

HOECHST AKTIENGESELLSCHAFT - Werk KALLE

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Radiation-curable composition and radiation-sensitive recording material prepared therefrom for use with high-energy radiation

- 5 The invention relates to a negative-acting, radiation-curable composition comprising a compound that forms an acid under the action of high-energy radiation and an acid-hardening compound.
- 10 In conventional UV-lithography, the limit of resolution is predetermined by the wavelength of the radiation employed. Increasing miniaturization of dimensions in the fabrication of chips therefore requires new lithographic techniques in the submicron range, electron
- 15 beams or X-rays being used because of their extremely short wavelengths. It has been found that resist materials which are suitable for use as electron-beam resists can also be employed as X-ray resists, and vice versa.
- 20 Resist materials which are known for this application comprise acrylates and methacrylates [G.M. Taylor, "Solid State Technology", 124 (1984)]. In these materials, sensitivity and pattern resolution have, in most cases, proved to be incongruous properties. In order
- 25 to be able to obtain relatively high sensitivities, halogens are usually incorporated in the resist. In the case of positive-acting resists, fluorine and chlorine are generally employed, whereas negative-acting resists preferably contain bromine and iodine, apart from chlo-
- 30 rine [T. Yamaoka et al., Phot. Sci. Eng. 23, 196 (1979)].

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Negative-acting, i.e. radiation-curable resists generally show a higher sensitivity than positive-acting resists, however - as explained above - they cannot have a high resolution in the submicron range, at the same time. Positive-acting resists on a basis of methacrylate, on the other hand, yield a high resolution but, with the exception of the resists based on polymethacrylonitrile, they do not withstand the plasma-etching processes used for the patterning of semiconductors. The methacrylate resists, for their part, have an insufficient sensitivity.

Polyalkenesulfones, in particular polybutene-1-sulfone, are the polymers with the highest radiation sensitivity in view of electron beams and X-rays, so far known. It is, however, a disadvantage of compounds of this category that they have an inferior resistance to plasma etching processes; they can thus be used for the production of masks, but they are unsuitable for use in the fabrication of semiconductors with the aid of masks made of this material. It has therefore been suggested to combine polyalkenesulfones with novolac resins that are plasma-etch resistant, as is generally known [M.J. Bowden et al., J. Electrochem. Soc., 128, 1304 (1981); US-A-4,289,845]. However, the two polymers showed a severe incompatibility, which impairs resolution. Even when it was attempted to improve compatibility by admixing further components, a loss of sensitivity had to be accepted (US-A-4,398,001).

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To maintain high sensitivities within the context of improved general characteristics, in particular, improved plasma-etch resistance, photocatalytically acting resists were developed. Examples of positive-
5 acting systems of this type are described, inter alia, in DE-A-27 18 254, 29 28 636 and in German Patent Application P 37 30 784.3 of earlier date.

Corresponding negative-acting systems comprise, for
10 example, resists which, upon irradiation, are cross-linked in a dimerizing reaction, such as polymeric cinnamic acid derivatives and polyacrylates. Resists of this type are relatively insensitive. When the principle of photocatalysis is utilized in negative-
15 acting systems, a difference is made between resists that can be photopolymerized by free radicals and resists which, due to photoinduced reactions, are crosslinked cationically, by addition, substitution or condensation. The first-mentioned resists exhibit con-
20 siderable drawbacks in the imaging quality. Their applicability to uses in the submicrometer range is therefore limited.

The application of acid-hardening resins in photoresist
25 formulations has been known for a long time. As described, for example, in US-A-3,692,560 halogen-containing benzophenones in combination with melamine resins or urea-formaldehyde resins can be used as UV resists. DE-A 27 18 259 (= US-A-4,189,323) describes the use of
30 halogenated derivatives of s-triazine as photolytically



activatable acid donors for positive and negative-acting systems, for example, for acid-hardening urea formaldehyde, melamine-formaldehyde and phenol formaldehyde resins (column 5). Examples of formulations of this
5 kind are also specified by Vollenbroek et al., Micro-electronic Engineering 6, 467, (1987).

It is also possible to use onium salts, such as diphenyl
10 iodonium salts of non-nucleophilic acids, e.g. of HSbF_6 , HAsF_6 or HPF_6 , as photolytically activatable acid formers. DE-A-27 30 725 describes the use of starters of this kind in resist formulations containing epoxides as acid-hardening materials. A general account of the use
15 of onium salts in acid-hardening systems is given by J.V. Crivello, Polym. Eng. Sci. 23, 953 (1983).

