

The present invention relates to a positive-working photosensitive composition comprising a photosensitive compound, a binder that is insoluble in water and soluble or swellable in an aqueous-alkaline solution, and a dye.

Photosensitive compositions containing a novolak or a polyvinyl phenol as the binder and, for example, an o-quinone diazide as the photosensitive compound have been in use for a long time for the preparation of high-resolution patterns in the fabrication of semiconductor devices. Due to the advancing miniaturization of functional element increasingly high requirements are demanded of the optical resolution of these photosensitive compositions. Difficulties have, in particular, to be expected when patterning is effected in the vicinity of the limit of resolution of the optical exposure systems. In these critical areas, resolution is, above all, influenced by disturbing optical effects, such as interference phenomena and undesirable reflexions of scattered light from the substrate surface. Effects of this kind can partly be avoided by increasing the non-bleachable absorption of the photosensitive compositions. For this purpose, for example, substances which absorb light in the actinic region are added to the photosensitive compositions.

It has been known for a long time to add absorbing substances to photosensitive compositions. As described in EP-A 0 026 088, for example, the image pattern produced can be improved by adding dyes to negative-working photoresists.

The addition of dyes to positive-working photoresists has been described for the first time by A. R. Neureuther and F. H. Dill ("Photoresist Modeling and Device Fabrication Applications", in Proceedings of Symposium on Optical and Acoustical Micro-Electronics, Polytechnic Institute of New York, April 16 to 18, 1974, pages 223-249). According to this publication, the dye addition, in the first place, reduces the adverse influences of interference effects on the optical resolution.

According to the paper "Submicron Optical Lithography: I-line Lens and Photoresist Technology" [SPIE Proceedings, Vol. 470, pages 22-23 (1984)] by H. L. Stover, M. Nagler, I. I. Bol and V. Miller, optical resolution is markedly improved by the addition of an absorbing dye which absorbs light in the region of the exposure wavelengths of $\lambda = 436$ nm while, at the same time, the exposure time required to generate image patterns has to be considerably extended, compared with a system which does not contain this absorbing substance.

PCT WO 86/01914 describes a process, in which the production of photoresist patterns is also improved by the use of a non-bleachable, light-absorbing addition. Also in this case it is pointed out that the exposure time has to be extended by about 50 to 150 %, compared with a photoresist without additive substance. Particularly preferred dyes mentioned comprise coumarin derivatives.

A coumarin derivative is also described by I. I. Bol in "High-Resolution Optical Lithography Using Dyed Single-Layer Resist" (Proceedings Kodak Microelectronics Seminar 1984, pages 19-22) and the significant improvement of the photolithographic properties of a photoresist is confirmed.

The influence of substances absorbing light in the actinic region on the photolithographic properties of positive-working photoresists is described in detail by A. V. Brown and W. H. Arnold in "Optimization of Resist Optical Density for High Resolution Lithography on Reflective Surfaces" [SPIE Proceedings, Vol. 539, pages 259-266 (1985)] and by M. P. C. Watts, D. DeBruin and W. H. Arnold in "The Reduction of Reflective Notching Using Dyed Resists" (Proceedings of Seventh International Technical Conference on Photopolymers, Ellenville, N.Y., October 1985, pages 285-296). According to these investigations, the solubility of the photoresist compositions in the aqueous-alkaline developers used is reduced by the addition of substances absorbing light in the actinic region and, as a consequence, the photosensitivity of these photoresists is lowered considerably.

In their paper "Improving Linewidth Control over Reflective Surfaces Using Heavily Dyed Resists" [Journal of the Electrochemical Society, Vol. 133, No. 1, pages 192-196 (1986)], T. R. Pampalone and K. A. Kuyan describe the influence of high concentrations of absorbing substances in a photoresist. According to these investigations particularly good results are obtained with photoresists having a very high absorption in the actinic region. Also in this

case it is found that the absorbing compound added clearly reduces photosensitivity, i.e. by the factor 5 or even more.

US-A 4,575,480 also describes photoresist formulations containing substances which absorb light in the actinic region. The compounds mentioned are distinguished by their low tendency to sublimation and their high absorption in the actinic region. It is a disadvantage of these photoresist formulations that - depending on the concentration of the substance added - they partly have a markedly reduced photosensitivity.

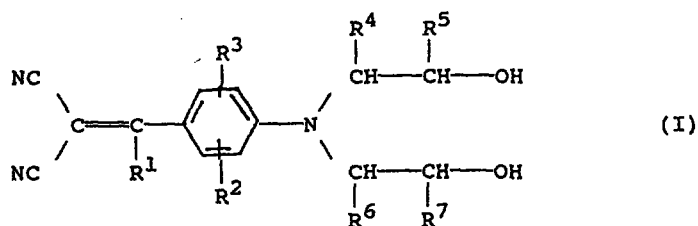
Similarly, Japanese Patent Applications 86-159626/25, 86-165777/26, 86-174465/27 and 86-174466/27 describe photoresist formulations which contain absorbing substances that are non-bleachable and do not sublime. In all cases, however, the exposed portions of the resists have a noticeably reduced solubility in the developer solutions.

