

HOECHST AKTIENGESELLSCHAFT - WERK KALLE-ALBERT

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Positive-working radiation-sensitive mixture and radiation-sensitive copying material produced therefrom

5 The invention relates to a positive-working radiation-sensitive mixture which contains as essential constituents:

- 10 a) a compound which forms a strong acid on irradiation,
b) a compound having at least one C-O-C- or C-O-Si-bond which can be cleaved by acid, and
c) a water-insoluble binder which is soluble or at least swellable in aqueous alkaline solutions.

15 The invention furthermore relates to a radiation-sensitive copying material produced therefrom which is suitable for producing photoresists, electronic components, printing plates or for chemical milling.

20 In UV lithography, the limit of resolution is governed by the wavelength of the radiation used. The continuous miniaturization of the structural dimensions, for example in chip production, therefore requires modified lithographic techniques in the submicron region. Owing to their short wavelength, high-energy UV light or electron beams and X-ray beams, for example, are used. However, the modification of the lithographic techniques expresses
25 itself, in particular, in a modification of the requirements imposed on the radiation-sensitive mixture. A summary of these requirements is given, for example, in the treatise by C.G. Willson entitled "Organic Resist Materials - Theory and Chemistry" (Introduction to Micro-
30 lithography, Theory, Materials, and Processing, edited by L.F. Thompson, C.G. Willson, M.J. Bowden, ACS Symp. Ser., 219, 87 (1983), American Chemical Society, Washington). There is therefore an intensified requirement for radiation-sensitive mixtures which are preferably sensitive in

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5 a wide spectral range and can accordingly be used in conventional UV lithography or, without losses in sensitivity, in the advanced technologies such as, for example, the mid-UV or deep-UV, electron or X-ray lithography.

10 Mixtures of the abovementioned composition are in principle known and are described, for example, in DE-A 2,306,248 (= US-A 3,779,778), 2,610,842 (= US-A 4,101,323), 2,718,254 (= US-A 4,247,611), 2,718,259 (= US-A 4,189,323), 2,928,636 (= US-A 4,311,782), 3,151,078 (= US-A 4,506,006), 3,544,165 (= US-A 4,786,577), 3,601,264, 3,730,783, 3,730,785 and 3,730,787, in EP-A 0,006,626 (= US-A 4,250,247), 0,006,627 (US-A 4,248,957), 0,042,562 (= US-A 4,506,003), 0,202,196 and 0,302,359, and also in US-A 15 4,491,628 and 4,603,101.

20 On irradiating the materials described above, photolysis of the compound (a) forms an acid which brings about a cleavage of the C-O-C- or C-O-Si-bond of the compound (b) in a manner such that the irradiated regions of the photosensitive layers become soluble in an aqueous alkaline developer.

25 As compounds (a) which can be characterized as photolytic acid donors, in particular, onium salts such as diazonium, phosphonium, sulfonium and iodonium salts of non-nucleophilic acids, for example of HSbF_6 , HAsF_6 , or HPF_6 (J.V. Crivello, Polym. Eng. Sci., 23, 953 (1983)), halogen compounds (EP-A 0,232,972, DE-A 1,572,089 (= GB-A 1,163,324), DE-A 1,817,540 (= US-A 3,615,455), DE-A 1,949,010 (= US-A 3,686,084), DE-A 2,317,846 (= GB-A 30 1,381,471 and 1,381,472), US-A 3,912,606), in particular trichloromethyl triazine derivatives (DE-A 1,298,414 (= GB-A 1,234,648), 2,243,621 (= GB-A 1,388,492), 2,306,248, 2,718,259, 3,333,450 (= ZA 84/7165) and 3,337,024 (= US-A 4,619,998 and 4,696,888) and also US-A 35 3,515,552, 3,536,489 and 3,615,630) or trichloromethyl



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oxadiazole derivatives (DE-A 2,851,472 (= US-A 4,212,970 and 4,232,106), 2,949,396 (= US-A 4,279,982), 3,021,590 (= US-A 4,371,607), 3,021,599 (= US-A 4,371,606) and DE-A 3,333,450), o-quinonediazidesulfochlorides or organometal/organohalogen combinations have hitherto been recommended.

The use of such photolytic acid donors, however, involves certain disadvantages which drastically restrict their possible uses in various fields of application. Thus, for example, many of the onium salts are toxic. Their solubility in many solvents is inadequate, which results in a limitation of the choice of resist-coating solvents. In addition, if the onium salts are used, some undesirable foreign atoms are introduced which may result in processing troubles, in particular in microlithography. Furthermore, during the photolysis they form Brønstedt acids with very strong corrosive action which render the use of radiation-sensitive mixtures containing them unsatisfactory on sensitive substrates. The halogen compounds and also the quinonediazide sulfonyl chlorides also form hydrohalic acids with strong corrosive action. Furthermore, on certain substrates, such compounds have only a limited storage life which, according to the teachings of DE-A 3,621,376 (= US-A 4,840,867) was improved in the past by introducing an intermediate layer between substrate and radiation-sensitive layer containing compounds of the type (a), but this resulted in an undesirable increase in defects and a reduction in the process reproducibility. In addition, there was the view that compounds of the type (b) can be cleaved only by the acid types described above which have good mobility in the photosensitive layer.

However, recent work by F.M. Houlihan et al., SPIE 920, 67 (1988) has shown that, in addition to the above-mentioned acid donors, nitrobenzyl tosylates, which form sulfonic acids of low mobility on exposure to light, can

be used in certain acid-labile resist formulations. The sensitivities achieved in such cases and the thermal stabilities of the photoresists have, however, proven inadequate.

5 Owing to the disadvantages cited there is therefore a need for further acid donors which act photolytically, which do not have the disadvantages described above as constituents of radiation-sensitive mixtures and which consequently have sufficient reactivity and acid strength
10 to convert compounds of the type (b) into their cleavage products even with short exposure times.

