DIOLS, METHODS FOR THE PREPARATION THEREOF, METHODS USING THEREOF; AND USES THEREOF

FIELD OF THE INVENTION

The invention relates to a compound, compositions comprising the polyol, and to methods for the preparation of the polyol. Further, the invention relates to a use of the compound or the composition in a lithography method. Still further, the invention relates to a lithography method, and an optical element, optically active device, optical device, or semiconductor device obtained by the lithography method. In particular, the compound is a polyol.

BACKGROUND

Spin-on carbon (SOC) materials are widely used in semiconductor manufacturing, particularly in advanced lithography processes. These materials may serve as hard masks in multilayer lithography schemes, which are essential for creating the intricate patterns required in semiconductor devices. However, common SOC materials have challenges associated with their use.

Polyarylene ether-based SOCs are popular due to their excellent thermal stability and low dielectric constant. They are often used in applications requiring high-temperature processing. Another class of SOC material is aromatic hydrocarbon-based SOCs that are known for their good etch resistance and mechanical strength, and these materials may be suitable for processes involving aggressive etching environments. Further, fullerene derivatives may offer unique properties such as high etch selectivity and low defectivity, making them suitable for advanced patterning techniques. Further, hydrogenated amorphous carbon is valued for its high etch resistance and ability to form smooth, defect-free films.

However, common problems SOC materials include pattern deformation (wiggling), solubility issues, non-uniform film thickness, and chemical-mechanical planarization (CMP) challenges. One of the significant challenges with SOC materials is pattern deformation (wiggling) during reactive ion etching (RIE). As the aspect ratios of SOC layers increase and feature sizes decrease, the patterns can deform, leading to issues in pattern transfer. High-temperature post-application baking (PAB) may mitigate this problem, but it adds complexity to the process. High-temperature-stable SOC polymers often have poor solubility in common organic solvents. This can

complicate the application process and limit the choice of solvents for cleaning and processing. Further, when using common SOC material achieving uniform film thickness across a wafer can be challenging, especially for thick SOC layers. Variations in film thickness can lead to non-uniform etching and pattern transfer issues. SOC films often require chemical-mechanical planarization (CMP) to achieve a smooth surface. However, the hardness of SOC materials can vary, making it difficult to achieve consistent polishing rates. For instance, SOC films with high hardness may resist polishing, while softer films may polish too quickly, leading to non-uniform surfaces.

Further problems associated with common SOC materials are problems associated with the removal of the SOC material after pattern transfer, and hydrophilicity and absorption issues of the SOC material. Removing SOC materials after pattern transfer without damaging the underlying substrate may be a challenge. Some SOCs can be removed using common developers, but others may require additional plasma etching steps, which can introduce defects and damage. Regarding hydrophilicity and absorption issues, during CMP, the surface properties of SOC films can change, affecting their hydrophilicity and absorption characteristics. This can impact the polishing rate and the overall quality of the SOC film.

While SOC material offer several benefits, including high etch resistance and thermal stability, they also present challenges such as pattern deformation, solubility issues, and difficulties in achieving uniform film thickness. Addressing these challenges requires careful material selection and process optimization to ensure successful pattern transfer and device fabrication.

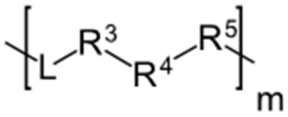
A good high temperature spin-on carbon (SOC) material should have one or more of the following main characteristics, ideally all: (a) ideally, an excellent planarization of a substrate surface having irregularities such as holes and trenches; (b) target thin film thickness under process conditions; (c) target high etch resistance, which is in demand for plasma etching process under process conditions; (d) outgassing and sublimate reduction for defect free coating; (e) ability to be spin coated from safe solvents; (f) spin bowl compatibility (compatible with all the solvents and materials that they can come in contact with in the spin bowl); (g) excellent storage stability; and (h) excellent thermal stability.

Due to high carbon content, which is typically required for excellent thermal stability and high etch resistance, conventional high temperature spin-on carbon (SOC) materials have limited spin bowl compatibility and are usually coated from very polar solvents, such as n-methyl pyrrolidone (NMP). I.e., such SOC becomes insoluble upon a contact with regular solvents used for lithography. Moreover, often outgassing and planarization properties could be significantly improved for conventional high temperature spin-on carbon (SOC) materials.

SUMMARY

This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

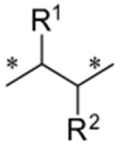
It is an object of the present invention to provide a compound of formula (I):



(I)

, wherein

L represent a moiety of formula (Ia):



(Ia)

, wherein

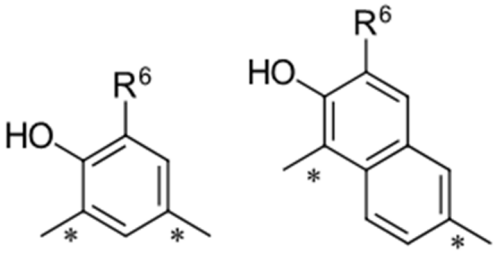
R^1 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R';

R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic

hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R''; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

R^3 is selected from a moiety of formula (Ib) or a moiety of formula (Ic):

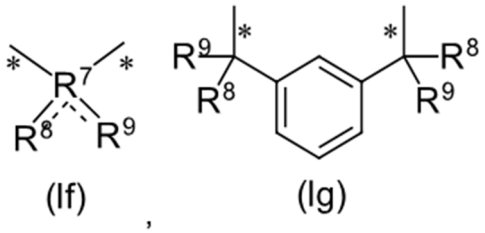


(Ib) , (Ic) , wherein

R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl; and

one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^5;

R^4 is absent, or is selected from a moiety of formula (If) or a moiety of formula (Ig):



(If) , (Ig) , wherein

each dotted line represents an optional bond;

R^7 is C or S;