Photoresists which, apart from a dye absorbing light in the actinic region, also contain a component which increases their solubility, in particular a trihydroxybenzophenone, are described in US-A 4,626,492. The trihydroxybenzophenone is added in quantities ranging from 12.8 to 13.1 % by weight, which, however, leads to a considerable deterioration of the thermal stability of the photoresist. Moreover, a decline in the processing latitude of the resist is observed, since the developing rate strongly depends on the pre-baking temperature of the resist film.

It is therefore an object of the present invention to provide a positive-working photosensitive composition containing a non-bleachable dye which absorbs light in the actinic region and which should either have or produce the following properties:

- good solubility in the solvent or solvent mixture of the photosensitive composition, so that undesirable deposits are not formed during storage of the composition, in particular at low temperatures,
- good thermal stability and low tendency to sublime, so that, on the one hand, constant absorption of actinic radiation is ensured - even at high temperatures - and, on the other hand, contamination of process equipment is kept as low as possible,
- high absorption in the region of actinic radiation in order to minimize undesirable optical effects in an efficient manner.

The object of the invention is achieved by providing a positive-working photosensitive composition comprising a photosensitive compound, a binder that is insoluble in water and soluble or swellable in an aqueous-alkaline solution, and a dye, wherein the dye comprises a non-bleachable compound which absorbs light in the actinic region and corresponds to the general formula I



wherein

R₁ denotes hydrogen, alkyl, aryl, alkoxy or nitrilo,

R₂ and R₃ are identical or different and denote
hydrogen, hydroxy, alkyl, aryl, alkoxy, aryloxy,
nitrilo, amino, alkylamino or halogen,

R₄, R₅, R₆ and R₇ are identical or different and denote
hydrogen, hydroxy, alkyl, aryl, alkoxy, aryloxy,
amino, alkylamino or halogen.

Compounds corresponding to the above-indicated general
formula I are characterized in that they meet the
requirements of high absorption in the actinic region
to a special degree.

Particularly unexpected properties of the photosensiti-
ve composition according to the invention, which may be
mentioned in addition to those indicated above,
include:

- higher photosensitivity of the composition accor-
ding to the present invention, compared with photo-
sensitive compositions containing other dyes which
are not claimed, but which also absorb light in the
actinic region,
- no or only slight reduction of the photosensitivity
of the photosensitive composition of the invention,
compared with photosensitive compositions that do
not contain dyes or contain other dyes.

Preferred dyes absorbing light in the actinic region are, in particular, those which, corresponding to the general formula I, contain as

R_1 hydrogen, (C_1-C_3) alkyl or phenyl,

R_2 and R_3 hydrogen, hydroxy, (C_1-C_3) alkyl, (C_6-C_{10}) aryl, (C_1-C_3) alkoxy, amino, (C_1-C_3) alkylamino, halogen, in particular, chlorine or bromine and as

R_4 , R_5 , R_6
and R_7 hydrogen, (C_1-C_3) alkyl, (C_6-C_{10}) aryl, (C_1-C_3) alkoxy, amino or halogen, in particular chlorine.

Preference is given to those dyes of the general formula I, in which

R_1 denotes hydrogen,

R_2 and R_3 denote hydrogen, hydroxy, (C_1-C_3) alkyl, phenyl, amino or chlorine, R_2 and/or R_3 being, in particular, hydroxy, (C_1-C_3) alkyl or phenyl and these being, in each case, preferably in the o-position with respect to the tertiary aromatic amino group and

R_4 and R_6
and

R_5 and R_7 are identical and denote hydrogen, (C_1-C_3) alkyl, (C_1-C_3) alkoxy, amino or chlorine.

Particularly preferred are those dyes of the general formula I, in which

R_1 denotes hydrogen,

R_2 and R_3 denote hydrogen, hydroxy or (C_1-C_3) alkyl and

R_4 and R_6
and

R_5 and R_7 are identical and denote hydrogen or
 (C_1-C_3) alkyl

and of these those are preferred, in which the radicals R_1 to R_7 are consistently hydrogen and those, in which the radicals R_1 and R_3 to R_7 are consistently hydrogen and R_2 is methyl.

Of these dyes those are preferably employed, which have absorption capacities coinciding as exactly as possible with the wavelength of the actinic radiation used and being, in particular, in the emission range of mercury vapor lamps, especially in the range from 365 to 436 nm and particularly preferably at wavelengths of $\lambda = 365$, 405 or 436 nm. The quantity of dye required to obtain the desired absorption is thus reduced to the minimum.