The object of the invention was therefore to propose a radiation-sensitive mixture based on acid-forming compounds in combination with compounds which can be cleaved
15 by acid, in which mixture the compound (a) which forms an acid photolytically should be as stable as possible on all known substrates and generate an acid with noncorrosive action as the photo product.

According to the invention, a radiation-sensitive mixture
20 is proposed which contains as essential constituents:

- a) a compound which forms a strong acid on exposure to actinic radiation,
- b) a compound having at least one C-O-C- or C-O-Si-bond which can be cleaved by acid, and
- 25 c) a water-insoluble binder which is soluble or at least swellable in aqueous alkaline solutions.

The mixture according to the invention is one wherein the compound (a) which forms a strong acid on irradiation is an α, α -bis(sulfonyl)diazomethane of the general formula
30 I



in which

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R is an optionally substituted alkyl, cycloalkyl, aryl or heteroaryl radical.

5 According to the invention, a radiation-sensitive copying material is proposed in addition which contains the mixture described above as a radiation-sensitive layer on a support.

10 The radiation-sensitive mixture according to the invention is notable for a high sensitivity over a wide spectral range. It exhibits a high thermal stability and provides the possibility of reproducing even the finest structures of a master with structural precision. No corrosive photolysis products are formed by the exposure to light, with the result that the mixture can be used even on sensitive substrate materials.

15 For the preparation of the radiation-sensitive mixture, it is possible to use compounds of the general formula I in which R is an optionally substituted alkyl or cycloalkyl radical, an optionally substituted aryl radical or an optionally substituted heteroaryl radical.

20 Examples of suitable substituents R in α,α -bis(sulfonyl)-diazomethanes of the general formula I are:

25 Methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl, nonyl, decyl, or undecyl groups, and also their positional isomers, aryl such as benzene and naphthalene, hetero-aromatic compounds containing O, N or S as heteroatom and also their derivatives in which one or more hydrogen atoms are substituted for example by alkyl, alkoxy, alkoxyalkyl, aryl, aryloxy, arylalkoxy, halo, cyano, nitro, carbonyl, carboxyl, amido or similar radicals. Particularly preferred substituents are alkyl, alkoxy, alkoxyalkyl, carbonyl, amido, nitro radicals or halogens, alkyl or alkoxy radicals containing in particular 1 to 4 carbon atoms.
30 If there is polysubstitution of the aromatic radicals,



- suitable substituents are pre-dominantly alkyl or halogens. In particular, these are then disubstituted radicals R. If, however, fluorine is a substituent of the radical R, more than two fluorine atoms may also be encountered as substituents of the radical R; the latter are not, however, preferred. If R is heteroaryl, it comprises at most predominantly one heteroatom, even if R is a binuclear radical. If N is chosen as a heteroatom, it may occur at most twice per nucleus.
- 10 Among the compounds of the general formula I which contain R=alkyl as a radical, those are preferred which contain 1 to 6 carbon atoms, and among those which contain R = aryl as a radical, those are preferred in which R is a mononuclear or binuclear aromatic radical.
- 15 Examples of particularly suitable α,α -bis(sulfonyl)-diazomethanes of the general formula I are:
- Bis(methylsulfonyl)diazomethane
Bis(ethylsulfonyl)diazomethane
Bis(propylsulfonyl)diazomethane
- 20 Bis(1-methylpropylsulfonyl)diazomethane
Bis(2-methylpropylsulfonyl)diazomethane
Bis(butylsulfonyl)diazomethane
Bis(1-methylbutylsulfonyl)diazomethane
Bis(2-methylbutylsulfonyl)diazomethane
- 25 Bis(3-methylbutylsulfonyl)diazomethane
Bis(allylsulfonyl)diazomethane
Bis(heptylsulfonyl)diazomethane
Bis(octylsulfonyl)diazomethane
Bis(nonylsulfonyl)diazomethane
- 30 Bis(decylsulfonyl)diazomethane
Bis(dodecylsulfonyl)diazomethane
Bis(trifluoromethylsulfonyl)diazomethane
Bis(hexadecylsulfonyl)diazomethane
Bis(cyclohexylsulfonyl)diazomethane
- 35 Bis(2-oxapentylsulfonyl)diazomethane
Bis(benzylsulfonyl)diazomethane



	Bis(2-chlorobenzylsulfonyl)diazomethane
	Bis(4-chlorobenzylsulfonyl)diazomethane
	Bis(4-methoxysulfonyl)diazomethane
	Bis(phenylsulfonyl)diazomethane
5	Bis(2-methylphenylsulfonyl)diazomethane
	Bis(3-methylphenylsulfonyl)diazomethane
	Bis(4-methylphenylsulfonyl)diazomethane
	Bis(4-ethylphenylsulfonyl)diazomethane
	Bis(2,4-dimethylphenylsulfonyl)diazomethane
10	Bis(2,5-dimethylphenylsulfonyl)diazomethane
	Bis(3,4-dimethylphenylsulfonyl)diazomethane
	Bis(4-t-butylphenylsulfonyl)diazomethane
	Bis(2-methoxyphenylsulfonyl)diazomethane
	Bis(3-methoxyphenylsulfonyl)diazomethane
15	Bis(4-methoxyphenylsulfonyl)diazomethane
	Bis(2-chlorophenylsulfonyl)diazomethane
	Bis(3-chlorophenylsulfonyl)diazomethane
	Bis(4-chlorophenylsulfonyl)diazomethane
	Bis(2,5-chlorophenylsulfonyl)diazomethane
20	Bis(2,6-chlorophenylsulfonyl)diazomethane
	Bis(3,4-chlorophenylsulfonyl)diazomethane
	Bis(2-bromophenylsulfonyl)diazomethane
	Bis(3-bromophenylsulfonyl)diazomethane
	Bis(4-bromophenylsulfonyl)diazomethane
25	Bis(4-fluorophenylsulfonyl)diazomethane
	Bis(2,4-difluorophenylsulfonyl)diazomethane
	Bis(pentafluorophenylsulfonyl)diazomethane
	Bis(4-nitrophenylsulfonyl)diazomethane
	Bis(4-acetamidophenylsulfonyl)diazomethane
30	Bis(4-acetoxyphenylsulfonyl)diazomethane
	Bis(2-naphthalinsulfonyl)diazomethane
	Bis(furfurylsulfonyl)diazomethane
	Bis(imidazolylsulfonyl)diazomethane
	Bis(2-methylimidazolylsulfonyl)diazomethane
35	Bis(benzimidazol-2-sulfonyl)diazomethane
	Bis(benzoxazol-2-sulfonyl)diazomethane
	Bis(benzothiazol-2-sulfonyl)diazomethane.



