

HOECHST AKTIENGESELLSCHAFT - WERK KALLE-ALBERT

REPLACED SHEETS 50

91/K 015

☒ Description : paged ... to paged ...
☒ Claim(s) : paged ... to paged ...
☐ Drawing(s) : paged ... to paged ...
☒ Abstract : paged ... to paged ...

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Radiation-sensitive mixture containing (naphthoquinone diazide)sulfonic acid mixed esters and radiation-sensitive recording material prepared therewith

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The invention relates to a radiation-sensitive mixture containing a resinous binder which is insoluble in water, but soluble or at least swellable in aqueous alkaline solutions and at least one radiation-sensitive compound.

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The radiation-sensitive layer of conventional copying materials is essentially composed of a mixture of an alkali-soluble cresol-formaldehyde novolak and radiation-sensitive compounds, such as 1,2-benzo- or o-naphthoquinone 2-diazide derivatives. The novolak is soluble per se in aqueous alkaline solutions, but the radiation-sensitive o-quinone diazide compounds act as solution inhibitors. During the imagewise exposure of the layer to actinic radiation, the radiation-sensitive diazocarbonyl compound is converted into a carboxylic acid via a ketene intermediate. The carboxylic acid is readily soluble in aqueous alkaline solution and, consequently, also enhances the solubility of the novolak. The preparation of novolaks is described, for example, by A. Knop and W. Scheib in "Chemistry and Application of Phenol Resins", Chapter 4, Springer, New York 1979.

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The exposed regions of the copying layer dissolve in the alkaline developer solution, while the unexposed regions remain essentially unaltered and intact, with the result that a positive relief image of the master is produced on the layer support.

The solubility behavior described can, however, also be reversed. For this purpose, the recording layer is subjected to a heat treatment after imagewise irradiation.

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tion. Under these circumstances, the resin molecules of the layer crosslink in the regions of the layer affected by the light. The process, referred to as "curing", requires, as a rule, the presence of a "crosslinking agent" which brings about the crosslinking and, consequently, the curing during the heat treatment, under the influence of the acid which has been produced from the o-quinone diazide during the exposure. During curing, heating is carried out to temperatures below the decomposition temperature of the o-quinone diazide. The heating can be carried out by irradiation, placing in a stream of hot gas, contact with heated surfaces, for example with heated rollers, or by immersion in a heated bath of an inert liquid, for example water. The temperature is in general between 100 and 150°C, preferably between 90 and 130°C.

Efficient crosslinking agents are generally compounds which readily form a carbonium ion under the acid and temperature conditions described. Examples of these are the hexamethylolmelamine esters in accordance with DE-A 33 25 022 (= US-A 4,581,321) and also the compounds described in EP-A 0 212 482, such as 1,4-bishydroxymethylbenzene and 4,4'-bismethoxymethyl diphenyl ether, which contain two or more aromatically bound hydroxymethyl or alkoxymethyl groups. 2,6-Bishydroxymethyl-4-methylphenol in accordance with US-A 4,404,272 is also known as a crosslinking agent.

After the heat treatment, the photoresist layer is, as a rule, subjected to a whole-surface exposure ("flood exposure") in order to render the still radiation-sensitive layer regions completely alkali-soluble.

The flood exposure is in general carried out with the same light source as was also used for the image exposure.

The development following the flood exposure is in



general carried out with one of the aqueous alkaline solutions which are also used to develop a positive-working photoresist. These are, for example, aqueous solutions of sodium hydroxide, tetramethylammonium hydroxide, trimethyl(hydroxyethyl)ammonium hydroxide, alkali-metal phosphates, alkali-metal silicates or alkali-metal carbonates, which solutions may contain wetting agents or fairly small amounts of organic solvents. During the development, the layer regions not affected by light in the original image exposure are washed out, with the result that a negative resist image of the master is obtained.

In most cases, the exposed and developed resist material is then treated with an etchant, in which process the etchant is only able to act on the layer support in the non-image regions. In this way, a negative etching image is produced on the layer support in the case of a positive-working copying layer and a positive etching image in the case of a negative-working copying layer.

The positive or negative relief image of the copying layer produced on the layer support by the processes described is suitable for various application purposes, inter alia as exposure mask or as an image in the production of semiconductor components in microelectronics, as a printing form for letterpress, gravure or lithographic printing, and also for the production of nickel rotary cylinders in an electroplating process.