The concentration of the absorbing dye can range from 0.05 to 2 % by weight, preferably from 0.2 to 0.8 % by weight, based on the non-volatile constituents of the photosensitive composition.

The quantity of dye added in each case is naturally dependent on the molar coefficient of extinction of the dye at the respective exposure wavelength. If the quantity of absorbing dye used is too low, the effects of reflexion are only insignificantly reduced and the photolithographic properties are either not at all or

only slightly improved. On the other hand, too high a concentration of absorbing compound leads to a deterioration of image quality, since the areas of the resist layer which are relatively close to the exposure source are too strongly exposed, while the areas of the layer which are in the vicinity of the substrate are still insufficiently exposed.

The compounds which absorb light in the actinic region, corresponding to formula I, can be prepared according to the processes described in US-A 2,206,108 and US-A 2,583,551 and in DE A-31 28 159.

The photosensitive compositions according to the present invention also contain a radiation-sensitive or photosensitive compound or a radiation-sensitive or photosensitive combination of compounds. Compounds which may be used are positive-working compounds, i.e. those which are rendered soluble upon exposure. These include, on the one hand, o-quinone diazides and, on the other hand, combinations of photolytic acid donors with acid-cleavable compounds, for example, orthocarboxylic acid or acetal compounds.

O-quinone diazides are known, for example, from DE-C 9 38 233 and DE-C 15 43 721 and from DE-A 23 31 377, DE-A 25 47 905 and DE-A 28 28 037. Preferably used o-quinone diazides comprise 1,2-naphthoquinone-2-diazide-4- or -4-sulfonic acid esters or amides. Of these, the esters, especially the esters of sulfonic acids, are particularly preferred. The quantity of o-quinone diazide compounds contained in the photosensitive composition of the present invention usually ranges from 3 to 50 % by weight, preferably from 7 to 35 % by weight, based on the non-volatile constituents of the composition.

Of the acid-cleavable materials the following are used:

- a) Compounds containing at least one orthocarboxylic ester and/or carboxyamide acetal group; it being possible for the compounds to have a polymeric character and for the groups mentioned to be present as linking members in the principal chain or as lateral substituents;
- b) oligomeric or polymeric compounds containing recurrent acetal and/or ketal groups in the principal chain;
- c) compounds having at least one enol ether or N-acyliminocarbonate group; and
- d) cyclic acetals or ketals of β -ketoesters or amides;
- e) compounds containing silylether groups;
- f) compounds containing silylenolether groups;
- g) monoacetals or monoketals, the aldehyde or ketone components of which have a solubility in the developer, which varies between 0.1 and 100 g/l;
- h) ethers based on tertiary alcohols; and
- i) carboxylic acid esters and carbonates of tertiary allylic or benzylic alcohols.

Acid-cleavable compounds of type a), which are used as components of radiation-sensitive compositions are described in detail in DE-A 29 28 636

(= EP-A 0 022 571) and DE-A 26 10 842 and in US-A 4,101,323; compositions containing compounds of type b) are described in DE-C 23 06 248 (= US-A 3,779,778) and DE-C 27 18 254; compounds of type c) are described in EP-A 0 006 626 and EP-A 0 006 627 and compounds of type d) in EP-A 0 202 196; compounds corresponding to type e) are presented in DE-A 35 44 165 and DE-A 36 01 264; compounds of type f) are disclosed in DE-A 37 30 783, and compounds of type g) in DE-A 37 30 785 and 37 30 787. Compounds of type h) are described, for example, in US-A 4,603,101 and compounds of type i), for example, in US-A 4,491,628 and by J. M. Fréchet et al. in J. Imaging Sci., 30, 59-64 (1986).

Preferred compounds contain C-O-C groups which can be split by acid.

US-A 4,101,323 describes orthocarboxylic acid derivatives and of these the bis-1,3-dioxan-2-yl ethers of aliphatic diols are used in particular. Of the polyacetals described in DE-C- 27 18 254 those containing aliphatic aldehyde and diol units are preferred.

Other suitable compositions are disclosed in EP-A 0 022 571. This publication describes polymeric orthoesters with recurrent orthoester groups in their principal chain, as acid-cleavable compounds. These groups comprise 2-alkylethers of 1,3-dioxo-cycloalkanes having 5 to 6 ring members. Particularly preferred are polymers with recurrent 1,3-dioxo-cyclohex-2-yl alkylether units, wherein the alkylether group can be interrupted by ether oxygen atoms and is preferably linked to the 5-position of the adjacent ring.