The compounds cited above have absorption maxima in the region between 220 and 270 nm, and are therefore very well suited for irradiation with high-energy UV radiation.

- 5 Of the abovementioned compounds of the general formula I in which R is a substituted aryl radical, the following compounds are particularly preferred:

- Bis(2-methylphenylsulfonyl)diazomethane
Bis(3-methylphenylsulfonyl)diazomethane
10 Bis(4-methylphenylsulfonyl)diazomethane
Bis(4-ethylphenylsulfonyl)diazomethane
Bis(2,4-dimethylphenylsulfonyl)diazomethane
Bis(3,4-dimethylphenylsulfonyl)diazomethane
Bis(4-t-butylphenylsulfonyl)diazomethane
15 Bis(4-methoxyphenylsulfonyl)diazomethane
Bis(2-chlorophenylsulfonyl)diazomethane
Bis(3-chlorophenylsulfonyl)diazomethane
Bis(4-chlorophenylsulfonyl)diazomethane
Bis(2,5-dichlorophenylsulfonyl)diazomethane
20 Bis(2,6-dichlorophenylsulfonyl)diazomethane
Bis(3,4-dichlorophenylsulfonyl)diazomethane
Bis(3-bromophenylsulfonyl)diazomethane
Bis(4-bromophenylsulfonyl)diazomethane
Bis(4-fluorophenylsulfonyl)diazomethane
25 Bis(2,4-difluorophenylsulfonyl)diazomethane
Bis(4-nitrophenylsulfonyl)diazomethane
Bis(4-acetoxyphenylsulfonyl)diazomethane.

- 30 These compounds are particularly suitable because, on the one hand, they have a high photolysis reactivity, and, on the other hand, they have an adequate thermal stability.

The preparation of the α,α -bis(arylsulfonyl)diazomethane derivatives according to the invention is known per se. Their preparation has been described, for example, by F. Klages et al., Chem. Ber., 97, 735 (1964).



5 In addition, their use as dissolution inhibitors for positive-working materials, in particular for printing plates, has been investigated in the past by A. Poot et al., J. Photogr. Sci., 19, 88 (1971); their practical suitability in photoresist formulations was, however, ruled out because of inadequate photosensitivity.

10 It was therefore particularly surprising that the compounds of the general formula I used according to the invention form, during their photolysis, adequate quantities of sufficiently strong acids which make it possible to produce the highly sensitive, positive-working radiation-sensitive mixture according to the invention. Although there are no precise ideas about the extent and the nature of the acids formed, it may nevertheless be
15 assumed that sulfonic and sulfinic acids form as a result of the photolysis and these are capable of cleaving the labile bond of the compounds of the type (b).

20 Compared with the photolytically produced acids hitherto used such as, for example, hydrochloric acid, these acids have, as a consequence of their high molecular weight, a much lower diffusion tendency or mobility in the radiation-sensitive mixture according to the invention, with the result that it was surprising, on the one hand, that it was possible to achieve an image differentiation satisfying the highest requirements, and on the other hand, it was, however, all the more surprising that, for comparable sensitivity, the contrast, and consequently the resolving power, of the radiation-sensitive mixture was increased further. Furthermore it was surprising that the α,α -
25 bis(sulfonyl)diazomethanes of the general formula I can also be activated by high-energy short-wave radiation and it is consequently possible, for example, to produce a highly sensitive photoresist for high-energy UV2 radiation (248 nm). In particular, however, it was unexpected that
30 an adequate spectral sensitivity is still present even in the conventional optical lithography region (436 nm).
35



In this connection, actinic radiation is to be understood to mean any radiation whose energy is equivalent at least to that of short-wave visible light. In this connection, in particular, UV radiation in the range from 190 to 450 nm, preferably from 200 to 400 nm, particularly preferably from 200 to 300 nm, but also electron radiation and X-rays are suitable.

The preparation of the α,α -bis(arylsulfonyl)diazomethanes used according to the invention, some of which are novel, is illustrated on the basis of the preferred bis(4-t-butylphenylsulfonyl)diazomethane (pbw = parts by weight):

37.3 pbw of 4-t-butylthiophenol are added to 100 pbw of sodium hydroxide and stirred at room temperature until a clear solution forms. 18.2 pbw of dichloromethane are added to the thiophenol solution. The mixture is heated under reflux for 8 hours. The formaldehyde bis(4-t-butylphenylmercaptal) produced is taken up in ether and washed with 2 x 200 ml of water. Drying is then carried out over magnesium sulfate and the ether is distilled off. 36 pbw of a colorless oil are left behind.