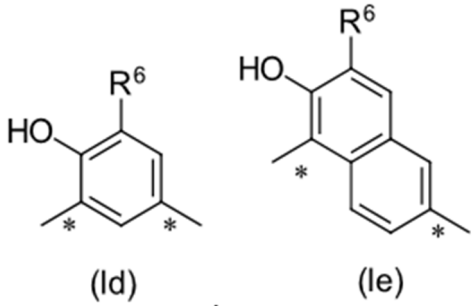
R^8 and R^9, provided that R^7 is C, together with the carbon they are attached to, form an aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

R^8 and R^9 are selected from the group consisting of a 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

both R^8 and R^9 are O, provided that R^7 is S and the dotted lines represent bonds; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

R^5 is selected from a moiety of formula (Id) or a moiety of formula (Ie):



(Id) , (Ie) , wherein

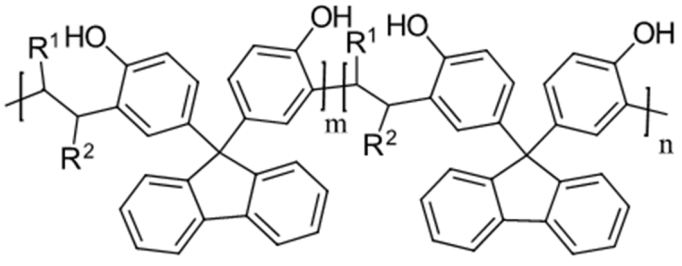
R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl; and

one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^3;

wherein each R', R'' and R''' is independently selected from the group consisting of halogen, and C_{1-3} -alkyl; and

m is an integer selected from 1-100.

It is another object of the present invention to provide a compound of formula (III):



(III) , wherein

each of R^1 and R^2 is as defined in the present disclosure, provided that the compound of formula (III) comprises at least two different R^1 and/or at least two different R^2;

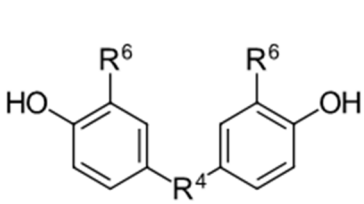
m is as defined in the present disclosure; and

n is an integer selected from 1-100.

It is another object of the present invention to provide a composition comprising the compound as defined in the present disclosure.

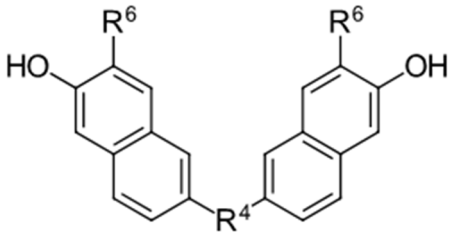
It is a further object of the present invention to provide a method for the preparation of a compound as defined in the present disclosure, wherein the method comprises:

i) providing a polymerization composition comprising a compound of formula (IVa) and/or formula (IVb):



(IVa)

,

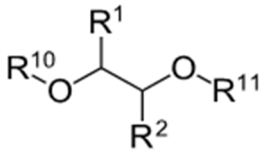


(IVb)

, wherein

R^4 and R^6 are as defined in any of claims 1 – 12; and

a compound of formula (V):



(V)

, wherein

R^1 and R^2 are as defined in the present disclosure;

R^{10} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -hydrocarbyl; and

R^{11} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -acyl; and

ii) polymerizing the polymerization composition to form the compound as defined in the present disclosure.

It is a further object of the present invention to provide a use of a compound or a composition as defined in the present disclosure in a lithography method.

As further object, the present invention provides a lithography method comprising:

i) applying a compound or a composition as defined in the present disclosure on a substrate, thereby forming a film on the substrate; and

ii) heating the formed film to form a spin-on carbon hardmask.

Another object of the invention is to prove an optical element, optically active device, optical device, or semiconductor device obtained by a method as defined in the present disclosure.

More specifically, the present invention is characterized by what is stated in the characterizing part of the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

Considerable advantages are obtained by the present invention.

Surprisingly, it has been found that polymerization of specific diols, such as bisphenols, with a 1,2-diol, such as hydrobenzoin, or a masked 1,2-diol, such as propylene glycol monomethyl ether acetate (PGMEA), as a comonomer results into a novel low molecular weight compound, typically a polymer, with a C-C bridge between the diol moieties. Surprisingly, it has been found that compounds as disclosed in the present disclosure may be used to prepare high temperature spin-on carbon (SOC) materials, such as spin-on carbon hardmasks, that overcome, at least partially, drawbacks of the prior art. Typically, high temperature SOC materials as disclosed in the present disclosure, obtained from compounds as disclosed in the present disclosure, have an excellent balance of all or at least a part of required properties.

Other advantages of the present invention include a faster and more economical method to prepare compounds of the disclosure.

Further features and advantages of the present technology will appear from the following detailed discussion of embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a lithography method disclosed in the present disclosure to form a spin-on carbon hardmask on a substrate; and
Figure 2 shows a lithography method disclosed in the present disclosure.

DETAILED DESCRIPTION

“Comprises” or “comprising” denotes that the subsequently described feature(s) or act(s) may but need not include other feature(s) or act(s). It will further be understood that reference to 'an' item refers to one or more of those items.

“Optional” or “optionally” denotes that the subsequently described event or circumstance may but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not.

The term “polyol” as used herein and hereafter refers to an alcohol comprising two or more hydroxy groups. It is to be understood that phenols comprising two or more, such as four or more, or six or more, hydroxy groups are also polyols, said polyols can be aliphatic or aromatic.

The terms “diol” and “diols” refer similarly to alcohols having two hydroxy groups, said alcohols can be aliphatic or aromatic.

The term “halogen” as used herein and hereafter by itself or as part of other groups refers to the Group VIIa elements and includes F, Cl, Br and I groups.

