-1,4-diol, 2-methyl-2,4-pentanediol, hexanediol, glycerol, ethylene glycol monomethyl ether diethylene glycol monomethyl ether, propylene glycol dimethyl ether, and 2-(2-butoxyethoxy)-ethanol.
17. A process according to claim 13 wherein the organic co-solvent is a co-solvent having a solubility parameter of from about 8 to about 15.
18. A process according to claim 17 wherein the co-solvent is at least one compound selected from the group consisting of 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, 1-ethyl-2-pyrrolidinone, 1-propyl-2-pyrrolidinone, 1-hydroxyethyl-2-pyrrolidinone, a dialkyl sulfone, dimethyl sulfoxide, a tetrahydrothiophene-1,1-dioxide, dimethylacetamide and dimethylformamide.
19. A process according to Claim 18 wherein the solvent is selected from the group consisting of sulfolane and 1-methyl-2-pyrrolidinone, the nucleophilic amine is selected from the group consisting of monoethanolamine and 1-amino-2-propanol, component (c) is selected from the group consisting of ethylene glycol, propylene glycol, 2-methyl-2,4-pentanediol, glycerol, 2-butene-1,diol, isopropanol and 2-(2-butoxyethoxy)ethanol.

20. A process according to claim 13 wherein the acid component (b) is at least one acid having a pKa value of from 2 to 5.
- 5 21. A process according to claim 19 wherein the acid component (b) is at least one acid having a pKa value of from v 2 to 5.
22. A process according to claim 13 wherein component (b) comprises at least one acid selected from the group consisting of acetic acid, propanoic acid,
10 malonic acid, phenylacetic acid and hypophosphorus acid.
23. A process according to claim 19 wherein component (b) comprises at least one acid selected from the group consisting of acetic acid, propanoic acid, malonic acid, phenylacetic acid and hypophosphorus acid.
- 15 24. A process according to claim 13 wherein the nucleophilic amine comprises monoethanolamine, the co-solvent comprises 1-methyl-2-pyrrolidinone, the compound of component (c) is ethylene glycol and the acid of component (b) is acetic acid.
- 20 25. A process according to claim 13 wherein the microelectronic substrate is a substrate for a flat panel display.
26. A process according to claim 25 wherein the substrate has an
25 aluminum/neodymium layer.