20 pbw of this oil are dissolved in 40 ml of glacial acetic acid and added dropwise to a mixture of 200 pbw of glacial acetic acid and 60 pbw of hydrogen peroxide preheated to 90°C, the drop rate being so regulated that the temperature remains below 100°C. After completion of the initially strongly exothermic reaction, heating is carried out for a further 2 hours at 100°C, the mixture is cooled and poured into water. This produces 16 pbw of bis(4-t-butylphenylsulfonyl)methane. The product is recrystallized from ethanol and is obtained with a melting point of 150 to 152°C.

10 pbw of the product obtained above are dissolved together with 4.8 pbw of tosylazide in 90 pbw of acetonitrile and cooled to 0°C. 2.5 pbw of triethylamine are



added dropwise to this mixture in a manner such that the temperature remains below 10°C. Stirring of the mixture is continued for 4 hours at room temperature and the solvent is then removed from the mixture. The residue is taken up in methylene chloride and extracted twice with 100 pbw of 5%-strength aqueous sodium hydroxide solution, washed until neutral and dried. After evaporating off the solvent, an oil is left behind which is filtered through a silicic acid with methylene chloride as solvent. Re-evaporation of the solution produces a solid having a decomposition point of 153 to 155°C, which proves to be analytically pure bis(4-t-butylphenylsulfonyl)diazomethane.

The analysis of this compound yielded the following values:

calc.: C 58.04%, H 6.03%, N 6.45% S 14.75%

found: C 57.9 %, H 6.1 %, N 6.5 % S 14.4 %

¹H-NMR (CDCl₃): 1.4 ppm (s, 18 H), 7.4 to 8.2 ppm (q, 8 H)

$\lambda_{\max}$ (CHCl₃) = 238, 248 nm.

The other abovementioned compounds of the general formula I can be prepared in an analogous manner.

The photolytic acid donors contained in the radiation-sensitive mixture according to the invention can be used alone or in combination with other acid donors of the category mentioned. Combinations with other photolytic acid donors are, however, also possible, for which purpose, in particular, the α -sulfonyl- α -carbonyldiazomethanes described in application P3,930,087.0 filed simultaneously are suitable.

In addition, the acid donors of the general formula I according to the invention can also be combined with



onium salts such as diazonium, phosphonium, sulfonium and
iodonium salts of non-nucleophilic acids, for example of
HSbF₆, HASF₆, or HPF₆ (J.V. Crivello, Polym. Eng. Sci.,
23, 953 (1983)), halogen compounds (DE-A 1,572,089,
5 1,817,540, 1,949,010 and 2,317,846, EP-A 0,232,972, US-A
3,912,606), in particular trichloromethyl triazine deri-
vatives (DE-A 1,298,414, 2,243,621, 2,306,248, 2,718,259,
3,333,450 and 3,337,024, US-A 3,515,552, 3,536,489 and
3,615,630) or trichloromethyloxadiazole derivatives (DE-A
10 2,851,472, 2,949,396, 3,021,590, 3,021,599 and 3,333,450
and also EP-A 135,348), o-quinonediazidesulfochlorides or
organometal/organohalogen combinations. Such combinations
are not, however, on the whole preferred since the
disadvantages mentioned in the preamble again occur in
15 such radiation-sensitive mixtures.

The content of acid donors of the general formula I in
the mixture according to the invention is in general
between 0.5 and 25% by weight, preferably 1 to 10% by
weight, based in each case on the total weight of the
20 layer.

As the material which can be cleaved by acid in the
radiation-sensitive mixture according to the invention
the following compound categories, in particular, have
proven successful:

- 25 a) those containing at least one orthocarboxylic acid
ester and/or carboxylic acid amide acetal grouping,
the compounds also being capable of having a poly-
meric nature and the groupings mentioned being
capable of occurring as linking elements in the main
30 chain or as lateral substituents,
b) oligomeric or polymeric compounds containing repeat-
ing acetal and/or ketal groupings in the main chain,
c) compounds containing at least one enol ether or N-
acyliminocarbonate grouping,
35 d) cyclic acetals or ketals of β -keto esters or β -keto
amides,



- e) compounds containing silyl ether groupings,
- f) compounds containing silyl enol ether groupings,
- g) monoacetals or monoketals whose aldehydes or ketone components have a solubility in the developer of 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.

As components of radiation-sensitive mixtures, compounds of the type (a) which can be cleaved by acids are described in detail in DE-A 2,610,842 and 2,928,636. Mixtures which contain compounds of the type (b) are disclosed in DE-C 2,306,248 and 2,718,254. Compounds of the type (c) are described in EP-A 0,006,626 and 0,006,627. Compounds of the type (d) are disclosed in EP-A 0,202,196 and compounds which are to be assigned to the type (e) are disclosed in DE-A 3,544,165 and 3,601,264. Compounds of the type (f) are found in DE-A 3,730,785 and 3,730,783, while compounds of the type (g) are dealt with in DE-A 3,730,787. Compounds of the type (h) are described, for example, in US-A 4,603,101 and compounds of the type (i), for example, in US-A 4,491,628 and also in J.M. Fréchet et al., J. Imaging Sci. 30, 59-64 (1986).

Mixtures of the materials mentioned which can be cleaved by acids may also be used. Preferred, however, is a material which can be cleaved by acid, which material is to be assigned to the abovementioned types, including, in particular, those which have a C-O-C-bond which can be cleaved by acid. Particularly preferred are those materials which belong to the types (a), (b), (g) and (i). Among type (b), the polymeric acetals must, in particular, be highlighted; of the materials of the type (g) which can be cleaved by acid, in particular those whose aldehyde or ketone component has a boiling point of higher than 150°C, preferably higher than 200°C, must be highlighted.



5 The content of material which can be cleaved by acid in the radiation-sensitive mixture according to the invention should be 1 to 50% by weight, preferably 5 to 25% by weight, based in each case on the total weight of the layer.