The term “hydrocarbyl” as used herein and hereafter refers to a monovalent hydrocarbon, such as, but not limited to, an alkyl, an alkenyl, an arenyl, and an cyclic alkyl. The hydrocarbyl may comprise 1-4 heteroatoms each selected from N, O, and S. Therefore, a $C_{1\text{-}10}$ -hydrocarbyl refers to hydrocarbyl comprising 1 – 10 carbons, optionally comprising 1-4 heteroatoms each selected from N, O, and S.

Embodiments of the present invention relates also to the use of the compound of formula (I), the compound of formula (II), or the composition comprising the compound of formula (I) and/or the compound of formula (II) to cast coating on semiconductor substrates to form patterns through subsequent bake, irradiation and development steps. In particular, the invention relates to the ability to control the microstructure of films or layers present on the substrate used in a lithography method in such way it is industrially feasible and solves, at least partially, drawbacks of prior art.

In the present context, the term “unsaturated moieties” stands for structures which exhibit double or triple bonds, in particular between carbon atoms. Such bonds are referred to as “unsaturated bonds”. The unsaturated moieties can contain one or

several unsaturated bonds. The unsaturated bonds can be conjugated or non-conjugated.

An unsaturated moiety may contain at least one ethylenically unsaturated bond. Examples of unsaturated moieties include groups or structures containing a double or triple bond, such as an alkylene group, an alkenylene group, a cycloalkylene group, an aryl group, an aralkyl group, a halogenated alkyl or alkylene group, a halogenated aryl group, a halogenated aralkyl group, an alkenyl group, an alkoxyalkyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them. Each may, of course, also contain substituents, typically selected from the group of halides, alkoxy groups, hydroxyl groups, thiol groups, ester groups, oxo groups, ketone groups, carboxylic acid groups, amines and amides.

Specific examples of unsaturated moieties include vinyl, vinyl ethers, acrylate, alkacrylate, allyl, norbornylene, and combinations thereof.

“Alkoxy” and “alkyl”, “alkylene”, and “alkenylene” groups are linear, branched or cyclic groups derived from alkanes comprising 1 to 10 carbon atoms. In embodiments of the present technology, alkoxy and alkyl are preferably linear or branched groups, in particular lower alkoxy and lower alkyl groups. Such groups contain 1 to 6, in particular 1 to 4 carbon atoms.

In particular, the term “alkyl” as used herein and hereafter is an aliphatic linear, branched or cyclic, especially linear or branched, hydrocarbon group having the indicated number of carbon atoms, for example C_{1-6}-alkyl has 1 to 6 carbon atoms in the alkyl moiety and thus, for example, C_{1-4}-alkyl includes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, and C_{1-6}-alkyl additionally includes, but is not limited to, branched and straight chain pentyl and hexyl. Other examples of alkyl are benzyl (may be a protecting group), 2-methoxybenzyl (CH_2Ph(o-OMe)), 2-hydroxybenzyl (CH_2Ph(o-OH)), and 2-cyano-1-phenylethyl.

“Cycloalkylene” groups comprise at least 3, preferably at least 4, and in particular at least 5 carbon atoms and up to 10 carbon ring atoms.

The terms “aromatic hydrocarbyl” refers to a monovalent hydrocarbon that is aromatic, said monovalent hydrocarbon may comprise 1-4 heteroatoms each selected from N, O, and S. Therefore, it is to be understood that aromatic

hydrocarbyl may be a heteroaryl if said aromatic hydrocarbyl comprises 1-4 heteroatoms each selected from N, O, and S. Examples of 5-14 membered aromatic hydrocarbyl include, but are not limited to, aryl, CH_2-Aryl, such as CH_2Ph; 9H-fluoren-9-yl, and 9,10-dihydroanthr-9-yl.

Similarly, the terms “aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group” refers to cyclic groups that may be aliphatic or aromatic, said group being a hydrocarbon having 3-14 atoms in the cycle and said group may comprise 1-4 heteroatoms each selected from N, O, and S. Therefore, it is to be understood that an aliphatic 3-14 membered cyclic hydrocarbon group may be a heterocyclic group if the group comprises 1-4 heteroatoms each selected from N, O, and S. Said aliphatic membered cyclic hydrocarbon group may be aliphatic, unsaturated or partially unsaturated, and it may comprise single bonds, double bonds and/or triple bonds. Further, it is to be understood that an aromatic cyclic hydrocarbon group may be heterocyclic group, i.e., a heteroaromatic group, if said group comprises 1-4 heteroatoms each selected from N, O, and S. Further, it is to be understood that an aromatic cyclic hydrocarbon group can be a 5-14 membered aromatic cyclic hydrocarbon group.

Examples of aliphatic 3-14 membered cyclic hydrocarbon groups optionally comprising 1-4 heteroatoms each selected from N, O, and S include, but are not limited to cyclopropan, cyclopentan, and cyclohexan.

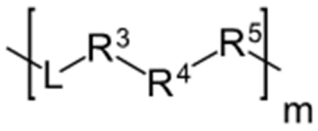
Examples of aromatic 3-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S include, but are not limited to, 9H-fluorene, and 9,10-dihydroanthracene.

The terms “cyclic C_{1-10} -hydrocarbyl “ as used in the present disclosure includes both monovalent cycloalkyls and heterocyclics. Examples of cycloalkyls include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. “Heterocyclics” are cycloalkyl groups as defined above where at least one of the carbon atoms of the ring is substituted with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorous.

“Aryl” bears the conventional meaning of a functional group or substituent derived from an aromatic ring, usually an aromatic hydrocarbon, such as phenyl and

naphthyl or antracenyl. The aryl groups typically contain 1 to 5 aromatic rings, which can be fused or partially fused.