The photosensitive or radiation-sensitive acid donors contained in these compositions primarily comprise organic halogen compounds. The halogen compounds include, in particular, the triazine derivatives disclosed in US-A 3,515,552; US-A 3,536,489 and US-A 3,779,778 and in DE-C 27 18 259, 33 27 024, 33 33 450, 23 06 248, 22 43 621 and 12 98 414. These triazine derivatives can, however, also be used in combination with other photoinitiators, for example, oxazoles, oxadiazoles or thiazoles or in mixtures with each other.

Oxazoles, oxadiazoles, thiazoles or 2-pyrones containing trichloro or tribromomethyl groups are also known (DE-A 30 21 599, 30 21 590, 28 51 472, 29 49 396; EP-A 0 135 348 and 0 135 863).

This general term also includes, in particular, aromatic compounds, in which halogen, preferably bromine, is attached to the aromatic ring. Compounds of this type are, for example, known from DE-A 26 10 842.

The amount of acid-cleavable compounds contained in the photosensitive composition according to the present invention is, in general, in the range from 8 to 65 % by weight, preferably from 14 to 44 % by weight, based on the non-volatile constituents of the composition. The amount of acid-forming compounds ranges from 0.1 to 10 % by weight, preferably from 0.2 to 5 % by weight, also based on the non-volatile constituents of the composition.

In addition to the above-described photosensitive constituents the coating solutions of the present invention comprise polymeric binders. The preferred polymers are insoluble in water and soluble or at least swellable in aqueous-alkaline solutions.

Alkali-soluble or at least alkali-swellaable binders which may be mentioned comprise natural resins, such as shellac and colophony, and synthetic resins, such as copolymers of styrene and maleic anhydride or copolymers of acrylic acid or methacrylic acid, in particular, with acrylic or methacrylic acid esters, and especially novolak resins.

Novolak condensation resins which have proved suitable include, in particular, the relatively highly condensed resins with substituted phenols as the condensation partners of formaldehyde. Examples of these are phenol-formaldehyde resins, kresol-formaldehyde resins, the co-condensates and mixtures thereof and phenol and kresol condensates with formaldehyde.

Instead of or in admixture with novolaks, phenolic resins of the type of poly(4-vinylphenol) can also advantageously be used.

The type and quantity of the alkali-soluble resins used can vary according to the intended application; preference is given to amounts ranging from 30 to 90 % by weight, particularly preferably from 55 to 85 % by weight, based on total solids contained in the composition.

A great number of other resins can additionally be used; preferred are vinyl polymers, such as polyvinyl acetates, poly(meth)acrylates, polyvinyl ethers, polyvinyl pyrrolidones and styrene polymers, which themselves may be modified by comonomers. The following are mentioned in particular: polymers of styrene containing units of alkenylsulfonyl-aminocarbonyloxy- or cyclo-

alkenylsulfonyl-aminocarbonyloxy- (EP-A 0 184 804); polymers of acrylic, methacrylic, maleic, itaconic acid, etc. having lateral, crosslinking $-CH_2OR$ groups (EP-A 0 184 044); polymers of vinyl monomers containing alkenyl phenol units (EP-A 0 153 682); polyvinyl phenols as substitutes for novolak (DE-C 23 22 230); polymeric binders with lateral phenolic hydroxyl groups (EP-A 0 212 439 and EP-A 0 212 440); styrene-maleic anhydride copolymers (DE-A 31 30 987); polymers formed from unsaturated (thio)-phosphinic acid iso(thio)cyanates with a polymer containing active hydrogen (DE-A 36 15 612 and 36 15 613); polymers containing vinyl acetate, vinyl alcohol and vinyl acetal units (EP-A 0 216 083) and polyvinyl acetals having units of hydroxyaldehydes DE-A 36 44 162).

The most favorable amount of these resins used in the binder of the photosensitive composition according to the present invention depends on application-related requirements and on their influence on development conditions and is, in general, not more than 20 % by weight of the alkali-soluble resin.

The photosensitive compositions of the present invention can optionally also be admixed with dyes, finely divided pigments, plasticizers, wetting agents and levelling agents and, in addition, polyglycols, cellulose derivatives, e.g. ethyl cellulose, to improve specific properties, such as flexibility, adhesion and gloss.

Also, the photosensitive composition may be admixed with customary crosslinking substances. Compounds of this kind are stated in EP-A 0 212 482.

The photosensitive composition of the invention is preferably dissolved in solvents comprising, for example, ethylene glycol; glycol ethers, such as glycol monomethyl ether, glycol dimethyl ether, glycol monoethyl ether or

propylene glycol monoalkyl ethers, in particular propylene glycol methyl ether; aliphatic esters, such as ethyl acetate, hydroxyethyl acetate, alkoxyethyl acetate, n-butyl acetate, propylene glycol monoalkylether acetate, in particular propylene glycol methyl ether acetate or amyl acetate; ethers, such as dioxane; ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone and cyclohexanone; dimethylformamide, dimethylacetamide, hexamethyl phosphoric acid amide, N-methylpyrrolidone, butyrolactone, tetrahydrofuran and mixtures thereof. Glycol ethers, aliphatic esters and ketones are particularly preferred.