10 The radiation-sensitive mixture according to the invention furthermore contains at least one polymeric water-insoluble binder which is, however, soluble, but at least swellable, in aqueous alkaline solutions. The binder is distinguished, in particular, by the fact that it readily dissolves the constituents of the radiation-sensitive mixture according to the invention and has as low as possible inherent absorption, i.e. a high transparency, in particular in the wavelength range from 190 to 300 nm.

15 This does not include, in particular, those binders based on novolak condensation resins which have been used, as a rule, in combinations of naphthoquinonediazides as photo-active components. Although novolak condensation resins reveal a drop in solubility compared with aqueous

20 alkaline developers in the unexposed regions after exposure to an image, their inherent absorption is undesirably high in the wavelength range required for the exposure to light.

25 The novolak condensation resins mentioned may, however, be used in a mixture with other resins having high transparency and being suitable as binders. In this connection, the mixing ratios depend predominantly on the nature of the binder to be mixed with the novolak resin. In particular, a decisive role is played by its degree of

30 inherent absorption in the wavelength range mentioned, but also by the miscibility with the other constituents of the radiation-sensitive mixture. In general, however, the binder of the radiation-sensitive mixture according to the invention may contain up to 30% by weight, in particular

35 up to 20% by weight, of a novolak condensation resin.



5 Suitable binders are homopolymers or copolymers of p-hydroxystyrene and also of its alkyl derivatives, for example of 3-methylhydroxystyrene, and also homopolymers or copolymers of other polyvinylphenols, for example of 3-hydroxystyrene or the esters or amides of acrylic acids with aromatics containing phenolic groups. Polymerizable compounds such as styrene, methacrylic acid methacrylate, acrylic acid methac or the like can be used as comonomers in the copolymer.

10 Mixtures with increased resistance to plasma etching are obtained if vinyl monomers containing silicon, for example vinyl-trimethylsilane, are used to prepare copolymers of the above type. The transparency of these binders is in general higher in the range of interest, with the result
15 that an improved patterning is possible.

Homopolymers or copolymers of maleinimide can also be used with the same success. These binders also exhibit high transparency in the wavelength range described. Styrene, substituted styrenes, vinyl ethers, vinyl
20 esters, vinylsilyl compounds or (meth)acrylic acid esters are also used as comonomers.

Finally, it is possible, in addition, also to use copolymers of styrene with comonomers which bring about an increase in solubility in aqueous alkaline solutions.
25 These include, for example, maleic anhydride, maleic acid half-esters or the like.

The binders mentioned may occur in mixtures if they are miscible and do not impair the optical qualities of the radiation-sensitive mixture. Preferred, however, are
30 binders containing one species of the abovementioned types.

The quantity of binder is, in general, 1 to 90% by weight, in particular 5 to 90% by weight, preferably 50



to 90% by weight, based on the total weight of the radiation-sensitive mixture.

5 Optionally, dyestuffs, pigments, plasticizers, wetting agents and leveling agents, but also polyglycols, cellulose ethers, for example ethylcellulose, may furthermore be added to the radiation-sensitive mixtures according to the invention to improve specific requirements such as flexibility, adherence and lustre.

10 Preferably, the radiation-sensitive mixture according to the invention is dissolved in solvents [for example ethylene glycol, glycol ether, glycol monomethyl ether, glycol dimethyl ether, glycol monoethyl ether or propylene glycol monoalkyl ether, in particular propylene glycol methyl ether, aliphatic esters (for example ethyl acetate, hydroxyethyl acetate, alkoxyethyl acetate, 15 n-butyl acetate, propylene glycol monoalkyl ether acetate, in particular propylene glycol methyl ether acetate or amyl acetate), ethers (for example dioxan), ketones (for example methyl ethyl ketone, methyl isobutyl ketone, 20 cyclopentanone and cyclohexanone), dimethylformamide, dimethyl acetamide, hexamethylphosphoric acid amide, N-methylpyrrolidone, butyrolactone, tetrahydrofuran and mixtures of the same]. Particularly preferred are glycol ether, aliphatic esters and also ketones.

25 Ultimately the choice of solvents depends on the coating method used, the desired layer thickness and the drying conditions. The solvent must also be chemically neutral, i.e. it must not react irreversibly with the other layer components.

30 The solutions produced with the constituents of the radiation-sensitive mixture have, as a rule, a solids content of 5 to 60% by weight, preferably up to 50% by weight.



According to the invention, a radiation-sensitive copying material is furthermore claimed which essentially comprises a substrate and a radiation-sensitive mixture applied thereto.

5 Suitable substrates are all those materials which capacitors, semiconductors, multilayer printed circuits or integrated circuits are composed of or produced from. In particular, mention may be made of surfaces composed of thermally oxidized silicon material and/or silicon
10 material coated with aluminum which may optionally also be doped, including all the other substrates common in semiconductor technology such as, for example, silicon nitride, gallium arsenide and indium phosphide. Furthermore, the substrates known from liquid crystal display
15 production such as, for example, glass and indium tin oxide, furthermore metal plates and metal foils (for example composed of aluminum, copper or zinc), bimetal and trimetal foils, but also electrically non-conducting sheets which are vapor-coated with metals, SiO_2 materials
20 optionally coated with aluminum, and paper, are suitable. These substrates may be subjected to a thermal pretreatment, superficially roughened, incipiently etched or treated with reagents to improve the desired properties, for example increase the hydrophilic nature.

25 In a particular embodiment, the radiation-sensitive mixture may contain an adhesion promoter to improve adhesion in the resist or between the resist and the substrate. In the case of silicon or silicon dioxide
30 substrates, adhesion promoters of the aminosilane type such as, for example, 3-aminopropyltriethoxysilane or hexamethyldisilazane are suitable for this purpose.