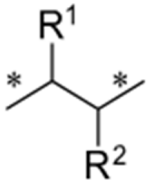
In one aspect is disclosed a compound of formula (I):



(I)

, wherein

L represent a moiety of formula (Ia):



(Ia)

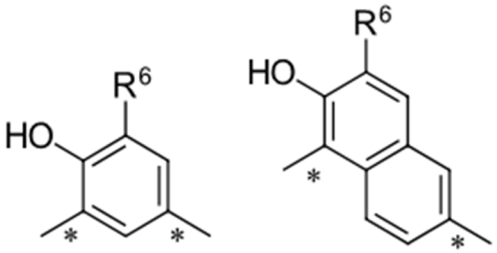
, wherein

R^1 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R';

R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R''; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

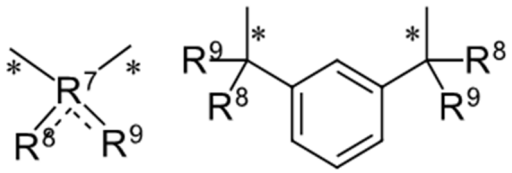
R^3 is selected from a moiety of formula (Ib) or a moiety of formula (Ic):



(Ib) , (Ic) , wherein

R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl, preferably methyl; and one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^5;

R^4 is absent, or is selected from a moiety of formula (If) or a moiety of formula (Ig):



(If) , (Ig) , wherein

each dotted line represents an optional bond;

R^7 is C or S;

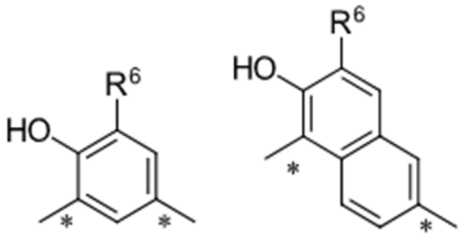
R^8 and R^9, provided that R^7 is C, together with the carbon they are attached to, form an aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

R^8 and R^9 are selected from the group consisting of a 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

both R^8 and R^9 are O, provided that R^7 is S and the dotted lines represent bonds; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

R^5 is selected from a moiety of formula (Id) or a moiety of formula (Ie):



(Id) , (Ie) , wherein

R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl; and

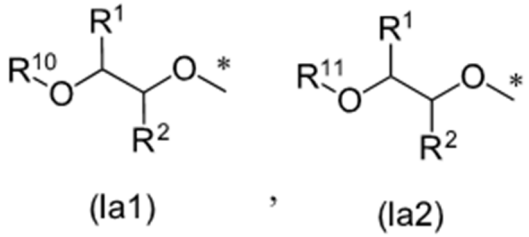
one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^3;

wherein each R', R'' and R''' is independently selected from the group consisting of halogen, and C_{1-3} -alkyl; and

m is an integer selected from 1-100.

Therefore, in particular when m is an integer selected from 2-100, it should be understood that the compound of formula (I) is a polymer, such as a linear polymer, comprising repeating units of formula (I), and that L is connected to R^5 of an adjacent repeating unit and to R^3; R^5 is connected to L of an adjacent repeating unit and to R^4 or, if R^4 is absent, to R^3; and R^3 is connected to L and to R^4 or, if R^4 is absent, to R^5.

Additionally, or alternatively, m is 1; L represents a moiety of formula (Ia1) or a moiety of formula (Ia2):



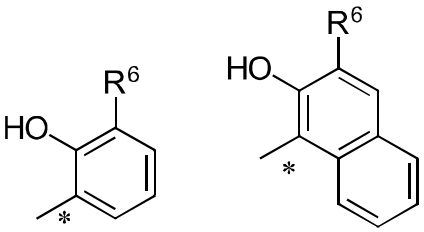
(Ia1) , (Ia2) , wherein

R^{10} is selected from the group consisting of H, and a C_{1-10} -hydrocarbyl;

R^{11} is selected from the group consisting of H, and a C_{1-10} -acyl; and

R^1 and R^2 are as defined in the present disclosure;

R^5 is selected from a moiety of formula (Id1) or a moiety of formula (Ie1):



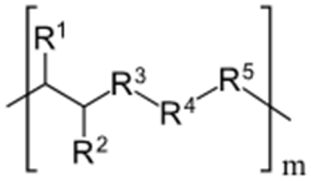
(Id1) (Ie1) , wherein

R^6 is as defined in the present disclosure; and the bond marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^3.

Further, it is to be understood that the terms “optionally comprising heteroatoms”, such as “optionally comprising 1-4 heteroatoms” as used herein and hereafter refers to each of the alternatives preceding the terms. Therefore, for example, but not limited to, the terms “H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S” refers to that the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl may optionally comprise 1-4 heteroatoms each selected from N, O, and S (it is clear to a person skilled in the art that a H may not comprise 1-4 heteroatoms).

Additionally, or alternatively, R^6 is H or methyl, preferably H.

Additionally, or alternatively, the compound has formula (Ih):

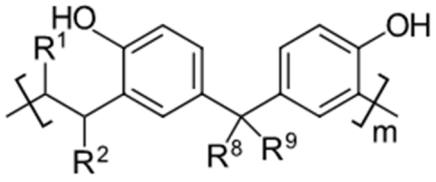


(Ih)

wherein

R^1, R^2, R^3, R^4, R^5, and m are as defined in the present disclosure. It should be understood that in these embodiments R^3 is connected to the carbon that R^2 is attached to, and to R^4 or, if R^4 is absent, to R^5, and R^5 is connected to a carbon that R^1 is attached to, and to R^4 or, if R^4 is absent, to R^3.

Additionally, or alternatively, the compound has formula (Ii):



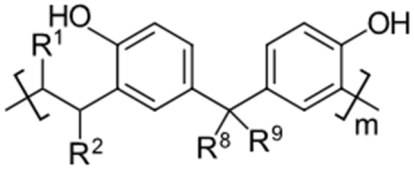
(Ii)

, wherein

R^8 and R^9, together with the carbon they are attached to, form an aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 3-14 membered, cyclic, aliphatic or aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R'''; and

R^1, R^2, R''' and m are as defined in the present disclosure.