Depending on the types of photosensitive compounds and binders used and also on the intended application, the total solids content of the composition according to the present invention generally varies between about 10 to 50 % by weight, preferably between about 15 to 35 % by weight.

The invention also provides a photosensitive recording material which essentially comprises a substrate and the photosensitive composition applied to this substrate.

Substrates which may be used include any materials which are suitable for the production of capacitors, semiconductors, multilayer printed circuits or integrated circuits. Particularly suitable surfaces are those which comprise a thermally oxidized and/or aluminum-coated silicon material and which are optionally doped, including any other substrates customarily used in semiconductor technology, for example, silicon nitride, gallium

arsenide and indium phosphide. Other appropriate substrates are those known from the manufacture of liquid crystal displays, such as glass and indium/tin oxide; and, in addition, metal plates and foils, e.g. comprising aluminum, copper or zinc; bimetallic and trimetallic foils and also electrically nonconductive sheets which are vacuum metallized, optionally aluminum-coated SiO_2 materials and paper. These substrates may be subjected to a thermal pretreatment, roughened on their surfaces, slightly etched or treated with chemicals, in order to obtain desirable properties, e.g. an improvement of the hydrophilic character.

In a special embodiment, the photosensitive recording material may comprise an adhesion promoter dissolved in the resist formulation or applied between the resist and the substrate in order to improve the adhesion of the resist. Adhesion promoters of the aminosilane type, for example, 3-aminopropyl-triethoxysilane or hexamethyldisilazane are appropriately used in the case of silicon or silicon dioxide substrates.

Examples of supports which may be used in the production of photomechanical recording materials, for example, printing plates for relief printing, lithographic printing, screen printing or gravure printing and in the production of relief copies, include optionally anodically oxidized aluminum plates, grained and/or silicated aluminum plates, zinc plates, steel plates, optionally coated with chromium, and also plastic sheets or paper.

The photosensitive composition can be applied to the support to be coated using customary methods, such as dip-coating, flow-coating, spin-coating, spraying, roller-coating or application through slot dies.

The recording materials according to the present invention are exposed imagewise. Sources of actinic light include: metal halide lamps, carbon arc lamps, xenon lamps and mercury vapor lamps, which have emission peaks in the near ultraviolet or short-wave visible light. Imaging can also be effected by means of electron-beam, x-ray or laser radiation. Suitable lasers are, in particular, helium/neon lasers, argon lasers, krypton lasers and helium/cadmium lasers.

With the recording material having eventually been heated, the layer may, if it contains a crosslinking agent, be post-treated with overall actinic radiation in order to achieve image reversal.

The layer thickness of the photosensitive layer depends on the intended field of application and varies between 0.1 to 100 μm , in particular, between 1 and 10 μm .

Aqueous-alkaline solutions of graduated alkalinity, i.e. preferably having a pH of 10 to 14, and which may also contain minor amounts of organic solvents or wetting agents are used for development. These solutions remove the exposed areas of the recording layer and thus produce a positive image of the original.

In the following examples preferred embodiments of the invention are described. Quantitative ratios and percentages relate to weight units, unless otherwise indicated.

Example 1

A photosensitive composition comprising

7.0 pbw of the esterification product of 1 mol of
2,3,4-trihydroxybenzophenone and 2 mols of
1,2-naphthoquinone-diazide-5-sulfonyl chloride,

23.0 pbw of a poly-p-vinylphenol having a glass transition temperature of 165 °C ,
0.8 pbw of 4-bis-(2-hydroxyethyl)aminophenyl-methylene-propanedinitrile,
28.0 pbw of ethylene glycol monoethyl ether acetate,
3.5 pbw of n-butyl acetate, and
3.5 pbw of xylene

was applied to a silicon wafer by spin-coating at 4,000 rpm and dried in a circulating air oven at 90 °C for 30 minutes. The 2.03 μm thick layer was exposed to actinic radiation of wavelength $\lambda = 436 \text{ nm}$ in 8 different places using energies from 31.4 to 169 mJ/cm^2 . The exposed layer was developed in a solution comprising

0.61 pbw of sodium metasilicate $\cdot 9\text{H}_2\text{O}$
0.46 pbw of trisodium phosphate $\cdot 12\text{H}_2\text{O}$
0.04 pbw of monosodium phosphate, anhydrous in
98.89 pbw of deionized water.

After a development time of 60 seconds at 21 °C, 1 μm of resist thickness had been detached from the area exposed at 104.8 mJ/cm^2 .