35 Examples of supports which can be used to produce photo-mechanical copying layers such as printing forms for letter press printing, lithographic printing and screen printing and also of embossed copies are aluminum plates,



optionally anodically oxidized, grained and/or silica-
tized, zinc plates and steel plates which have optionally
been chromium-plated, and also plastic sheets or paper.

5 The copying material according to the invention is
imagewise exposed. Sources of actinic radiation are:
metal halide lamps, carbon arc lamps, xenon lamps and
mercury vapor lamps. An exposure to high-energy radiation
such as laser radiation, electron radiation or X-rays may
also take place. Particularly preferred, however, are
10 lamps which are able to radiate light of a wavelength
from 190 to 260 nm, i.e. in particular xenon and/or
mercury vapor lamps. In addition, laser light sources,
for example excimer lasers, in particular KrF or ArF
lasers which emit at 249 or 193 nm respectively, may also
15 be used. The radiation sources must have an adequate
emission in the wavelength ranges mentioned.

The layer thickness varies as a function of its field of
application. It is between 0.1 and 100 μm , in particular
between 1 and 10 μm .

20 The invention furthermore relates to a method of producing
a radiation-sensitive copying material. The radiation-
sensitive mixture can be applied to the substrate by
spraying-on, flow coating, rolling, spin coating and
immersion coating. The solvent is then removed by evapor-
25 ation, with the result that the radiation-sensitive layer
remains behind on the surface of the substrate. The removal
of the solvent can be promoted optionally by heating the
layer to temperatures of up to 150°C. The mixture may, how-
ever, first be applied in the abovementioned manner to an
30 intermediate support from which it is transferred under pres-
sure and elevated temperature to the final support material.
As intermediate supports, all the materials also identified
as support materials can be used. The layer is then irradiated
imagewise. Then an image pattern is revealed in the
35 radiation-sensitive layer by development, the layer being



treated with a developer solution which dissolves or removes the irradiated regions of the material.

As developers, solutions of reagents such as, for example, silicates, metasilicates, hydroxides, hydrogen-
5 or dihydrogenphosphates, carbonates or hydrogencarbonates, of alkali metals and/or alkaline earth metals, in particular of ammonium ions, but also ammonia and the like are used. Metal-ion-free developers are described in US-A 4,729,941, EP-A 0,062,733, US-A 4,628,023, US-A 4,141,733, EP-A
10 0,097,282 and EP-A 0,023,758. The content of these substances in the developer solution is in general 0.1 to 15% by weight, preferably 0.5 to 5% by weight, based on the weight of the developer solution. Metal-ion-free developers are used in particular. Optionally, smaller
15 quantities of a wetting agent may be added to the developers in order to facilitate the dissolution of the exposed areas in the developer.

The developed resist structures are optionally post-hardened. This is done, in general, by heating the resist
20 structure on a hot plate to a temperature below the flow temperature and then exposing it to the UV light of a xenon-mercury vapor lamp (range from 200 to 250 nm) over its whole area. This post-hardening crosslinks the resist structures with the result that the structures have a flow
25 resistance in general up to temperatures of over 200°C. The post-hardening may also be carried out without raising the temperature by irradiation with high-energy UV light.

The radiation-sensitive mixture is preferably used in lithographic processes for producing integrated circuits
30 or discrete electrical components. The copying material produced from the mixture then serves as a mask for the subsequent processing steps. These include, for example, the etching of the support, the implantation of ions in the support or the deposition of metals or other
35 materials on the support.



The examples described below are only a selection of the invention. This is therefore not intended to be limited to the examples.

5 Examples 1 to 8 confirm the suitability of the mixture according to the invention for copying materials in microlithography using radiation of a very wide range of energy. The Comparison Examples 9 and 10 confirm the superiority of the mixtures according to the invention over the prior art. The Examples 11 and 12 document the
10 usability of the mixture in macroapplications, for example lithographic plates.

Example 1:

A coating solution was prepared from

15 7.5 pbw of a kresol-formaldehyde novolak having a softening range of 105 to 120°C,
2.0 pbw of a p-methoxybenzaldehyde bis(phenoxyethyl)-acetal prepared analogously to Preparation Example 1 of DE-A 3,730,787, and
20 0.7 pbw of bis(4-chlorophenylsulfonyl)diazomethane in
42 pbw of propylene glycol monomethyl ether acetate.

The solution was filtered through a filter having a pore diameter of 0.2 μm and spun onto a wafer treated with an adhesion promoter (hexamethyldisilazane) at 3,000 revolutions. After drying at 100°C for 1 min on a hot plate, a
25 layer thickness of 1.04 μm was obtained.

The copying material was exposed imagewise under a master using the UV radiation of a xenon-mercury vapor lamp at 365 nm having an energy of 124 mJ/cm².

30 The copying material was developed with a 0,3 N alkaline developer of the following composition:

5.3 pbw of sodium metasilicate nonahydrate,



3.4 pbw of trisodium phosphate dodecahydrate,
0.3 pbw of sodium dihydrogenphosphate and
91 pbw of completely deionized water.

5 After a development time of 60 s, a fault-free image of the mask having steep resist edges was obtained, even structures of $< 1 \mu\text{m}$ being resolved in true detail. An examination of the edges of the resist profiles by means of scanning electron microscopy confirmed that these were virtually perpendicular to the substrate surface.

10 Example 2:

A coating solution was prepared from

7.5 pbw of a copolymer of styrene/p-hydroxystyrene
(20/80) having an average molecular weight of
32,000,
15 2.0 pbw of 3,4-dimethoxybenzaldehydebis(phenoxyethyl)-
acetal prepared analogously to Preparation
Example 1 of DE-A 3,730,787 and
0.7 pbw of bis(4-bromophenylsulfonyl)diazomethane in
42 pbw of propylene glycol monomethyl ether acetate.