The commercial suitability of a copying layer, for example a photoresist layer, is assessed, inter alia, on the basis of the radiation sensitivity, the development and image contrast, the resolution and the adhesion to the layer support.

A high radiation sensitivity of the mixture is an important factor in the manufacture of microelectronic circuits or components, especially in the so-called "in-line"



processing of wafers, in which the throughput of wafers is determined by the longest lasting process step. With the relatively long exposure times hitherto necessary, the exposure equipment throughput is the limiting factor.

5 The exposure equipment cycle times are too long, especially with monochromatic irradiation and with irradiation using shorter-wave actinic light, and this results in an unduly low production rate.

The resist resolution relates to the capability of a photoresist system to reproduce even the finest lines and gaps of a mask used for the exposure, the exposed and developed regions being required to exhibit a high degree of edge steepness and sharpness.

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In many technical application fields, in particular in the production of semiconductor components in microelectronics, the photoresist has to achieve a particularly high resolution as very small line and gap widths ($< 1 \mu\text{m}$) have to be reproduced. The ability to reproduce extremely small details in the order of magnitude of $1 \mu\text{m}$ and less is of the greatest importance for the large-scale production of integrated circuits on silicon chips and similar components. If photographic processes are used, the integration density on such a chip can be increased by increasing the resolving power of the photoresist.

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It is known that the resolution of a photoresist increases if photoactive compounds containing a plurality of radiation-sensitive radicals in one molecule are present in it, since the radiation-sensitive component in the mixture is then increased. [P. Trefonas III and B. K. Daniels, "New Principle for Image Enhancement in Single Layer Positive Photoresists", SPIE Advances in Resist Technology and Processing IV, 771 (1987), 194-210; P. Trefonas III, B. K. Daniels and R. L. Fischer, "Photoresist Design for Submicron Optical Lithography: Application of Polyphotolysis", Solid State Technology 30

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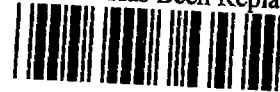
(1987), 131-137].

If the mixed esters mentioned in EP-A 0 244 762 and 0 244 763 are used, an improved resolution can already be observed. DE-A 38 37 500 reveals the superior properties of ring-substituted naphthoquinone diazide derivatives in lithographic applications. Esters of optionally substituted (o-naphthoquinone 2-diazide)-4- or -5-sulfonic acids with compounds which possess three or more aromatic hydroxyl groups often have, however, an unduly low solubility in the standard solvents, and this has the result that the resists prepared with these esters still do not achieve an adequate resolution.

The object was therefore to provide novel mixtures exhibiting increased radiation sensitivity and improved solubility in the solvents used in industry.

This object is achieved by a mixture which contains, as radiation-sensitive component, an ester of a) a compound containing 2 to 6 aromatic hydroxyl groups, b) a ring-substituted (o-naphthoquinone 2-diazide)-4-sulfonic acid (diazocompound D_1) and c) an (o-naphthoquinone 2-diazide)-4- or -5-sulfonic acid which is not further substituted (diazocompound D_2) and/or a non-radiation-sensitive organic acid (compound D_0), where the $D_1:(D_2 \text{ and/or } D_0)$ molar ratio is between 0.1:1 and 30:1. The esters and their preparation are described in the co-pending patent application, Serial No. (Hoe 91/K 014.). The alkali-soluble binder is preferably a novolak, a poly(vinylphenol) or a poly(vinylalkylphenol).

The radiation-sensitive mixture is, in general, applied to a support material in the form of a solution in an organic solvent. Suitable solvents are, for example, glycol ethers, such as ethylene glycol monomethyl ether or monoethyl ether and also their acetates, such as propylene glycol methyl ether acetate, esters, such as ethyl or butyl acetate, ketones, such as methyl ethyl



ketone, cyclopentanone and cyclohexanone and also aromatic hydrocarbons, such as toluene and xyleneol. Mixtures of these solvents can also be used.

5 The proportion of binder in the mixture is, in general, about 15 to 99% by weight, preferably about 50 to 97% by weight and particularly preferably about 63 to 93% by weight, based on the total weight of the solid constituents in the radiation-sensitive mixture.

10 The proportion of radiation-sensitive compound is about 1 to 50% by weight and preferably about 3 to 35% by weight, based on the total weight of the solid constituents in the mixture.

15 To prepare a solution of the radiation-sensitive mixture, the binder and the radiation-sensitive compound are mixed with a sufficient quantity of solvent to give a solvent proportion of about 40 to 90% by weight, preferably about 60 to 85% by weight.

