

Description

Dry-developable positive resist

The invention relates to a dry-developable positive TSI resist.

5 In the course of photolithographic patterning, dry-developable TSI single-layer resists (TSI = Top Surface Imaging) exhibit a number of advantages such as reflections being suppressed and topography effects being reduced. A detailed description of such systems can be
10 found in "Introduction to Microlithography", ACS Symposium Series 219 (1983), pages 287 to 350.

TSI resists are known both in the form of positive and of negative dry-developable single-layer systems. In contrast to negative systems, positive TSI
15 systems are much more suitable - owing to a lower defect density - for applications in the contact hole planes, which are highly critical.

Dry-developable single-layer systems function according to the following principle:

- 20 - application of the resist to a silicon wafer and drying;
- exposure and, if required, heating to generate a "latent" image;
- treatment with a metallizing agent, for example an
25 organometallic compound, which makes the resist - in the exposed areas (negative resist) or in the unexposed areas (positive resist) - resistant to dry development, particularly in an oxygen plasma;
- dry development.

This number of process steps should not be exceeded during production, if possible.

A high-resolution TSI system suitable for production should, in addition, meet the following requirements:

1. Simple and line-compatible processing

More process steps than the abovementioned mean higher costs, the possible causes for increased costs being investments for additional equipment and/or reagents, as well as the additional process steps.

2. High sensitivity

The lower the sensitivity, the lower is the throughput with the expensive exposure equipment (stepper) and the higher are the costs. Of particular importance in this context is high sensitivity in the DUV region (DUV = Deep UV).

3. High Resistance to plasma development

High resistance of the areas treated with the metallizing agent is important to provide as much scope to the process as possible during dry-developing.

To overcome the problem of low DUV sensitivity of photoresist, resist systems were developed whose base polymer contains t-butyl ester or t-butoxycarbonyloxy groups (cf. EP-A 0 102 450 and 0 161 476, and the corresponding US Patents 4 491 628 and 4 552 833). During exposure in the presence of a strong acid former, for example a Crivello salt, carboxyl groups or phenolic OH groups are generated, a single proton - according to the principle of so-called chemical amplification - cleaving off more than one group (cf., for example, "J. Electrochem. Soc.", Vol. 136 (1989), pages 1453 to 1456).

Catalysis by means of strong acids provides another way to carry out cationic polymerizations or cross-linkings which are suitable for use in resist systems having high DUV sensitivity. A negative TSI resist which is highly sensitive in the DUV range and operates on the principle of acid-catalyzed polymerization is described, for example, in EP-A 0 192 078 or the corresponding US Patent 4 551 418. The use of acid-catalyzed cross-linking in photoresist systems, for example by electrophilic substitution on activated aromatic compounds in the presence of Crivello salts has been reported during the 8th International Conference on Photopolymers, Ellenville, N.Y. (1988) (see Conference Report: pages 63 to 72).

A number of positive TSI systems have indeed been disclosed previously, but none of them entirely meets the abovementioned requirements:

- EP-A 0 136 130

The method described can be used - by means of UV light or electron beams - to generate positive and negative patterns. A drawback is the need for special equipment (for vacuum) and the requirement of metallization by means of corrosive or toxic gases such as B_2H_6 , $SiCl_4$ and $TiCl_4$, which is of little use for production.

- EP-A 0 204 253 (and US Patent 4 613 398)

Positive and negative systems are described, the permeability of the resist with respect to the metallizing agent being altered by exposure. A drawback of this system in the positive mode are low DUV sensitivity (from 50 to 300 mJ/cm²) and the requirement of silylation by means of hexyamethylcyclotrisilazane in o-xylene at 65°C, calling for special apparatus resulting in low line compatibility.

- EP-A 0 229 917 (and US Patent 4 657 845)

5 A method is described which is based on the principle of chemical amplification and has high DUV sensitivity (approx. 6. mJ/cm²). This does, however, require two additional process steps, i.e. a metal-free treatment with methyl isocyanate, in a vacuum oven, moreover, and an overall-exposure step.

- EP-A 0 248 779

10 While the method described manages with few process steps, it does require a special apparatus for gas-phase silylation at elevated temperature.

- EP-A 0 281 182 and EP-A 0 352 739 (and US Patent 4 921 778)

15 While the systems described exhibit good DUV sensitivity, they do have the drawback that special equipment is required for silylation from the gas phase at elevated temperature. Moreover, these silylated areas, owing to the incorporation of monomer silicon fragments such as Si(CH₃)₃ groups, have only a moderate etching resistance (cf: "Micro-electronic Engineering", Vol. 3 (1985), pp. 279 to 291).