20 The solution was filtered through a filter having a pore diameter of $0.2 \mu\text{m}$ and spun onto a wafer treated with an adhesion promoter (hexamethyldisilazane) at 3,000 revolutions. After drying at 100°C for 1 min on a hot plate, a layer thickness of $1.18 \mu\text{m}$ was obtained.

25 The copying material was exposed imagewise under a master using the UV radiation of a xenon-mercury vapor lamp at 260 nm having an energy of 103 mJ/cm^2 and then processed with the developer described in Example 1.

30 After a development time of 60 s, a fault-free image of the mask having high edge stability was obtained, structures of $< 1 \mu\text{m}$ also being resolved in this case in true detail.



Example 3:

5 A wafer prepared in accordance with Example 2 was irradiated under a master using the UV light of a KrF excimer laser having a wavelength of 248 nm with an energy of 92 mJ/cm². After development, an image of the master in which even structures in the submicron region were reproduced in true detail was obtained similarly to Example 2.

Example 4:

10 The experiment of Example 1 was repeated, but UV light of a wavelength of 436 nm was used. In order to obtain an image of the master with sharp edges, an exposure energy of 280 mJ/cm² had to be used.

Example 5:

A coating solution was prepared from

- 15 7.5 pbw of a 1:1 copolymer of styrene and maleimide having a softening range of 165 to 180°C,
2.0 pbw of benzaldehyde bis(phenoxyethyl)acetal prepared analogously to Preparation Example 1 of DE-A 3,730,787, and
20 0.7 pbw of bis(phenylsulfonyl)diazomethane in
42 pbw of propylene glycol monomethyl ether acetate.

25 The solution was filtered through a filter having a pore diameter of 0.2 μm and spun onto a wafer treated with an adhesion promoter (hexamethyldisilazane) at 3,500 revolutions. After drying at 100°C for 1 min on a hot plate, a layer thickness of 1.08 μm was obtained.

The copying material was exposed imagewise under a master using the UV radiation of a xenon-mercury vapor lamp at 260 nm having an energy of 88 mJ/cm².

30 The copying material was developed with a 0.02 N aqueous solution of tetramethyl ammonium hydroxide, the exposed regions being stripped to leave no residue within 60 s.



Once more a fault-free image of the mask with satisfactorily steep resist edges was obtained. The removal of unexposed area was < 20 nm; even structures of < 1 μ m were resolved in true detail.

5 Example 6:

A coating solution was prepared from

7.5 pbw of a 1:1 copolymer of styrene and maleimide
having a softening range of 165 to 180°C,

10 2.0 pbw of 3,4-methylenedioxybenzaldehyde bis(phenoxy-
ethyl)acetal,

0.8 pbw of bis(t-butylphenylsulfonyl)diazomethane in
42 pbw of propylene glycol monomethyl ether acetate.

15 The solution was filtered through a filter having a pore
diameter of 0.2 μ m and spun onto a wafer treated with an
adhesion promoter (hexamethyldisilazane) at 3,500 revolu-
tions. After drying at 100°C for 1 min on a hot plate, a
layer thickness of 1.06 μ m was obtained.

20 The copying material was exposed imagewise under a
master using the UV radiation of a xenon-mercury vapor
lamp at 260 nm having an energy of 92 mJ/cm².

25 The copying material was developed with a 0.02 N aqueous
solution of tetramethylammonium hydroxide, the exposed
regions being stripped to leave no residue within 60 s
and a true-to-detail image of the master being obtained.
The edge steepness of the image was more than 85°.

Example 7:

A coating solution was prepared from

7.5 pbw of the copolymer described in Example 2,

30 2.0 pbw of a polyorthoester, prepared by condensation,
of 1 mol of 7,7-bishydroxymethylnonanol with 1
mol of methyl orthoformate,



0.8 pbw of bis(t-butylphenylsulfonyl)diazomethane in
42 pbw of propylene glycol monomethyl ether acetate

5 The solution was filtered through a filter having a pore diameter of 0.2 μm and spun onto a wafer treated with an adhesion promoter (hexamethyldisilazane) at 3,500 revolutions. After drying at 100°C for 1 min on a hot plate, a layer thickness of 0.98 μm was obtained.

10 The copying material was exposed imagewise under a master using the UV radiation of a xenon-mercury vapor lamp at 260 nm having an energy of 78 mJ/cm².

15 The copying material was developed with a 0.27 N aqueous solution of tetramethylammonium hydroxide, the exposed areas being stripped to leave no residue within 60 s and a true-to-detail image of the master being obtained. Lines and gaps down to 0.7 μm were reproduced with faithfulness to the mask.

Example 8:

20 The copying material from Example 7 was irradiated with synchrotron radiation (BESSY, Berlin, 754 MeV) through a gold-on-silicon mask with a dose of 160 mJ/cm². The experimental setup is to be found in A. Heuberger, Microelectr. Eng., 3, 535 (1985). After development with the developer described in Example 7 and a development time of 70 s, a fault-free image of the mask was obtained
25 down to structures of < 0.6 μm . The resist edges were virtually vertical to the planar substrate surface.

Examples 9 and 10 (comparison examples):

30 The resist formulation of Example 7 was modified in a manner such that the acid-forming compound used therein was replaced by an equal quantity of

triphenylsulfonium hexafluorophosphate (Example 9) or 2-nitrobenzyl tosylate (Example 10).



5 After exposure to radiation of a wavelength of 260 nm and an energy of 105 or 140 mJ/cm² and development with a developer of the composition specified in Example 1, structures which exhibited no image differentiation suitable for practical work were obtained.

10 On using the onium salt (Example 9), structures with so-called "resist foot" were obtained, i.e. resist residues adhered to the substrate in the exposed regions, while on using the tosyl ester (Example 10) surface crosslinkings ("lips") were visible and these spanned the substrate areas which had been bared. In both cases no acceptable patterning was consequently obtained.