20 Before application to a layer support, additives may also be added to the radiation-sensitive solution, such as, for example, crosslinking agents, dyes, levelling agents, plasticizers, adhesion promoters, development accelerators, surfactants, for example non-ionic surfactants.

25 Suitable as dyes are, for example, methyl violet 2B (C.I. 42 535), crystal violet (C.I. 42 555), malachite green (C.I. 42 000), Victoria blue B (C.I. 44 045), neutral red (C.I. 50 040), coumarine dyes and styryl dyes, in accordance with EP-A 0 070 445 or DE-A 37 35 852. These dyes are added in an amount of 1 to 10% by weight, based on
30 the total weight of binder and radiation-sensitive compound.

Levelling agents can be used in an amount of up to 5% by weight, based on the total weight of binder and radi-



ation-sensitive compound.

Suitable plasticizers are, for example, phosphate tri-(β -chloroethyl), stearic acid, dicamphor, polypropylene, acetal resins, phenoxy resins and alkyd resins, which can be added in proportions of 1 to 10% by weight, based on the total weight of binder and radiation-sensitive compound. The plasticizers added improve the coating characteristics of the mixture and make it possible to apply the mixture in a smooth and uniformly thick layer to the layer support.

Suitable adhesion promoters for improving the adhesion of the mixture on the support comprise specific organo-silicon compounds, for example 3-aminopropyltriethoxysilane, in a proportion of up to 4% by weight, based on the total weight of binder and radiation-sensitive compound.

The development accelerators added may be aromatic carboxylic acids or aromatic polyhydroxy compounds, such as polyhydroxybenzophenone, picric, nicotinic and nitrocinnamic acids, in a proportion of up to 20% by weight, based on the total weight of binder and radiation-sensitive compound. These accelerators lead to an increase in the solubility of the radiation-sensitive layer, both in the exposed and unexposed regions. They are therefore used in those applications in which the speed of development is of prime importance. While the exposed regions of the layer are more rapidly dissolved by the developer as a result of the addition of accelerators, the development accelerators also give rise at the same time to a relatively large loss of layer from the unexposed regions, with the result that a loss of contrast may occur.

Suitable non-ionic surfactants are, for example, polyethylene glycol monononylphenyl ether, polyethylene glycol mono-octylphenyl ether and polyethylene glycol monodinonylphenyl ether, which are used in a proportion



of up to 10% by weight, based on the total weight of binder and radiation-sensitive compound.

Suitable crosslinking agents are described in EP-A 0 212 482 and US-A 4,404,272. These are generally added to a radiation-sensitive mixture intended for use in a negative-working layer, for example a negative-working photoresist. The crosslinking agents are mainly aromatic compounds containing two or more hydroxymethyl or alkoxy-methyl groups in a molecule, such as 1,2-bishydroxymethylbenzene, 1,2-bismethoxymethylbenzene, 1,2-bis-hydroxymethylfuran, 2,6-bishydroxymethyl-4-methylanisole, 1,4-bis(α -hydroxybenzyl)benzene, 2,5-dimethyl-1,4-bis-hydroxymethylbenzene, 4,4'-bishydroxymethyldiphenyl ether, 4,4'-dimethoxydiphenyl, 2,6-bishydroxymethyl-4-methoxy or -4-ethoxyphenol, 4,4'-bismethoxymethyldiphenyl ether and epoxycresol novolak resins and also alkoxy-methylmelamine derivatives. Particularly preferred are: 2,6-bishydroxymethyl-4-methyl-, -4-ethyl-, -4-propyl-, -4-isopropyl-, -4-n-butyl-, -4-tert-butyl- and -4-(2-phenyl-2-propyl)phenol.

The crosslinking agents can be used in proportions of 1.5 to 20% by weight, based on the total solids content of the radiation-sensitive mixture.

In the presence of acid and at elevated temperature, the binder molecules are "crosslinked" by said crosslinking agents, i.e. the radiation-sensitive layer is cured. The acid required to cure the layer is formed as a result of the photoreaction of the radiation-sensitive compound.

The radiation-sensitive mixture of the present invention exhibits an improved stability in solution and improved storability. The resolution is better than in comparable, prior art radiation-sensitive mixtures.

The invention furthermore relates to a radiation-sensitive recording material which essentially comprises



a a layer support and a radiation-sensitive layer formed from a mixture of the above-described type and to a process for preparing the recording material.