EP-A-0 164 248 describes photo-curable compositions on a basis of acid-hardening resins and naphthoquinone
20 diazides or o-nitrobenzoic acid derivatives.

In EP-A-0 232 972 halogenated compounds, such as DDT or Gammexan, are described, which show virtually no absorption above 299 nm and are used as photoinitiators in
25 acid-hardening negative photoresists.

The systems described above have the common feature that the initiator compounds do not participate in the actual crosslinking process and are themselves insoluble in
30 aqueous alkaline developers, with the exception of the onium salts. This leads to drastically reduced develop-



ment rates in those areas, where the non-exposed resist layer is to be removed by the developer. The amount of starter compound, which can be added - and consequently also the sensitivity of the resist prepared - is thus
5 clearly limited. The use of onium salts and also the use of the initiators described in EP-A-0 232 972, which are known as plant protection agents, are moreover critical for physiological reasons.

10 It was therefore the object to propose a negative-acting resist system for the recording of high-energy radiation, which system can be processed in daylight and artificial light substantially without any particular precautionary measures, but is nevertheless highly sensitive to high-energy radiation, in particular electron
15 emission and X-rays, yields resist patterns of high resolution after development with aqueous-alkaline developers, is physiologically safe and has a good resistance to liquid and plasma etching media.

20 According to the invention a composition is provided, which is curable by high-energy radiation and comprises a compound that forms an acid under the action of high-energy radiation and an acid-hardening substance.

25 In the composition of the present invention the compound that forms an acid contains chlorine or bromine linked to aromatic carbon atoms and has a pK_a value below 12.

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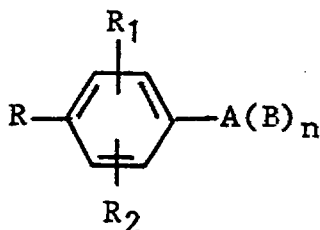


It was surprising to find that, using starters of this kind, even acid-hardening compositions of particularly high sensitivity are obtained without the high starter concentrations required having an adverse influence on the development characteristics or the thermal stability of the resist patterns obtained, as is the case when the starters described in EP-A-0 232 972 are employed. This is ascribed to the fact that the alkali-solubility of the non-exposed resist areas is considerably increased, due to the structure of the starter. In the exposed areas of the resist, on the other hand, the starter participates in the crosslinking reaction.

Of the acid-forming starters containing chlorine or bromine linked to aromatic carbon atoms those are preferred, which have a pK_a value in the range from 6 to 10.

The pK_a value of chemical compounds can be determined according to conventional methods, it is, however, also possible to make a theoretical calculation, e.g. using the "CAMEO" program.

Particular preference is given to acid-forming starters of the general formula I



(I)



containing at least one chlorine or bromine atom linked to an aromatic carbon atom, wherein

R is OH or COOH,

5 R₁ and R₂ are identical or different and denote hydrogen, chlorine, bromine, alkyl which may be substituted by aryl, alkoxy, aryloxy or hydroxyl groups or by fluorine atoms; or aryl which may be substituted by alkoxy, aryloxy or hydroxyl groups or by halogen atoms, and

10 n = 0 to 3,
if n = 0:

A denotes hydrogen, chlorine, bromine, alkyl which may be substituted by alkoxy, aryloxy, hydroxyl or aryl groups or by fluorine atoms; aryl which may be substituted by alkoxy, aryloxy, hydroxyl or carboxyl groups or by halogen atoms,
15 if n = 1:

A denotes a single bond, -O-, -S-, -SO₂-, -NH-,
20 -NR₃-, alkylene or perfluoroalkylene,

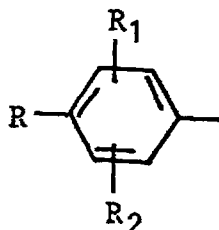
if n = 2:

A denotes $\begin{array}{c} \text{-CR}_3\text{-} \\ | \\ \text{ } \end{array}$ or $\begin{array}{c} \text{-N-} \\ | \\ \text{ } \end{array}$ and

if n = 3:

A denotes $\begin{array}{c} | \\ \text{-C-} \\ | \end{array}$ and

25 B denotes



30



carboxyl, substituted carbonyl, in particular alkylcarbonyl or arylcarbonyl, carboxyalkyl or substituted sulfonylimidocarbonyl and

5 R_3 denotes alkyl, in particular (C_1-C_3) alkyl, or aryl, in particular phenyl.

Preference is, in particular, given to compounds, in which

10 R_1 and R_2 are identical and denote, in particular, chlorine or bromine and are, in each case, in the o-position relative to R, and
R denotes a hydroxyl group.