Example 2 (Comparison Example):

A photosensitive composition comprising

7.0 pbw of the esterification product of 1 mol of 2,3,4-trihydroxybenzophenone and 2 mols of 1,2-naphthoquinonediazide-5-sulfonyl chloride,
23.0 pbw of a poly-p-vinylphenol having a glass transition temperature of 165 °C,

1.07 pbw of coumarin 338 (equimolar quantity to the absorbing compound specified in Example 1),
28.0 pbw of ethylene glycol monoethyl ether acetate,
3.5 pbw of n-butylacetate, and
3.5 pbw of xylene

was applied to a silicon wafer by spin-coating at 4,000 rpm and dried in a circulating air oven at 90 °C for 30 minutes. The 2.13 μm thick layer was exposed to actinic radiation of wavelength $\lambda = 436 \text{ nm}$ in 8 different places using energies from 50.7 to 273 mJ/cm^2 . The exposed layer was developed in a solution comprising

0.61 pbw of sodium metasilicate $\cdot 9\text{H}_2\text{O}$
0.46 pbw of trisodium phosphate $\cdot 12\text{H}_2\text{O}$
0.04 pbw of monosodium phosphate, anhydrous in
98.89 pbw of deionized water

After a development time of 60 seconds at 21 °C, 1 μm of resist thickness had been detached from the area exposed at 198 mJ/cm^2 .

Example 3 (Comparative Example):

A photosensitive composition comprising

7.0 pbw of the esterification product of 1 mol of 2,3,4-trihydroxybenzophenone and 2 mols of 1,2-naphthoquinonediazide-5-sulfonyl chloride,
23.0 pbw of a poly-p-vinylphenol having a glass transition temperature of 165 °C,
28.0 pbw of ethylene glycol monoethyl ether acetate,
3.5 pbw of n-butylacetate, and
3.5 pbw of xylene

was applied to a silicon wafer by spin-coating at 4,000 rpm and dried in a circulating air oven at 90 °C for 30 minutes. The 2.05 μm thick layer was exposed to actinic radiation of wavelength $\lambda = 436 \text{ nm}$ in 8 different places using energies from 25 to 136 mJ/cm^2 . The exposed layer was developed in a solution comprising

0.61 pbw of sodium metasilicate $\cdot 9\text{H}_2\text{O}$
0.46 pbw of trisodium phosphate $\cdot 12\text{H}_2\text{O}$
0.04 pbw of monosodium phosphate, anhydrous in
98.89 pbw of deionized water

After a development time of 60 seconds at 21 °C, 1 μm of resist thickness had been detached from the area exposed at 53 mJ/cm^2 .

Comparison between Examples 1 to 3 shows that, on condition that resolution is comparable, the photosensitivity of a photoresist formulation containing an absorbing compound according to formula I (Example 1) decreases by only 97 % as against a resist which is free of an additive compound (Example 3), whereas an addition of equimolar quantities of coumarin 338 (Example 2) reduces the practical photosensitivity by 273 %.

Example 4

A photosensitive composition comprising

3.0 pbw of the bis-(5-ethyl-5-butyl-1,3-dioxan-2-yl)-
ether of 2-ethyl-butyl-propane-1,3-diol,
10.0 pbw of a cresol formaldehyde novolak having a
melting range from 147 to 150 °C,

0.5 pbw of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloro-
methyl-s-triazine,
0.08 pbw of 4-bis-(2-hydroxyethyl)aminophenyl-
methylene-propanedinitrile, and
35.0 pbw of propylene glycol monomethyl ether acetate

was applied to a silicon wafer by spin-coating at
4,000 rpm and dried in a circulating air oven at 90 °C
for 30 minutes. The 0.93 μ m thick layer was exposed to
actinic radiation of wavelength $\lambda = 436$ nm in 8
different places using energies from 24.3 to
131 mJ/cm².

The exposed layer was developed in a 1 % aqueous
sodium hydroxide solution. At an exposure energy of
59.0 mJ/cm² the substrate was completely developed
after 60 seconds at 21 °C.

Example 5 (Comparison Example):

A photosensitive composition comprising

3.0 pbw of the bis-(5-ethyl-5-butyl-1,3-dioxan-2-yl)-
ether of 2-ethyl-butyl-propane-1,3-diol,
10.0 pbw of a cresol-formaldehyde novolak having a
melting range from 147 to 150 °C,
0.5 pbw of 2-(4-ethoxynaphth-1-yl)-4,6-bis-
trichloromethyl-s-triazine,
0.107 pbw of coumarin 338, and
35.0 pbw of propylene glycol monomethyl ether acetate

was applied to a silicon wafer by spin-coating at 4,000
rpm and dried in a circulating air oven at 90 °C for 30
minutes. The 0.94 μ m thick layer was exposed to actinic
radiation of wavelength $\lambda = 436$ nm in 8 different places
using energies from 24.3 to 131 mJ/cm².