- "Mat. Res. Soc. Symp. Proc.", Vol. 45 (1985), pages 197 to 202, and "IBM Techn. Discl. Bull.", Vol. 27, No. 4A (1984), p. 2197.

25 The method described is based on the decarboxylation of homo- or copolymers of (meth)acrylic acid and, where appropriate, its anhydride, by high-energy radiation and silylation of the unexposed areas from the gas phase. The drawbacks consist in gas-phase silylation (special equipment being required), the relatively low etching resistance in the oxygen plasma (owing to silylation with hexamethyldisilazane) and the reduced DUV sensitivity of a decarboxylation reaction of the abovementioned type.

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- "J. Vac. Sci. Technol. B", Vol. 10 (1992), pp. 2610 to 2614.

This describes the silylation of resists on a novolak basis from the liquid phase by means of hexamethylcyclotrisilazane. This silylation reagent does, however, owing to its sensitivity to moisture, require closed special equipment. Moreover, the novolak resists used contain OH groups which are silylated with the formation of O-Si bonds. The etching resistance of such systems is comparatively low, however.

Furthermore, a patterning method involving dry development had previously been proposed, which produces positive images and which - employing conventional equipment - makes it possible to generate sub-half-micron patterns (see EP-A 0 451 311 and the corresponding US Patent 5 229 258). This method, however, comprises two additional process steps, i.e. a treatment of the exposed photoresist layer with a polyfunctional organic compound, in particular a polyamine, and an overall-exposure step.

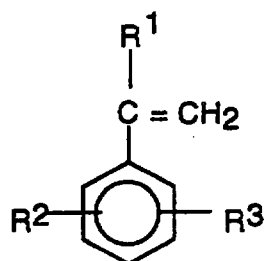
EP-A 0 492 256 discloses a method for photolithographic patterning in the submicron range and a dry-developable TSI resist system suitable for this purpose. To this end, a substrate is coated with a photoresist layer composed of a polymer which contains carboxylic acid anhydride groups and t-butylcarboxylate groups, of a photoinitiator which liberates an acid upon exposure, and of a suitable solvent. The photoresist layer is then dried and exposed imagewise, and the exposed layer is subjected to a thermal treatment, the thermal treatment being controlled in such a way that the photoresist becomes hydrophilic in the exposed areas. The photoresist layer thus treated is then subjected to liquid-phase silylation, and the silylated layer is dry-developed in an anisotropic oxygen plasma. While the known TSI resist system does have a high etching resistance and a high sensitivity, it is possible, however, for wetting problems during the treat-

ment with the silylation solution to occur, specifically during silylation with apolar, aprotic media, i.e. in the case of the positive mode.

It is an object of the invention to provide a dry-developable, positive TSI resist for the sub-half-micron range, which can be readily processed, is sensitive in particular to DUV radiation, and has a high etching resistance of the metallized areas to dry development. In particular it should be possible, with the TSI resist, for the metallization process to be carried out at room temperature and at room humidity and atmospheric pressure, without, specifically, use of special equipment.

This is achieved, according to the invention, by a resist which comprises the following components:

- a suitable solvent
- a strong acid former as a photoactive component, and
- a base polymer in the form of a co- or terpolymer comprising maleic anhydride as a base unit and glycidyl methacrylate and/or a styrene derivative of the following structure as a further base unit:



where $R^1 = H \text{ or } CH_3,$

$R^2 = H \text{ or } R^3,$

$R^3 = (CH_2)_m - OX,$

X having the following meaning:

$(CH_2)_a - CH_3, (CH_2)_b - OCH_3, CO - (CH_2)_c - CH_3,$ or
 $CO - (CH_2)_d - O - (CH_2)_e - CH_3,$



and m, a, b, c, d and e - independently of one another - each representing an integer from 0 to 5,

and

- 5 - optionally, but unconditionally for m = 0, an additive of the following structure:



where $R^4 = CO-(CH_2)_n-CH_3$ or $CO-C_6H_5$,

n representing an integer from 0 to 5.

10 In the case of the positive resist according to the invention it is essential for the base polymer to be composed of at least two different base units or for at least two different functional groups to be present. These functional groups are, firstly, carboxylic acid anhydride groups and, secondly, epoxide groups or
15 aromatic groups of the above-described type, the anhydride groups serving to form a chemical bond during silylation, the epoxide groups or the aromatic groups for acid-catalyzed cross-linking in the DUV range.