Example 11:

15 To prepare an offset printing plate, a mechanically roughened and pre-treated aluminum foil was spin-coated with a coating solution of the composition below:

20 7.5 pbw of a kresol-formaldehyde novolak having a softening range of 105 to 120°C,
2,3 pbw of a polyacetal prepared from 1 mol of 2-ethylbutyraldehyde and 1 mol of triethylene glycol,
0.5 pbw of bis(4-chlorophenylsulfonyl)diazomethane,
0.05 pbw of crystal violet base in
90 pbw of propylene glycol monomethyl ether acetate.

25 After drying the layer (layer weight approximately 2.5 g/m²), exposure was carried out under a positive test master for 30 s and development was then carried out with a developer of the following composition:

30 0.5 pbw of sodium hydroxide,
0.8 pbw of sodium metasilicate nonahydrate,
1.0 pbw of 2-n-butoxyethanol in
97.7 pbw of completely deionized water.



After rinsing with water, the plate was made ready for printing by wiping over with 1%-strength phosphoric acid. After clamping in a printing press, 72,000 perfect imprints of the master were obtained.

5 Example 12:

The solution of an etch and electroplating positive dry resist was prepared by making up the following composition:

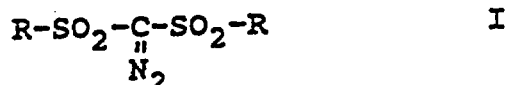
- 12.5 pbw of the novolak described in Example 11,
10 10.0 pbw of an oligomeric aliphatic polyacetal having a mean molecular weight of approximately 1,400 prepared by condensation of butyraldehyde with diethylene glycol,
0.5 pbw of bis(4-methylphenylsulfonyl)diazomethane,
15 0.1 pbw of crystal violet in
30 30 pbw of butanone.

- A polyethylene terephthalate film of 25 μ m thickness, which is standard for this purpose, was coated with this solution, with the result that a dry layer thickness of
20 18 μ m was produced. The surface of the dry resist film was clad with a further polyethylene terephthalate film. The dry film was laminated onto a brass sheet after peeling off the covering film, under pressure and heat. After cooling and peeling off the temporary support film, the sheet
25 was exposed through a master, in which process a good image contrast became visible. The exposed areas were spray-developed with a developer of the composition specified in Example 11. The sheet was then etched with commercial ferrichloride solution until the smooth edges
30 had been etched through. The shaped parts obtained may be processed still further before separation into singles.



Patent claims

1. A positive-working radiation-sensitive mixture essentially containing
- 5 a) a compound which forms an acid on irradiation,
- b) a compound having at least one C-O-C- or C-O-Si-bond which can be cleaved by acid, and
- c) a water-insoluble binder which is soluble or at least swellable in aqueous alkaline solutions,
- 10 wherein the compound (a) is an α,α -bis(sulfonyl)diazomethane derivative of the formula I



in which R is an alkyl, cycloalkyl, aryl or heteroaryl radical.

- 15 2. A positive-working radiation-sensitive mixture as claimed in claim 1, wherein the radical R of the compound of the formula I is an optionally substituted alkyl or cycloalkyl radical, an optionally substituted aryl radical or a heteroaryl radical.

- 20 3. A positive-working radiation-sensitive mixture as claimed in claim 1 or 2, wherein the radical R of the compound of the formula I is an optionally substituted alkyl radical containing 1 to 6 carbon atoms or an optionally substituted aryl radical.

- 25 4. A positive-working radiation-sensitive mixture as claimed in claims 1 to 3, wherein the radical R of the compound of the formula I is an optionally substituted aryl radical.

- 30 5. A positive-working radiation-sensitive mixture as claimed in any of claims 1 to 4, wherein the substituents of the aromatic radical are selected from the group comprising alkyl, alkoxy, alkoxyalkyl, nitro, carbonyl and amido radicals or halogen atoms.



6. A positive-working radiation-sensitive mixture as claimed in claims 1 to 5, wherein UV light having a wavelength of 190 to 450 nm is used as radiation.

5 7. A positive-working radiation-sensitive mixture as claimed in claims 1 to 6, wherein UV light having a wavelength of 200 to 400 nm is used as radiation.

10 8. A positive-working radiation-sensitive mixture as claimed in claims 1 to 7, wherein the concentration of the acid-forming compound of the formula I is 0.5 to 25% by weight.

9. A positive-working radiation-sensitive mixture as claimed in claims 1 to 8, wherein the binder has an absorbance of $< 0.5 \mu\text{m}^{-1}$ in the wavelength range of the irradiation.

15 10. A positive-working radiation-sensitive mixture as claimed in claims 1 to 9, which contains up to 30% by weight, in particular up to 20% by weight, of a novolak condensation resin as binder.

20 11. A positive-working radiation-sensitive mixture as claimed in claims 9 and 10, wherein the binder contains phenolic hydroxyl groups.

25 12. A positive-working radiation-sensitive mixture as claimed in claims 9 to 11, wherein the binder is contained in a concentration of 60 to 96% by weight, in particular 70 to 94% by weight, in the radiation-sensitive mixture.

13. A positive-working radiation-sensitive mixture as claimed in claims 9 to 12, wherein the binder has an absorbance of $< 0.3 \mu\text{m}^{-1}$ above 240 nm.



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14. A positive-working radiation-sensitive mixture as claimed in claim 1, wherein the compound of the formula I has the highest molar absorption of all the resist constituents at 248 nm.

- 5 15. A positive-working radiation-sensitive copying material essentially composed of a support and a radiation-sensitive layer, wherein the layer is composed of a radiation-hardenable mixture as claimed in claims 1 to 14.



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