Also preferred are those compounds, in which

15 A (if $n = 1$ and $B = R-\text{C}_6\text{H}_2-\text{C}_6\text{H}_2$), denotes $-\text{SO}_2-$, propylene or perfluoropropylene, in the two last-mentioned instances, preferably propylidene or perfluoropropylidene, or
20 A (if $n = 1$ and $B = \text{alkylcarbonyl}$, in particular, methylcarbonyl, carboxyalkyl, in particular, carboxymethyl or substituted sulfonylimidocarbonyl, in particular, p-toluenesulfonylimidocarbonyl)
25 denotes $-\text{O}-$, $-\text{NH}-$ or $-\text{NR}_3-$, or
A (if $n = 0$) denotes hydroxyl, carboxyl or alkyl which is substituted, on every other carbon atom, by phenyl or chlorinated or brominated phenyl.

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Particular preference is also given to phenolic resins, in which the unsubstituted o- and/or p-positions relative to the hydroxyl function are partially or completely chlorinated or brominated.

5

Novolac types obtained by condensing p-chloro- or p-bromo-o,o'-bis-methylol-phenol and m-cresol which may be substituted by chlorine or bromine are particularly preferred.

10

Particularly preferred are compounds, in which, if $n = 0$ and $A =$ substituted carbonyl:

R denotes hydroxyl and

R_1 and R_2 , each being in the o-position relative to R , denote chlorine or bromine, or

15

if $n = 0$ and $A =$ alkyl which may be substituted:

R denotes hydroxyl and

R_1 and R_2 , each being in the o-position relative to R , denote hydrogen, chlorine or bromine.

20

The amount of acid-forming starters contained in the radiation-sensitive composition of the present invention is, in general, about 2 to 50 % by weight, preferably about 4 to 25 % by weight, in each case relative to the total weight of the radiation-sensitive layer.

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If the starter is in a polymeric form and is, in particular, part of the binder, the constituent amounts specified for the corresponding polymeric binders are

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regarded as an upper limit. The respective content of the starter or of the molecular groups in the polymer, which are responsible for the starting process, can be calculated from the mixing ratios of the monomeric initial ingredients.

Suitable systems which can be catalytically hardened by acid comprise crosslinkable systems, in which the crosslinking component and the functional group which is capable of crosslinking and reacts with the crosslinking component, are contained in one and the same molecule, preferably in an oligomeric or polymeric molecule. Examples are copolymers of N-alkoxymethylmethacrylamide, for example, with acrylic acid or pyrocatechol monomethacrylate, if appropriate, in the presence of further comonomers, as described, for example, in EP-A-0 184 044.

Acid-hardening components which can be used further comprise compounds containing cationically polymerizable groupings. Mention is made of vinyl ethers, epoxides, and the like. A general review is given in "Makromol. Chemie, Macromolecular Symposia", Vol. 13/14, Munic 1988. The preferably used compounds contain a plurality of the groupings indicated above.

Further suitable acid-hardening components include compounds which, when catalyzed by acid, enter into condensation reactions with themselves or with the binder. Melamine-formaldehyde resins, benzoguanamine-formaldehyde



hyde resins, glycoluril-formaldehyde resins, urea-formaldehyde resins and also hydroxymethylated phenols and cresols, as described, for example, in EP-A-0 212 482, are mentioned in this connection.

5

Preference is given to compositions, in which the reactive groups are present in different molecules. In that case, the binder contains a crosslinkable functional group. Examples are -SH, -OH, -CONH₂ and -COOH groups. Moreover, compositions are suitable, which can be hardened by condensation with formaldehyde in the presence of acid. These include, in particular, appropriately substituted phenolic resins. Instead of formaldehyde, compounds which release formaldehyde, for example, trioxane, can also be employed. The latter are preferably used in combination with phenolic resins.