5 Suitable support materials are, for example, silicon, aluminum or polymeric resins, silicon oxide, doped silicon oxide, silicon nitride, tantalum, copper, polysilicon, ceramics and aluminum/copper alloys.

10 To prepare the recording material according to the invention, the radiation-sensitive mixture, for example a photoresist, can be applied to the support by processes conventionally employed in industry, such as immersion, spraying and spin-coating. In the spin-coating process, the proportion of solids in the resist solution is adjusted in such a way that, depending on the spin-coating apparatus used in the individual case and the period of time fixed for the spin-coating operation, a coating in the desired thickness is obtained.

20 The radiation-sensitive mixtures prepared according to the process described are particularly well suited for application to silicon wafers which carry a layer of silicon oxide, such as those used in the manufacture of microprocessors and other semiconductor components used in microelectronics. A wafer of gallium arsenide, of aluminum having an oxide layer or of silicon having a layer of metallic aluminum or of oxidatively aftertreated aluminum may also be used. The support may also be made of various polymeric resins, in particular of transparent polymers, for example polyesters.

30 After applying the radiation-sensitive mixture to the layer support, the solid-liquid composite is subjected to a pre-drying operation at about 80 to 105°C. This heat treatment is continued until nearly all of the solvent has evaporated and a thin layer of about 1 μm is left on the layer support.



The coated support is then imagewise exposed in a known manner using actinic radiation, in particular UV radiation having wavelengths of 248, 365, 405 or 436 nm, through appropriate masks, negatives or stencils etc. or exposed to directed electron radiation or to the radiation of a laser. The term "actinic radiation" comprises both the X-ray region and electromagnetic radiation in the technically applicable wavelength range from 193 to 450 nm and also electron radiation.

For the purpose of development, the imagewise exposed recording materials are immersed in an aqueous alkaline developer solution. Spray developing processes are also frequently used in industry.

After removal from the developer solution, the material can be subjected to a heat treatment or baking treatment, respectively, to increase the adhesion and the chemical resistance of the layer to etching solutions and other substances. Heat treatment after development may comprise oven curing of layer and support at temperatures below the softening point of the layer.

For industrial applications, in particular in the manufacture of semiconductor components on silicon supports having a silicon oxide layer, the developed supports can be treated with a buffered etching solution based on hydrofluoric acid. The photoresist mixtures according to the invention are resistant to acidic etching solutions and guarantee an effective protection of the unexposed regions of the support, which are coated with the photoresist mixture.

The radiation-sensitive mixtures according to this invention are not only suitable for use as photoresist mixtures, but can also be used for printing plates and color proofing films.

If the recording material which is produced by coating a



support with the mixture according to the invention and which may additionally contain a crosslinking agent is used in the negative-working image reversal process, imagewise exposure is followed by a second, brief heat treatment at a temperature between 90 and 150°C. During this heat treatment, the binder is cured in the exposed regions of the photoresist layer. The heat treatment time is between 10 and 90 seconds. After heat treating and cooling the recording material, the photoresist layer is developed or is, preferably prior to developing, subjected to a whole-surface UV irradiation (flood exposure). The developers used comprise aqueous alkaline solutions containing inorganic or quaternary organic bases. The developers may be buffered or contain additional additives (for example wetting agents). In this process, the regions of the layer, which were not exposed during imagewise exposure, are washed out, while the regions of the layer, which were exposed during imagewise exposure, are not attacked (negative process). As a result, a negative relief copy of the exposure mask is obtained.

It is also possible to combine positive and negative processes on one layer support (photocomposing).

In the examples which follow, the radiation-sensitive mixtures and recording materials are explained in greater detail.

Examples

For the lithographic comparison, radiation-sensitive mixtures were formulated. They exclusively contain completely esterified derivatives of 2,3,4,4'-tetrahydroxybenzophenone (Examples 1 to 6) and of 2,3,4,3',4',5'-hexahydroxybenzophenone (Examples 7 to 10).

The derivatives are esterified with 7-methoxy(1,2-naphthoquinone 2-diazide)-4-sulfonic acid (D_1) and



(1,2-naphthoquinone 2-diazide)-4-sulfonic acid (D_2) in the $D_1:D_2$ molar ratio of 0.33:1 (Example 1) or 4.71:1 (Example 2). In Comparative Examples 3, 4 and 10, the hydroxybenzophenones are esterified only with (1,2-naphthoquinone 2-diazide)-4-sulfonic acid and in Comparative Examples 5 and 6 only with 7-methoxy(1,2-naphthoquinone 2-diazide)-4-sulfonic acid.