Additionally, or alternatively, the compound has formula (Ii):

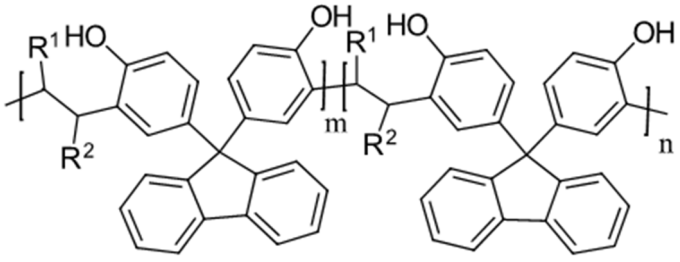


(Ii)

, wherein

R^8 and R^9, together with the carbon they are attached to, form a group selected from 9*H*-fluoren-9-ylidene, 9,10-dihydroanthr-9-ylidene, cyclohexylidene, and cyclopentylidene, optionally substituted with 1-4 substituents each independently selected from the group represented by R''', and R''' is as defined in the present disclosure.

Additionally, or alternatively, the compound has formula (II):

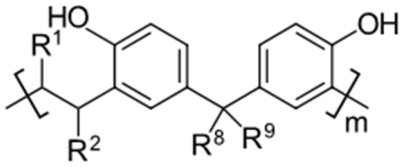


(III)

, wherein

R^1 and R^2 are as defined in the present disclosure. These compounds are in particular useful in lithography methods as disclosed in the present disclosure, in particular to prepare an optical element, optically active device, optical device, or semiconductor device.

Additionally, or alternatively, the compound has formula (Ii):

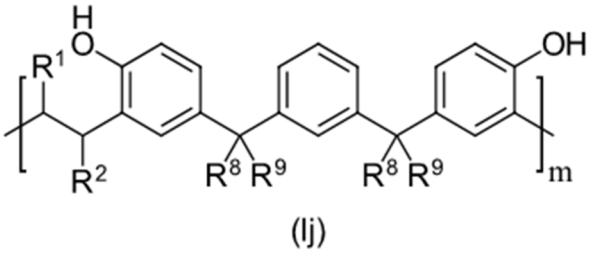


(Ii)

, wherein

R^8 and R^9 are each selected from a 1-10 membered aliphatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-10 membered aliphatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R’’’, preferably R^8 and R^9 are selected from phenyl, methyl, and trifluoromethyl, and R’’’ is as defined in the present disclosure.

Additionally, or alternatively, the compound has formula (Ij):



(Ij)

, wherein

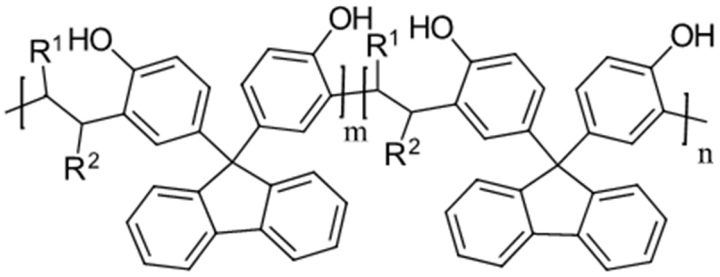
each R^8 and R^9 is independently selected from a 1-10 membered aliphatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-10 membered aliphatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R’’’, preferably R^8 and R^9 are phenyl, methyl, or trifluoromethyl, and R’’’ is as defined in the present disclosure.

Additionally, or alternatively, R’, R’’ and R’’’ are each independently selected from the group consisting of Br, F, and methyl.

Additionally, or alternatively, R^1 and R^2 are phenyl, optionally R^1 is substituted with 1-4 substituents each independently selected from the group represented by R', and optionally R^2 is substituted with 1-4 substituents each independently selected from the group represented by R'', and R' and R'' are as defined in the present disclosure.

Additionally, or alternatively, one of R^1 and R^2 is H, and the other one of R^1 and R^2 is a saturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, preferably methyl.

In one aspect is disclosed a compound of formula (III):



(III)

, wherein

each of R^1 and R^2 is as defined in the present disclosure, provided that the compound of formula (III) comprises at least two different R^1 and/or at least two different R^2;

m is as defined in any of the preceding claims; and

n is an integer selected from 1-100.

Additionally, or alternatively, wherein the compound of formula (I), the compound of formula (II), or the compound of formula (III) has a number average molar mass (Mn) of 500 – 5000 g/mol or 1000 – 5000 g/mol.

Additionally, or alternatively, spin-on carbon hardmask has a number average molar mass (Mn) of 500 – 5000 g/mol or 1000 – 5000 g/mol.

Additionally, or alternatively, the n(193 nm) value of the compound is 1 – 2, preferably 1.2 – 1.6, such as 1.30 – 1.50. Additionally, or alternatively, the n(193 nm) value of the spin-on carbon hardmask is 1 – 2, preferably 1.2 – 1.6, such as 1.30 – 1.50.

Additionally, or alternatively, the k(193 nm) value of the compound is 0.20 – 0.90, such as 0.40 – 0.80. Additionally, or alternatively, the k(193 nm) value of the spin-on carbon hardmask is 0.20 – 0.90, such 0.40 – 0.80.

In one aspect is disclosed a composition comprising a compound as defined in the present disclosure.

Additionally, or alternatively, the composition further comprises a solvent, optionally the composition further comprises a crosslinking agent, optionally further a catalyst, such as an acid generator, thermal acid generator or a polymerization catalyst, optionally the composition further comprises a surfactant.

Additionally, or alternatively, the crosslinking agent is selected from the group consisting of tetra-alkoxyalkyl glycouril, hexa(methoxymethyl)melamine and an aromatic compound having multi-functional groups suitable for acid catalyzed crosslinking. Additionally, or alternatively, the content of the crosslinking agent is 4 – 25 wt %, for example, 10 – 22 wt %, based on the total weight of the solids of the composition. In these embodiments, a reduced baking temperature and outgassing may be achieved.