The binders used in the composition according to the present invention are insoluble in water, but soluble in aqueous-alkaline media and in organic solvents. To achieve this, the binders contain functional groups having a pK_a below 12, preferably between 6 and 10. Typical examples are phenols, carboxylic acids, but also sulfonamides and imides.

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Phenolic resins of the novolac type, for example, phenol-formaldehyde resins, cresol-formaldehyde resins, co-condensates and mixtures thereof, and phenol and cresol condensates with other aldehydes are preferably used.

30



In addition, the following can be used:

- Polymers of styrene containing units of alkenylsulfonyl-aminocarbonyloxy- or cycloalkenylsulfonyl-aminocarbonyloxy- (EP-A-0 184 804), polymers of acrylic, methacrylic, maleic and itaconic acids etc., which may have lateral, crosslinking $-CH_2OR$ groups (EP-A-0 184 044), polymers of vinyl monomers with alkenylphenol units (EP-A-0 153 682), polyvinylphenols (DE-C-23 22 230),
 5 polymeric binders with lateral, phenolic hydroxyl groups (EP-A-0 212 439 and 0 212 440), copolymers of styrene and maleic anhydride (DE-A-31 30 987), polymers of 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 units, vinyl alcohol units and vinyl acetal units (EP-A-0 216 083) and also polyvinyl acetals containing units of hydroxyaldehydes (DE-A-36 44 162).
 10
 15
 20 The amount of binder generally ranges from 1 to 90 % by weight, in particular, from 5 to 90 % by weight and preferably from 50 to 90 % by weight, relative to the total weight of the radiation-sensitive composition.
 25 If polymeric starters are used, the above-indicated binders which are insoluble in water and soluble in aqueous alkali may, if appropriate, also be dispensed with. For this purpose, chlorinated or brominated polystyrenes or polyvinyl phenols are used, in particular.
 30 As a consequence, the content of polymeric starter



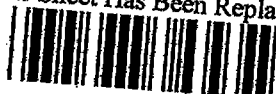
can even exceed the quantitative range specified for the starter. It is, in particular, possible to employ amounts of over 50 % by weight and up to 100 % by weight, minus the content of the acid-cleavable compound.

Aside from this, the binder can also be prepared by condensing a chlorine or bromine-containing aromatic starter with an initial monomer which can be used for the preparation of conventional binders. It is then a prerequisite that the acid-forming chlorine or bromine-containing compound contains groups which are capable of condensation or polymerization.

Of the monomeric constituents of conventional binders, phenols and cresols, specifically m-cresol, are particularly preferred for this condensation. Condensation is advantageously carried out using approximately equimolar quantities.

In addition to this incorporation of the halogen-containing starter into known binders to form a polymeric starter which simultaneously acts as a binder, simple mixing of polymeric starters with customary binders is also possible. In particular, chlorine or bromine-containing styrene derivatives are mixed with novolac resins, preferably in approximately equimolar quantities.

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It is possible to add to the radiation-sensitive compositions according to the invention, if desired, dyes, pigments, plasticizers, wetting agents and levelling agents, but also polyglycols and cellulose ethers, for example ethylcellulose, for improving special requirements such as flexibility, adhesion and gloss.

Preferably, the radiation-sensitive composition according to the invention is dissolved in solvents such as 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 monoalkyl ether 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, hexamethylphosphoric amide, N-methyl-pyrrolidone, butyrolactone, tetrahydrofuran and in mixtures thereof. Particular preference is given to glycol ethers, aliphatic esters and ketones.

The solutions that are formed with the components of the radiation-sensitive composition usually have a solids content of 5 to 60 % by weight, preferably up to 50 % by weight.

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A radiation-sensitive recording material is also claimed according to the invention, consisting essentially of a support with the radiation-sensitive composition applied thereon.

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Suitable supports include all materials of which capacitors, semiconductors, multi-layer printed circuits and integrated circuits consist or can be prepared.

10

Surfaces made of pure silicon and thermally-oxidized and/or aluminum-coated silicon that, if desired, can also be doped, including all other supports or substrates customary in semiconductor technology, such as silicon nitride, gallium arsenide and indium phosphide, are particularly mentioned. Further suitable are those

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substrates known from the production of liquid crystal displays, such as glass and indium/tin oxide; and also metal sheets and foils, for example made of aluminum, copper, zinc; bimetallic and trimetallic foils; electrically non-conducting films which are vacuum-metalized, SiO_2 materials optionally coated with aluminum and paper. These substrates can be subjected to a prior heat treatment, roughened on the surface, etched or treated with chemicals to improve desirable properties, for example, to increase hydrophilicity.