20 The base units used for the base polymer are therefore, firstly, maleic anhydride and, secondly, either glycidyl methacrylate or a styrene derivative of the structure (1). If the styrene derivative does not contain a group $(CH_2)_m-OX$ with $m \geq 1$, the resist composition additionally contains an additive having the structure (2). This additive, which is preferably p-bis(ace-
25 toxymethyl)benzene, may be present, however, even if the styrene derivative does comprise a group of the abovementioned type.

30 The base polymer may be a copolymer or a terpolymer. What is present in the former case is a copolymer of maleic anhydride and glycidyl methacrylate or of maleic anhydride and



a styrene derivative of the abovementioned type. In the latter case a third base unit is added which may, for example, be maleic acid or styrene. Alternatively, the terpolymer may be composed of maleic anhydride, glycidyl methacrylate and a styrene derivative of the abovementioned type.

The photoactive component in the case of the TSI resist according to the invention is a strong acid former, i.e. a compound which upon exposure forms a strong acid. This purpose is served, in particular, by so-called Crivello salts. These are onium compounds such as diphenyliodonium triflate and triphenylsulfonium triflate ("triflate" is the trifluoromethanesulfonyl radical). Generally photoactive sulfonic-acid formers can be used, however. The photoactive component is generally used in an amount of from 0.5 to 5 % by weight, based on the resist composition.

The solvents used for the photoresist according to the invention are solvents known per se. Preferably, the resist solvent is methoxypropyl acetate or diethylene glycol dimethylether; it is also possible, for example, for cyclohexanone to be used. The only important criterion in selecting the solvent is that both the base polymer and the photoactive component and, if required, the additive must be dissolved.

Photopatterning in the case of the TSI resist according to the invention requires only the minimum number of process steps. After application of the resist to the substrate and drying, exposure takes place through a mask, followed by tempering. This results in acid-catalyzed cross-linking of the exposed areas, so that during the subsequent liquid-phase silylation any penetration of the silylation solution into these areas is prevented and the unexposed areas are silylated selectively. The silylation reagent used is in the form of oligomeric bisaminosiloxanes. Compounds of this type

ensure high plasma etching resistance during the dry-developing step. The silylation itself is carried out in conventional spray or puddle development equipment at room temperature and room humidity, and at atmospheric pressure. After silylation a dry-developing step is carried out in an anisotropic oxygen plasma. We found, in the process, that the etching resistance of the silylated resist areas to the oxygen plasma is very high. After the dry-developing step, sub-half-micron patterns with steep sidewalls are obtained.

The invention will be described in even more detail with reference to specific embodiments. These make use of the following starting materials and reagents (PM = parts by mass):

- 15 - Base polymer (1):
Copolymer of maleic anhydride and 4-(acetoxymethyl)-styrene, prepared by free-radical polymerization of the monomers, using azoisobutyronitrile as the initiator.
- 20 - Base polymer (2):
Terpolymer of maleic anhydride, 4-(acetoxymethyl)-styrene, and maleic acid, prepared by free-radical polymerization of the monomers, using azoisobutyronitrile as the initiator.
- 25 - Base polymer (3):
Copolymer of maleic anhydride and glycidyl methacrylate, prepared by free-radical polymerization of the monomers, using azoisobutyronitrile as the initiator.
- 30 - Base polymer (4):
Copolymer of maleic anhydride and p-methoxystyrene, prepared by free-radical polymerization of the monomers, using azoisobutyronitrile as the initiator.
- 35 - Photoactive component (1):
Triphenylsulfonium trifluoromethanesulfonate
- Photoactive component (2):
Diphenyliodonium trifluoromethanesulfonate
- Additive (1):

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p-bis(acetoxymethyl)-benzene

- Silylating solution (1):
Aqueous organic solution comprising 8 PW of diamino-siloxane (Tegomer A-Si 2120 from Goldschmidt), 61.3 PW of isopropanol, 18.4 PW of diethylene glycol dimethylether, and 12.3 PW of water
- Silylating solution (2):
Aqueous organic solution comprising 8 PW of diamino-siloxane, 51 PW of isopropanol, 26 PW of ethanol, and 15 PW of water
- Silylating solution (3):
Organic solution comprising 5 PW of diaminosiloxane, 76 PW of isopropanol and 19 PW of diethylene glycol dimethylether
- Silylating solution (4):
Aqueous organic solution comprising 8 PW of diamino-siloxane, 69 PW of isopropanol, 9.2 PW of diethylene glycol dimethylether, and 13.8 PW of water.