Additionally, or alternatively, the acid generator is selected from the group consisting of thermal acid generators (TAGs), photoacid generators (PAGs) and combinations thereof.

A thermal acid generator is a compound which is capable of generating an acidic moiety when heated. The thermal acid generator can be nonionic or ionic. Suitable nonionic thermal acid generators include, for example, cyclohexyl p-toluenesulfonate, methyl p-toluenesulfonate, cyclohexyl 2,4,6-triisopropylbenzene sulfonate, nitrobenzyl esters, benzoin tosylate, 2-nitrobenzyl tosylate, tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione, alkyl esters of organic sulfonic acids such as p-toluenesulfonic acid, dodecylbenzenesulfonic acid, oxalic acid, phthalic acid, phosphoric acid, camphorsulfonic acid, 2,4,6-trimethylbenzene sulfonic acid, triisopropylnaphthalene sulfonic acid, 5-nitro-o-toluene sulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzene sulfonic acid, 2-nitrobenzene sulfonic acid, 3-chlorobenzene sulfonic acid, 3-bromobenzene sulfonic acid, 2-fluorocaprylnaphthalene sulfonic acid, dodecylbenzene sulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzene sulfonic acid, and their salts, and combinations thereof. Suitable ionic thermal acid generators include, for example, dodecylbenzenesulfonic acid triethylamine salts, dodecylbenzenedisulfonic acid triethylamine salts, p-toluene sulfonic acid-ammonium salts, sulfonate salts, such as carbocyclic aryl (e.g., phenyl, napthyl,

anthracenyl, etc.) and heteroaryl (e.g., thienyl) sulfonate salts, aliphatic sulfonate salts and benzenesulfonate salts. Compounds that generate a sulfonic acid upon activation are generally suitable. Preferred thermal acid generators include p-toluenesulfonic acid ammonium salts or ammonium salts of antimony hexafluoride.

A photoacid generator is a compound which is capable of generating an acidic moiety when exposed to activating radiation. Suitable photoacid generators include, for example, sulfide and onium type compounds. Photoacid generators include but are not limited to diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, diphenyl p-tert-butylphenyl triflate, triphenylsulfonium hexafluororphosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, (4-tbutylphenyl)tetramethylenesulfonium (3-hydroxyadamantanyl ester)-tetrafluoro-butanesulfonate), (4-tbutylphenyl)tetramethylenesulfonium (adamantanyl ester)-tetrafluoro-butanesulfonate) and dibutylnaphthylsulfonium triflate. Preferred PAGs include tetramethylenesulfonium compounds. Certain photoacid generators can also function as thermal acid generators, generating an acid upon exposure to activating radiation or heat.

Additionally, or alternatively, the thermal acid generator is selected from the group consisting of p-toluenesulfonic acid ammonium salts and ammonium salts of antimony hexafluoride.

Additionally, or alternatively, the polymerization catalyst is selected from the group consisting of any free acid which is compatible with the compositions of the present invention and catalyzes crosslinking of the polymer and crosslinker is suitable for use in the present invention. Examples of free acids include, but are not limited to, sulfonic acids such as methane sulfonic acid, ethane sulfonic acid, propyl sulfonic acid, phenyl sulfonic acid, toluene sulfonic acid, dodecylbenzene sulfonic acid, and trifluoromethyl sulfonic acid.

Additionally, or alternatively, the Tg of the compound as disclosed herein is advantageous. Tg of the compound is advantageous to be low when coating, and prior to cure. This will permit the coating to reflow on a substrate containing topography, and hence permit the coating to reflow to allow greater planariztion. On

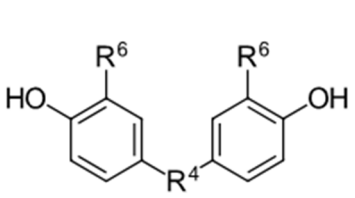
the contrary, high Tg for the crosslinked system is beneficial at a later stage where the coating may need to retain physical dimensions during heating (i.e., Tg should be above the process temperature).

Additionally, or alternatively, the constant of thermal expansion (CTE) of the compound or spin-on carbon hardmask as disclosed herein is advantageous. A low CTE is generally favored in application when there are heating steps involved. Mismatches in CTE may lead to wafer bowing, e.g., if the wafer is very thin. In worst case CTE mismatch may lead to delamination or cracks.

Additionally, or alternatively, the C:H:O ratio of the compound as disclosed herein is advantageous. Generally, maximum carbon content is preferred, more specifically maximum aromatic carbon content is preferred as it also reduces H-content. Typically, high carbon content leads to poor solubility but preferred etch performance. Low H-content and specifically low aliphatic H-content is preferred. Typically, this is due to replacement of hydrogen with fluorine leading to an increase in physical dimensions of a coating due to size difference between H and F. Addition of F to a coating is known to induce pattern deformation known as 'wiggling'. In addition, any oxygen added to a coating reduces carbon content, but may be needed to induce polarity in the material to permit desired solubility.

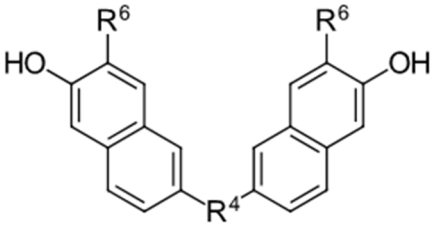
In one aspect is disclosed a method for the preparation of a compound as defined in the present disclosure, wherein the method comprises:

i) providing a polymerization composition comprising a compound of formula (IVa) and/or formula (IVb):



(IVa)

,

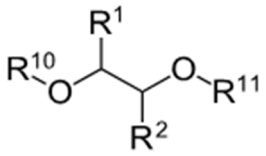


(IVb)

, wherein

R^4 and R^6 are as defined in the present disclosure; and

a compound of formula (V):



(V)

, wherein

R^1 and R^2 are as defined in the present disclosure;

R^{10} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -hydrocarbyl; and

R^{11} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -acyl; and

ii) polymerizing the polymerization composition to form the compound as defined in the present disclosure.