20

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In a particular embodiment, the radiation-sensitive composition can contain an adhesion promoter for better adhesion, in the resist or between the resist and the support or substrate. In the case of silicon or silicon dioxide substrates, suitable adhesion promoters are

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of the aminosilane type, such as, for example, 3-amino-propyltriethoxysilane or hexamethyldisilazane.

5 Examples of supports which can be used for the preparation of printing plates for letterpress printing, planographic printing, screen printing, gravure printing and also for relief copies are aluminum plates, optionally anodically oxidized, grained and/or silicated aluminum plates: zinc plates, steel plates, which may
10 have been treated with chromium, and also plastic sheets or paper.

The recording material according to the invention is subjected to imagewise irradiation using sources of
15 high-energy radiation; electron emission or X-rays are preferred. In the event of using sufficiently transparent binders, imagewise irradiation by means of deep UV is also feasible.

20 The layer thickness varies depending on its field of application. It is between about 0.1 and 1000 μm , in particular between about 1 and 10 μm .

The radiation-sensitive composition can be applied to
25 the support by spray-coating, flow-coating, roller-coating, spin-coating and dip-coating. The solvent is then removed by evaporation leaving the radiation-sensitive layer on the surface of the support. The removal of the solvent can, if necessary, be promoted
30 by heating the layer, to temperatures of up to 150 °C.



However, it is also possible initially to apply the mixture in the above-mentioned manner to a temporary support, from which it is transferred to the final support material under pressure and elevated temperature.

5 Any materials which have been mentioned for use as support materials can basically also be employed as temporary supports, provided they are flexible. The layer is then subjected to imagewise irradiation. Preference is given to high-energy radiation, such as

10 X-rays or electron beams. Particularly preferred is high-energy synchrotron radiation at dosage values from 20 to 200 mJ/cm² or the radiation of an electron beam recorder. In particular cases, the actual differentiating reaction (crosslinking) can take place at room

15 temperature. As a rule, however, it is advantageous to carry out a post exposure bake for about 1 to 30 minutes, preferably at temperatures from about 90 to 150 °C. An image pattern is then developed in the radiation-sensitive layer, by treating the layer with a

20 developer solution which dissolves or removes the non-irradiated portions of the material.

The developers used are solutions of alkaline reagents, such as, for example, silicates, metasilicates, hydrox-

25 ides, hydrogen phosphates and dihydrogen phosphates, carbonates and bicarbonates, in particular of alkali metal or ammonium ions, but also of ammonia or organic ammonium bases and the like. The content of these substances in the developer solution is in general 0.1 to

30 15 % by weight, preferably 0.5 to 5 % by weight, relative to the weight of the developer solution.



The following examples are intended to illustrate the preparation of the compounds containing aromatic chlorine or bromine, which are contained in the radiation-sensitive composition according to the present invention and some of which are new. Quantities are usually specified in parts by weight (pbw), quantitative ratios and percentages are by weight, unless stated otherwise.

Example 1

- 10 A coating solution was prepared, containing
 - 17 pbw of a cresol-formaldehyde novolac having a softening range from 105 to 120 °C;
 - 4 pbw of tetrabromo-bisphenol A,
 - 15 5 pbw of poly(alkoxymethyl)melamine; mixture of methoxy and higher alkoxy compounds (Cymel 1116; Cyanamide) and
 - 74 pbw of propylene glycol methyl ether acetate (PGMEA)
- 20 A silicon wafer which had been treated with an adhesion promoter (hexamethyl disilazane) was spin-coated with the solution, at 5,000 rpm. After drying for 3 minutes in a circulating air oven at 95 °C, a 1.0 µm thick layer
- 25 of synchrotron radiation (BESSY, Berlin, 2 mm air gap) at a dosage of 200 mJ/cm², through a gold-on-silicon mask. The experimental set-up is described in A. Heu-
- 30 berger, "X-Ray Lithography", Microelectronic Engineering 3, 535-556 (1985). After exposure, the wafer was heated for 10 minutes in a circulating air oven at 100 °C and then developed during 60 seconds in a solution of



- 1 % of NaOH,
- 0.4 % of alkylaryl disulfonic acid (sodium salt)
- and
- 0.1 % of a cation-active wetting agent (hetero-
- 5 cyclic quaternary ammonium base) in
- 98.5 % of fully demineralized water.