In Examples 7 to 9, the hexahydroxybenzophenones are in each case esterified with 7-methoxy(1,2-naphthoquinone 2-diazide)-4-sulfonic acid (D_1) and a non-radiation-sensitive acid (D_0) in the $D_1:D_0$ molar ratio of 5:1. The non-radiation-sensitive acid is stearic acid (Example 7), 2-ethylhexyl carbonate (used as 2-ethylhexyl chloroformate) (Example 8) or methanesulfonyl chloride (Example 9).

a) Mixtures according to the invention:

To the 26%-strength solution of a cresol/xlenol novolak in methoxypropanol acetate there are added, based on the novolak, 28% (in the case of derivatives of tetrahydroxybenzophenone) or 43% (in the case of derivatives of hexahydroxybenzophenone) of the photoactive compound and dissolved.

b) Comparative examples:

The corresponding naphthoquinone diazide is added to the novolak solution mentioned under a) until the solution is saturated and undissolved material is filtered off.

These resist solutions are used for spin-coating silicon wafers and the layers thus obtained are dried for 60 seconds on a hot plate at 90°C. The layer thickness is 1.30 μm . After exposure through a mask containing patterns of various dimensions using an exposure apparatus conventionally employed in industry, the layers are again heat-treated for 60 seconds on the hot plate at 100°C. The regions of the layer affected by the light



are then dissolved by means of a developer solution (development time 60 seconds) so that the unexposed regions of the layer remain on the silicon wafer.

As shown by the table below, considerably smaller patterns can be produced using the mixtures of the present invention.

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Lithographic characteristics

Example No.	Normality of developer	Smallest patterns which can be resolved*) (dimensionally true reproduction of mask patterns)	Layer removal rate in the non-exposed region (nm/min)
1	0.24	0.65 μm	36
2	0.24	0.65 μm	45
3 (comparison)	0.24	cannot be patterned	>1 300
4 (comparison)	0.15	cannot be patterned	46
5 (comparison)	0.24	cannot be patterned	>1 300
6 (comparison)	0.15	cannot be patterned	52
7	0.24	0.70 μm	33
8	0.24	0.65 μm	32
9	0.24	0.65 μm	36
10 (comparison)	0.24	1.15 μm	71

*) Larger patterns are, at the same time, reproduced true to the mask



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Patent Claims

- 5 1. A radiation-sensitive mixture containing a resinous binder which is insoluble in water, but soluble or at least swellable in aqueous alkaline solutions and at least one radiation-sensitive compound, wherein the radiation-sensitive compound is an ester of a) a compound
10 containing 2 to 6 aromatic hydroxyl groups, b) a ring-substituted (o-naphthoquinone 2-diazide)-4-sulfonic acid (diazocompound D_1) and c) an (o-naphthoquinone 2-diazide)-4- or -5-sulfonic acid which is not further substituted (diazocompound D_2) and/or a non-radiation-sensitive
15 organic acid (compound D_0), where the $D_1:(D_2 \text{ and/or } D_0)$ molar ratio is between 0.1:1 and 30:1.
2. The radiation-sensitive mixture as claimed in claim 1, wherein the resinous binder comprises a novolak, a poly(vinylphenol) or a poly(vinylalkylphenol).
- 20 3. The radiation-sensitive mixture as claimed in claim 1 or 2, wherein the mixture additionally contains cross-linking agents, dyes, levelling agents, plasticizers, adhesion promoters, development accelerators and/or surfactants.
- 25 4. The radiation-sensitive mixture as claimed in one or more of claims 1 to 3, wherein the binder is present in a proportion of 15 to 99% by weight of the solid constituents of the mixture.
- 30 5. The radiation-sensitive mixture as claimed in one or more of claims 1 to 4, wherein the radiation-sensitive compound is present in a proportion of 1 to 50% by weight, preferably 3 to 35% by weight, of the solid constituents of the mixture.





6. A radiation-sensitive recording material which essentially comprises a layer support and a radiation-sensitive layer, wherein the radiation-sensitive layer consists essentially of the radiation-sensitive mixture
5 as claimed in one or more of claims 1 to 5.

7. The recording material as claimed in claim 6, wherein the layer support comprises a silicon or gallium arsenide wafer to which at least one further layer is additionally applied between the semiconducting material
10 and the radiation-sensitive layer.