Additionally, or alternatively, R^1 and R^2 are phenyl; and R^{10} and R^{11} are H.

Additionally, or alternatively, R^{10} is a $C_{1\text{-}10}$ -hydrocarbyl, preferably methyl; and R^{11} is a $C_{1\text{-}10}$ -acyl, preferably acetyl.

Additionally, or alternatively, in i), providing a polymerization composition comprising a compound selected from bisphenol, such as bisphenol FL, bisphenol Z, or bisphenol BP; 4,4′-dihydroxybiphenyl, and 6,6′-(9H-fluoren-9,9-diyl)bis(naphthalen-2-ol); and a compound selected from PGMEA and hydrobenzoin.

The polymerizing may be carried out completely without solvents, or it is carried out in organic solvents, such as in a hydrocarbon, alcohol, ester, or an aromatic, such as toluene, or a combination thereof. Specific, suitable solvents are PGMEA, PGME, n-heptane, cyclohexane, and toluene. Particularly suitable solvents are hydrocarbons, ethers and aromatics. Such examples are PGMEA, PGME, n-heptane, cyclohexane, and toluene.

Additionally, or alternatively, the polymerization composition comprises a solvent, preferably the solvent is a compound of formula (V), or selected from PGMEA, PGME, n-heptane, cyclohexane, toluene.

Additionally, or alternatively, the polymerization composition comprises a solvent, preferably the solvent is a compound of formula (V), or toluene. Additionally, or alternatively, the compound of formula (V) and the solvent is PGMEA.

Additionally, or alternatively, the method further comprises, during and/or after ii) polymerizing, removing, preferably removing comprises distilling, at least partially, low boiling products, such as decomposition products, from the polymerization composition. A reduced polymerization time to obtain a specific yield of the product may be obtained if such products are removed from the polymerization composition during the polymerizing, such as a polymerization time from 5 days to less than a day.

Additionally, or alternatively, the polymerization composition comprises a catalyst, such as a polymerization catalyst, preferably the catalyst is an acid, such as sulfuric acid or sulfonic acid, optionally the polymerization composition is essentially free of air.

Organic or inorganic acid can be used in the polymerizing the polymerization composition. Inorganic acids such as nitric acid, sulfuric acid, hydrocholoric acid, hydriodic acid, hydrobromic acid, hydrofluoric acid, boric acid, perchloric acid, carbonic acid and phosphoric acid can be used. Typically, sulfuric acid is used. In other option, various organic acids can be used instead of inorganic acid. Organic acids are carboxylic acid, sulfonic acid, alcohol, thiol, enol, and phenol groups. Examples are methanesulfonic acid, acetic acid, ethanesulfonic acid, toluenesulfonic acid, formic acid, or oxalic acid.

Those familiar to the art knows that lower reaction temperatures provide improved control of the reaction but at the cost of long reaction times, while excessively high temperatures may make the process too fast for adequate control, or the yield of unwanted products may be too high. Thus, a reaction time of 1 – 48 h at a temperature of 0 – 145 °C or 100 – 160 °C is preferred. A reaction time of 2 – 24 h is even more preferred. Using appropriate conditions, methods according to the present invention yields a partially cross-linked polymer (compound of formula (I) or (III)) in an organic solvent system, said polymer having a number average molar mass (Mn) of about 500 to 10000 g/mol or 500 to 5000 g/mol, in particular about 700 to 5000 g/mol, measured against polystyrene standards.

Additionally, or alternatively, the polymerizing the polymerization composition comprises heating the polymerization composition to a temperature selected from 80 – 200 °C, preferably a temperature selected from 100 – 160 °C or 110 – 140 °C,

optionally the polymerizing is performed under an inert atmosphere, such as nitrogen.

Additionally, or alternatively, the polymerization composition is heated at the temperature selected from 80 – 200 °C, preferably a temperature selected from 100 – 160 °C or 110 – 140 °C, for 2 – 48 h, preferably for 4 – 42 h, more preferably for 5 – 42 h.

Additionally, or alternatively, the weight ratio of the compound of formula (IVa) to the compound of formula (V) is 20:80 – 80:20 in the polymerization composition, or the weight ratio of the compound of formula (IVb) to the compound of formula (V) is 20:80 – 80:20 in the polymerization composition.

Additionally, or alternatively, the method further comprises, after ii) heating, washing the formed product. Additionally, or alternatively, the washing the formed product comprises washing with one or more solvents selected from the group consisting of diluted nitric acid, diluted hydrochloric acid, deionized water, *tert*-butyl methyl ether (MTBE), and methyl isobutyl ketone (MIBK), or a combination thereof.

The solvent in which polymerization and/or washes are carried out may be changed after polymerization or washing for a solvent that provides the material better coating performance and product storage properties though some form of stabilization. Such stabilizing organic solvent system is formed by an organic ether optionally in mixture with other co-solvent or co-solvents. The organic ether is a linear, branched or cyclic ether comprising generally 4 to 26 carbon atoms and optionally other functional groups, such as hydroxyl groups. Particularly suitable examples are five and six membered cyclic ethers, which optionally bear substituents on the ring, and ethers, such as (C1-20) alkanediol (C1-6) alkyl ethers. Examples of said alkanediol alkyl ethers are propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol. dimethyl ether, dipropyleneglycol n-butyl ether, tripropylene glycol monomethyl ether and mixtures thereof. Particularly preferred examples of the present ethers are methyl tetrahydrofurfuryl ether, tetrahydrofurfuryl alcohol, propylene glycol n-propyl ether, dipropylene glycol dimethyl ether, propylene glycol n-methyl ether, propylene glycol n-ethyl ether and mixtures thereof. The stabilizing solvent system consists of a solvent comprising of the ether of this kind alone, or of a mixture-of such ether with a typical reaction medium of the hydrolyzation or other

solvents such as propylene glycol monomethyl ether acetate. The proportion of the ether is, in such a case, about 10 to 90 wt-%, in particular about 20 to 80 wt-% of the total amount of the solvent.