Example 1

A silicon wafer is spin-coated with a resist comprising 23.25 PW of base polymer (1), 1.75 PW of photoactive component (1) and 75 PW of methoxypropyl acetate, and is dried for 60 s and 100°C on a hot plate; the film thickness of the resist is 1.2 μm . The resist is then subjected to contact exposure at 6.8 mJ/cm² through a mask (apparatus MJB 3, from Karl Süss; exposure wavelength λ = 250 nm) and tempered for 90 s at 140°C. After cooling, the resist is treated in a puddle processor (Type CEM 2000, from Convac), at room temperature and room humidity, and atmospheric pressure, for 75 s with the silylating solution (1) and then rinsed for 30 s with isopropanol and dried. After drying the wafer is introduced into a plasma etching system (Type MIE 720, from Material Research Corporation) and the resist is dry-developed in an oxygen plasma (O₂/RIE: gas pressure 1.8 mtorr, gas flow rate 30 sccm, bias voltage 50 V, rating 1.2 kW, with magnet). Positive patterns up to 0.4 μm having a ridge/trench ratio of 1:1 are obtained.

Example 2

A silicon wafer is spin-coated with a resist comprising 21.4 PW of base polymer (2), 1.6 PW of photoactive component (1) and 77 PW of methoxypropyl acetate, and is dried for 60 s and 100°C on a hot plate; the film thickness of the resist is 1.2 μm . The resist is then subjected to contact exposure at 7 mJ/cm^2 through a mask (apparatus MJB 3, from Karl Süss; exposure wavelength $\lambda = 250 \text{ nm}$) and tempered for 90 s at 140°C. After cooling, the resist is treated in a puddle processor (Type CEM 2000, from Convac), at room temperature and room humidity, and atmospheric pressure, for 90 s with the silylating solution (2) and then rinsed for 30 s with isopropanol and dried. After drying the resist [sic] is introduced into a plasma etching system (Type MIE 720, from Material Research Corporation) and the resist is dry-developed in an oxygen plasma (O_2/RIE : gas pressure 1.8 mtorr, gas flow rate 30 sccm, bias voltage 50 V, rating 1.2 kW, with magnet, as in Example 1). Positive patterns up to 0.4 μm having a ridge/trench ratio of 1:1 are obtained.

Example 3

A silicon wafer (as the substrate) is spin-coated with a commercially available positive resist based on novolak and is dried for 1 min. on a hot plate at 90°C. After baking in a circulating oven (240°C, 35 min) the thickness of the resist serving as a planarizing layer is 1.3 μm .

The planarizing layer is spin-coated with a resist comprising 13.95 PW of base polymer (3), 1.05 PW of photoactive component (2) and 85 PW of diethylene glycol dimethylether. After drying at 90°C/60 s on a hot plate, the film thickness of the top resist is 0.35 μm . The resist is then subjected to contact exposure at 5.5 mJ/cm^2 through a mask (apparatus MJB 3, from Karl Süss; exposure wavelength $\lambda = 250 \text{ nm}$) and tempered for 60 s at 110°C. After cooling, the resist is treated in a puddle processor (Type CEM 2000, from Convec [sic]), at

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room tempe-

5 rature and room humidity, and atmospheric pressure, for
60 s with the silylating solution (3) and then rinsed for
30 s with isopropanol and dried. After drying the wafer
is introduced into a plasma etching system (Type MIE 720,
from Material Research Corporation) and the resist is
dry-developed in an oxygen plasma (O_2 /RIE: gas pressure
1.8 mtorr, gas flow rate 30 sccm, bias voltage 40 V,
rating 0.9 kW, with magnet). Positive patterns up to
0.4 μm with vertical sidewalls having a ridge/trench
10 ratio of 1:1 are obtained.

Example 4

A silicon wafer is spin-coated with a resist
comprising 13.6 PW of base polymer (4), 5.0 PW of addi-
tive (1), 1.4 PW of photoactive component (1) and 80 PW
15 of methoxypropyl acetate, and is dried for 60 s at 90°C
on a hot plate; the film thickness of the resist is
1.3 μm . The resist is then subjected to contact exposure
at 7.5 mJ/cm² through a mask (apparatus MJB 3, from Karl
Süss; exposure wavelength λ = 250 nm) and tempered for
20 60 s at 110°C. After cooling, the resist is treated in a
puddle processor (Type CEM 2000, from Convac), at room
temperature and room humidity, and atmospheric pressure,
for 45 s with the silylating solution (4) and then rinsed
for 30 s with isopropanol and dried. After drying the
25 resist [sic] is introduced into a plasma etching system
(Type MIE 720, from Material Research Corporation) and
the resist is dry-developed in an oxygen plasma (O_2 /RIE:
gas pressure 1.8 mtorr, gas flow rate 30 sccm, bias
voltage 50 V, rating 1.2 kW, with magnet, as in Example
30 1). Positive patterns up to 0.4 μm with vertical
sidewalls having a ridge/trench ratio of 1:1 are
obtained.