The exposed layer was developed in a 1 % aqueous sodium hydroxide solution. At an exposure energy of 131.0 mJ/cm² the substrate was completely developed after 60 seconds at 21 °C.

Example 6 (Comparison Example):

A photosensitive composition comprising

3.0 pbw of the bis-(5-ethyl-5-butyl-1,3-dioxan-2-yl)-
ether of 2-ethyl-butyl-propane-1,3-diol,
10.0 pbw of a cresol-formaldehyde novolak having a
melting range from 147 to 150 °C,
0.5 pbw of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloro-
methyl-s-triazine,
35.0 pbw of propylene glycol monomethyl ether acetate

was applied to a silicon wafer by spin-coating at 4,000 rpm and dried in a circulating air oven at 90 °C for 30 minutes. The 0.94 μm thick layer was exposed to actinic radiation of wavelength $\lambda = 436$ nm in 8 different places using energies from 24.3 to 131 mJ/cm².

The exposed layer was developed in a 1 % aqueous sodium hydroxide solution. At an exposure energy of 36.3 mJ/cm² the substrate was completely developed after 60 seconds at 21 °C.

Comparison between Examples 4 to 6 shows that, on condition that resolution is comparable, the photosensitivity of a photoresist formulation containing an absorbing compound according to formula I (Example 4) decreases by only 62 % as against a resist which is free of an additive compound (Example 6), whereas an addition of equimolar quantities of coumarin 338 (Example 5) reduces the practical photosensitivity by 261 %.

Examples 7 to 15:

A photosensitive composition comprising

- 3.5 pbw of the esterification product of 1 mol of
2,3,4-trihydroxybenzophenone and 2 mols of
1,2-naphthoquinonediazide-5-sulfonyl
chloride,
- 11.9 pbw of a cresol-formaldehyde novolak having a
melting range from 147 to 150 °C,
- 27.7 pbw of ethylene glycol monoethyl ether acetate,
- 3.45 pbw of n-butyl acetate, and
- 3.45 pbw of xylene

was, in each case, admixed with one of the absorbing substances listed in Table 1 and mixed to give a homogeneous solution. This solution was applied to a silicon wafer by spin-coating at 4,000 rpm and dried in a circulating air oven at 90 °C for 30 minutes. The layers having a thickness of about 1.8 μm were exposed to actinic radiation of $\lambda = 436 \text{ nm}$ in 8 different places using different exposure times. The wafers were then developed in an 0.27 N aqueous solution of tetramethyl ammonium hydroxide. After a development time of 60 seconds at 21 °C the thicknesses of the resist layers were measured in the differently exposed areas and the energy values required for detaching a 1 μm thick resist layer were determined.

Table 1:

Example No.	Absorbing compounds added	Energy required for detaching 1 μm of resist layer
7 (C)	without additive compound	42.8 mJ/cm^2
8 (C)	0.1006 g of coumarin 338	49.8 mJ/cm^2
9 (C)	0.0978 g of coumarin 314	49.2 mJ/cm^2
10 (C)	0.1041 g of coumarin 7	62.4 mJ/cm^2
11	0.0803 g of 4-bis-(2-hydroxyethyl)aminophenyl-methylene-propanedinitrile	43.6 mJ/cm^2
12 (C)	0.1241 g of 4-bis-(2-isopropyl-carbonyl-oxyethyl)aminophenyl-methylene-propanedinitrile	60.5 mJ/cm^2
13 (C)	0.1327 g of 4-bis-(2-tert.-butyl-carbonyl-oxyethyl)-aminophenyl-methylene-propanedinitrile	59.1 mJ/cm^2
14 (C)	0.0753 g of 4-(2-hydroxyethyl)-4'-(ethyl-aminophenyl-methylene-propanedinitrile)	48.3 mJ/cm^2
15 (C)	0.084 g of 4-(2-hydroxyethyl-n-butyl)aminophenyl-methylene-propanedinitrile	58.9 mJ/cm^2

Comparison between the energy values shows that the lowest energy for detaching the resist layer is required using a dye according to formula I (Example 11).

Example 16:

A photosensitive composition comprising

6.0 pbw of the esterification product of 1 mol of
2,3,4-trihydroxybenzophenone and 3 mols of
1,2-naphthoquinonediazide-4-sulfonyl
chloride,

89.0 pbw of a cresol-formaldehyde novolak having a
melting range from 147 to 150 °C,

5.0 pbw of hexamethylol-melamine-hexamethyl ether,

2.0 pbw of bis-(2-hydroxyethyl)aminophenyl-methylene-
propanedinitrile, and

370.0 pbw of propylene glycol monomethyl ether
acetate

was applied to a silicon wafer by spin-coating at 4,000 rpm and dried on a hotplate at 90 °C for 1 minute. The 1.4 µm thick layer was exposed to actinic radiation of $\lambda = 436$ nm in 8 different places and then developed with the following solution:

2.25 pbw of sodium metasilicate $\cdot 9\text{H}_2\text{O}$

1.7 pbw of trisodium phosphate $\cdot 12\text{H}_2\text{O}$

0.15 pbw of monosodium phosphate, anhydrous in

95.80 pbw of deionized water.