10 A faultless image was obtained showing all details of
the mask and perfectly rendering even lines and spaces
of 0.3 μ m. There was no undercutting of the resist
walls, which showed angles of nearly 90° in a micro-
graph taken under a scanning electron microscope.

15 Example 2

A coating solution was prepared, containing

- 15 pbw of the novolac specified in Example 1,
- 8.5 pbw of 1,1,1-tris-(3,5-dibromo-4-hydroxyphenyl)-
- 20 ethane,
- 5 pbw of Cymel 1116,
- 71.5 pbw of PGMEA.

25 The solution was applied by spin-coating as in Example
1. After drying on a hot plate (110 °C, 1 minute),
irradiation was carried out as in Example 1, at 90 mJ/cm².
Following a post exposure bake for 2 minutes at 110 °C
development was carried out for 150 seconds with a solu-
tion of

30



2.65 % of sodium metasilicate x $9H_2O$
1.7 % of trisodium phosphate x $12H_2O$ and
0.15 % of sodium dihydrogen phosphate in
95.5 % of fully demineralized water.

5

The patterns obtained corresponded to those of Example 1.

Preparation of 1,1,1-tris-(3,5-dibromo-4-hydroxyphenyl)
ethane

10

102 g of tris-(4-hydroxyphenyl)ethane were suspended in
a mixture of 500 ml of glacial acetic acid and 250 ml
of water. 334 g of bromine were then added dropwise to
the agitated suspension at 10 °C. After the reaction
15 of bromine had gone to completion, 750 ml of water were
added and the crystals which precipitated were filtered
off by suction. They were washed with water, recryst-
allized from toluene and then dried. The product
obtained had a melting point of 276-278 °C. The NMR
20 spectrum ($CDCl_3$) showed the following signals: CH_3 : δ
= 2.05 (3H)s; OH: δ = 5.89 (3H)s; phenyl: δ = 7.1 (6H)s.

Example 3

25

The procedure of Example 2 was repeated, except for the
fact that Cymel 1116 was replaced by the melamine resin
Maprenal 900 (Cassella AG), which is a similar polyalk-
oxymethylmelamine containing C_1 and n- C_4 -alkoxy groups.
The developing time was 20 seconds in the same developer
30 as used in Example 2.



Example 4

A coating solution was prepared, containing

- 20 pbw of the novolac of Example 1,
5 3.4 pbw of tetrachloro-bisphenol A,
5.1 pbw of Cymel 1116,
71.5 pbw of cyclohexanone.

After spin-coating upon a silicon wafer at 5000 rpm,
10 the layer was dried for 1 minute at 110 °C, then
irradiated imagewise at 30 mJ/cm², thereafter baked for
30 minutes at 105 °C and finally developed during 165
seconds in a solution of

- 15 5.3 % of sodium metasilicate x 9H₂O,
3.4 % of trisodium phosphate x 12H₂O and
0.3 % of sodium dihydrogen phosphate in
91 % of fully demineralized water.

20 Example 5

When the amount of tetrachloro-bisphenol A used in
Example 4 is reduced to 0.6 pbw a developing time of
420 seconds is required, at an otherwise identical
procedure.

25

Example 6

A coating solution was prepared, containing

- 20 pbw of novolac according to Example 1,
30 5.1 pbw of neopentyl-diglycidyl ether and



8.5 pbw of tetrabromo-bisphenol A in
71.4 pbw of PGMEA.

The layer obtained was dried for 1 minute at 110 °C.
5 After irradiation at 200 mJ/cm², a post exposure bake
was carried out for 3 minutes at 120 °C. The develop-
ing time was 60 seconds in the developer specified in
Example 4.

10 Example 7

A coating solution was prepared, containing

22.7 pbw of a copolymer comprising 84 % by weight of
pyrocatechol monomethacrylate and 16 % by
15 weight of N-methoxymethyl methacrylamide
and

5.7 pbw of tetrabromo-bisphenol A in
71.6 pbw of PGMEA.

20 The layer obtained was dried for 1 minute at 110 °C.
After irradiation at 200 mJ/cm² and a post exposure
bake for 3 minutes at 130 °C, development was effected
within 30 seconds in the developer specified in
Example 4.