Example 5

35 A resist corresponding to Example 1 is applied to
a silicon wafer, in the manner described there, and
dried. This is followed, in a corresponding manner, by
75 s, in a puddle processor, of the silylating solution

(1) treatment, then by rinsing with isopropanol for 30 s and drying. After drying, the wafer is introduced into a plasma etching system (Type MIE 720, from Material Research Corporation) and the resist is dry-etched for
5 200 s in an oxygen plasma (O_2 /RIE: gas pressure 1.8 mtorr, gas flow rate 30 sccm, bias voltage 40 V, rating 0.9 kW, with magnet). From the film thickness measurement before and after etching, an ablation rate of the silylated layer of 0.83 nm/s can be calculated.

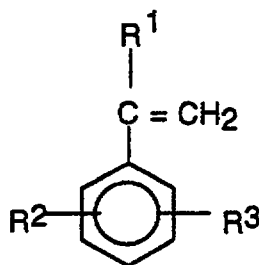
10 Example 6

A resist corresponding to Example 3 is applied to a silicon wafer, in the manner described there, and dried. This is followed, in a corresponding manner, by
15 60 s, in a puddle processor, of the silylating solution (3) treatment, then by rinsing with isopropanol for 30 s and drying. After drying the wafer is introduced into a plasma etching system (Type MIE 720, from Material Research Corporation) and the resist is dry-etched for
20 200 s in an oxygen plasma (O_2 /RIE: gas pressure 1.8 mtorr, gas flow rate 30 sccm, bias voltage 40 V, rating 0.9 kW, with magnet). From the film thickness measurement before and after etching, an ablation rate of the silylated layer of 0.78 nm/s can be calculated.

Patent claims:

1. A dry-developable positive TSI resist, characterized in that it comprises the following components:

- a suitable solvent
- 5 - a strong acid former as a photoactive component, and
- a base polymer in the form of a co- or terpolymer comprising maleic anhydride as a base unit and glycidyl methacrylate and/or a styrene derivative of the following structure as a further base unit:



- 10 where $R^1 = H \text{ or } CH_3$,
 $R^2 = H \text{ or } R^3$,
 $R^3 = (CH_2)_m-OX$,

X having the following meaning:

- 15 $(CH_2)_a-CH_3$, $(CH_2)_b-OCH_3$, $CO-(CH_2)_c-CH_3$, or
 $CO-(CH_2)_d-O-(CH_2)_e-CH_3$,
and m, a, b, c, d and e - independently
of one another - each representing an
integer from 0 to 5,
and

- 20 - optionally, but unconditionally for $m = 0$, an
additive of the following structure:



- where $R^4 = CO-(CH_2)_n-CH_3$ or $CO-C_6H_5$,
n representing an integer from 0 to 5.





2. The resist as claimed in claim 1, characterized in that the base polymer is a copolymer of maleic anhydride and glycidyl methacrylate.
3. The resist as claimed in claim 1, characterized in that the base polymer is a copolymer of maleic anhydride and 4-(acetoxymethyl)-styrene.
4. The resist as claimed in claim 1, characterized in that the base polymer is a terpolymer of maleic anhydride, 4-(acetoxymethyl)-styrene and maleic acid.
5. The resist as claimed in claim 1, characterized in that the base polymer is a copolymer of maleic anhydride and p-methoxystyrene.
6. The resist as claimed in claim 5, characterized in that it contains p-bis(acetoxymethyl)-benzene as an additive.
7. The resist as claimed in any one of claims 1 to 6, characterized in that the photoactive component is an onium salt.
8. The resist as claimed in claim 7, characterized in that the photoactive component is diphenyliodonium trifluoromethanesulfonate and/or triphenylsulfonium trifluoromethanesulfonate.
9. The resist as claimed in one or more of claims 1 to 8, characterized in that the solvent is methoxypropyl acetate, or diethylene glycol dimethylether.



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10. The use of the resist as claimed in one or more of claims 1 to 9 in single-layer resist technology.