After a development time of 60 seconds at 21 °C the resist layer exposed at 160 mJ/cm² had been cleaned out down to the substrate.

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A second silicon wafer was coated, prebaked and exposed in the same manner. It was thereafter heated at 120 °C for 60 seconds and then exposed overall to actinic radiation at 200 mJ/cm². The desired cross-linking of the areas exposed first was achieved at an exposure energy of 90 mJ/cm².

Example 17 (Comparison Example):

A photosensitive composition corresponding to that of Example 16, but without the addition of bis-(2-hydroxy-ethyl)aminophenyl-methylene-propanedinitrile was processed as described in Example 16.

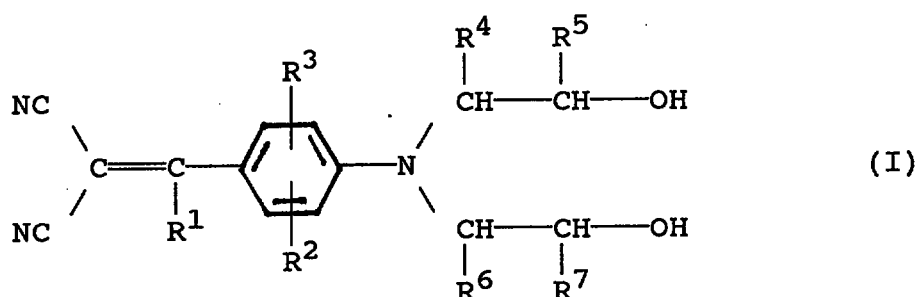
An exposure energy of 125 mJ/cm² was sufficient for the complete development of the resist layer.

The desired crosslinking of the resist layer was observed at an exposure energy of 75 mJ/cm².

Comparison between Examples 16 and 17 shows that by adding the dye according to formula I photosensitivity decreases by only 28 % (for the production of positive resist patterns) or 20 % (for the production of negative resist patterns).

Patent Claims

1. Positive-working photosensitive composition comprising a photosensitive compound, a binder that is insoluble in water and soluble or swellable in an aqueous-alkaline solution, and a dye, characterized in that the dye comprises a non-bleachable compound which absorbs light in the actinic region and corresponds to the general formula I



wherein

R^1 denotes hydrogen, alkyl, aryl, alkoxy or nitrilo,

R^2 and R^3 are identical or different and denote hydrogen, hydroxy, alkyl, aryl, alkoxy, aryloxy, nitrilo, amino, alkylamino or halogen,

R^4 , R^5
 R^6 and R^7 are identical or different and denote hydrogen, hydroxy, alkyl, aryl, alkoxy, aryloxy, amino, alkylamino or halogen.

2. A photosensitive composition as claimed in claim 1, characterized in that the dye has an absorption peak which is in the range of the emission of mercury vapor lamps.

3. A photosensitive composition as claimed in claim 1, characterized in that the dye has an absorption peak in the region from 365 to 436 nm.



4. A photosensitive composition as claimed in any one or several of claims 1 to 3, characterized in that an o-quinone diazide is present as the photosensitive compound.
5
5. A photosensitive composition as claimed in any one or several of claims 1 to 3, characterized in that a photolytic acid donor in combination with an acid-cleavable compound containing a C-O-C group is present as the photosensitive compound.
10
6. A photosensitive composition as claimed in claim 5, characterized in that an organic halogen compound is present as the photolytic acid donor.
15
7. A photosensitive composition as claimed in any one or several of claims 1 to 6, characterized in that a novolak condensation resin is present as the binder.
20
8. A photosensitive composition as claimed in claim 7, characterized in that the alkali-soluble novolak condensation resin is blended with other resins in a proportion of up to 20 % by weight.
25
9. A photosensitive composition as claimed in any one or several of claims 1 to 8, characterized in that the photosensitive composition comprises a crosslinking agent.
30
10. A process for the production of a relief pattern according to the image reversal process, the process essentially comprising the steps of coating a support with the photosensitive composition as



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claimed in claim 9, drying, imagewise exposing and optionally post-baking the layer, characterized in that an overall reexposure is carried out by means of actinic radiation.

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11. Positive-working photosensitive recording material essentially comprising a support and a photosensitive layer, characterized in that the material comprises a composition as claimed in claims 1 to 9 as the photosensitive layer.

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