25

Example 8 (Comparative Example)

A coating solution was prepared, containing

20 pbw of the novolac of Example 1, -----
30 3.4 pbw of DDT and



5.1 pbw of Cymel 1116 in
71.5 pbw of PGMEA

5 This formulation corresponds to that of Example 4,
however, using the known starter DDT which is not
alkali-soluble. The layer obtained was dried for 1
minute at 110 °C. Irradiation at 30 mJ/cm² followed by
a post exposure bake for 3 minutes at 105 °C produced a
10 resist film that could not be developed in the non-
exposed areas, even after treating it for 30 minutes
with the developer specified in Example 4.

Example 9 (Comparative Example)

15 When the amount of DDT is reduced to 0.6 pbw, analo-
gously to Example 5, development is possible using the
developer of Example 4, but it takes a considerably
longer time (18 minutes), as compared with Example 5.

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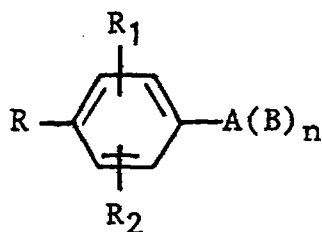
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What is claimed is:

1. A composition which is curable by high-energy radiation, comprising a compound that forms an acid under the action of high-energy radiation and an acid-hardening substance, wherein the compound that forms an acid contains chlorine or bromine linked to aromatic carbon atoms and has a pKa value below 12.
2. A radiation-curable composition as claimed in claim 1, wherein the acid-forming compound has a pKa value of 6 to 10.
3. A radiation-curable composition as claimed in claim 1, wherein the acid-forming compound comprises a compound of the general formula



containing at least one chlorine or bromine atom linked to an aromatic carbon atom, wherein

R is OH or COOH,

R₁ and R₂ are identical or different and denote hydrogen, chlorine, bromine, alkyl which may

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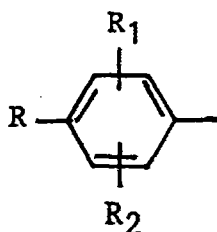
be substituted by aryl, alkoxy, aryloxy or hydroxyl groups or by fluorine atoms; or aryl which may be substituted by alkoxy, aryloxy or hydroxyl groups or by halogen atoms, and

5 n = 0 to 3,
if n = 0:
A denotes hydrogen, chlorine, bromine, alkyl which may be substituted by alkoxy, aryloxy, hydroxyl or aryl groups or by fluorine atoms;

10 aryl which may be substituted by alkoxy, aryloxy, hydroxyl or carboxyl groups or by halogen atoms,
if n = 1:
A denotes a single bond, -O-, -S-, -SO₂-, -NH-,

15 -NR₃-, alkylene or perfluoroalkylene,
if n = 2:
A denotes -CR₃- or -N- and
if n = 3:
A denotes -C- and

20 B denotes



carboxyl, substituted carbonyl, in particular alkylcarbonyl or arylcarbonyl, carboxyalkyl or

30 substituted sulfonylimidocarbonyl and





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R_3 denotes alkyl, in particular (C_1-C_3) alkyl, or aryl, in particular phenyl.

- 5 4. A radiation-curable composition as claimed in claim 1, wherein the acid-forming compound comprises a monomer and the composition contains a binder that is insoluble in water and soluble in aqueous alkali.
- 10 5. A radiation-curable composition as claimed in claim 1, wherein the acid-forming compound comprises a polymer.
- 15 6. A radiation-curable composition as claimed in claim 5, wherein the acid-forming compound comprises a hydroxystyrene polymer or copolymer or a phenolic resin.
- 20 7. A radiation-curable composition as claimed in claim 5, wherein the composition additionally contains a polymeric binder that is insoluble in water and soluble in aqueous alkali.
- 25 8. A radiation-curable recording material for use with high-energy radiation, essentially comprising a support and a radiation-sensitive layer, wherein the layer comprises a radiation-curable composition as claimed in any of claims 1 to 7.
- 30 9. A process for recording high-energy radiation by means of a radiation-curable recording material,

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5 wherein a radiation-curable composition according
to claims 1 to 7 is applied to a support, which may
have been provided with an adhesion promoter, the
material is dried, then irradiated imagewise with
high-energy radiation, in particular X-ray or
electron emission, thereafter baked at elevated
temperature, if required and the image is finally
developed by removing the non-irradiated portions
of the layer with an aqueous-alkaline developer.

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