Additionally, or alternatively, the method further comprises, after ii) heating, washing the formed product with one or more solvents selected from the group consisting of of diluted nitric acid, diluted hydrochloric acid, deionized water, *tert*-butyl methyl ether (MTBE), and methyl isobutyl ketone (MIBK); and performing a solvent exchange, preferably by adding a solvent, such as PGMEA, and distilling the thus formed composition.

In one aspect is disclosed a use of a compound or a composition as defined in the present disclosure in a lithography method, preferably as a spin-on carbon (SOC) material, an organic etch hard mask or a layer functioning as an etch hard mask.

In one aspect is disclosed a lithography method comprising:

i) applying a compound or a composition as defined in the present disclosure on a substrate, thereby forming a film on the substrate; and
ii) heating the formed film to form a spin-on carbon hardmask.

Additionally, or alternatively, in i), applying is spin coating a compound or a composition as defined in the present disclosure on a substrate, thereby forming a film on the substrate.

Additionally, or alternatively, in ii), heating the formed film at 200 – 400 °C, preferably for 1-2 min.

Additionally, or alternatively, i) applying, preferably spin coating, a composition as defined in the present disclosure on a substrate, wherein the composition further comprises a crosslinking agent, thereby forming a film on the substrate; and in ii), heating the formed film at 200 – 400 °C, preferably for 1-2 min.

Additionally, or alternatively, after ii) heating the formed film, the method further comprises:

iii) applying an organic or inorganic composition, such as a composition of high silicon content layer, silicon oxynitride, or metal oxide, on top of the formed spin-on carbon hardmask, thereby forming an additional layer, and baking the formed additional layer to form an organic or inorganic film;

iv) applying a composition for a functional coating layer, such as a composition comprising a poly(organosiloxane) on the formed organic or inorganic film, thereby forming a resist underlayer functional layer;

v) applying a composition for a resist onto the resist underlayer functional layer to form a resist film;

vi) exposing the formed resist film to light or electron beam radiation according to a predetermined pattern to form a photoresist pattern on the resist film, thereby forming a patterned resist film;

vii) developing the formed patterned resist film to form a developed patterned resist film;

viii) etching the resist underlayer functional film according to a pattern of the patterned resist film; and

ix) processing the substrate according to the pattern of the resist film and the resist underlayer functional film.

Additionally, or alternatively, processing comprises one or more of etching, and developing, preferably processing comprises etching, and developing, more preferably processing comprises etching and developing multiple times, such as two or three times.

Additionally, or alternatively, the substrate is a semiconductor substrate.

Additionally, or alternatively, the substrate consists essential of or comprises TiO_2, Si, GaAs, SiO2, TiN, TaN, GaN, SiC, glass, Al_2O_3, or HfO_2.

The solid content of the radiation sensitive formulation (composition) consisting of selected solvents and the compound of formula (I) or formula (I) (resin material) is in the range of 0.1% to no more than 50%. Most preferably in the range of 0.5% to 10%. The solid content (or polymer content) is used to adjust the resultant film thickness during the coating process. To improve the coating performance in terms of coating uniformity, different surfactants such as silicone or fluoro surfactant can be used can be used to lower surface tension of the compound of formula (I)- or formula (II) -formulation coating. The use of such surfactants may improve coating quality if needed. The amount of surfactant is in a range of 0.001 % to no more than 10 % by mass compared to the amount of compound of formula (I) or formula (II).

In one aspect is disclosed an optical element, optically active device, optical device, or semiconductor device obtained by a method as defined in the present disclosure. Surprisingly, it has been found that an optical element, such a layer or film formed in a lithography method as disclosed in the present disclosure have an excellent balance of all or at least a part of required properties: (a) an excellent planarization of a substrate surface having irregularities such as holes and trenches; (b) target thin film thickness under process conditions; (c) target high etch resistance, which is in demand for plasma etching process under process conditions; (d) outgassing and sublimate reduction for defect free coating; (e) ability to be spin coated from safe solvents; (f) spin bowl compatibility (compatible with all the solvents and materials that they can come in contact with in the spin bowl); (g) excellent storage stability; and (h) excellent thermal stability.

In certain embodiments, the present invention relates to the use of compositions described herein in the formation of patterns on a semiconductor substrate, as illustrated in Figures 1 and 2.

Thus, in a lithography method of the invention, applying 11a, such as coating 11a, a compound or a composition as defined in the present disclosure on a substrate 10, thereby forming a film 12 on the substrate 10 is illustrated in Figure 1. Heating 11b the formed film 12 forms a spin-on carbon hardmask 12a.

In Figure 2 is illustrated embodiments of the invention, wherein applying 11a, such as coating 11a, a compound or a composition as defined in the present disclosure on a substrate 10, thereby forming a film 12 on the substrate 10. Heating 11b the formed film 12 forms a spin-on carbon hardmask 12a. Applying 13 (such coating) an organic or inorganic composition, such as a composition of high silicon content layer, silicon oxynitride, or metal oxide, on top of the formed film/spin-on carbon hardmask 12b, thereby forming an additional layer (not shown), and baking the formed additional layer to form an organic or inorganic film 14. Applying 15, such as coating 15, a composition for a functional coating layer, such as a composition comprising a poly(organosiloxane) on the formed organic or inorganic film 14, forms a resist underlayer functional layer 16, and applying 15b, such as coating 15b, a composition for a resist onto the resist underlayer functional layer 16 forms a resist film 17. Exposing 18 the formed resist film 17 to light or electron beam radiation, preferably irradiating with light of 193 nm wavelength (shown as curly arrows),

according to a predetermined pattern forms a photoresist pattern on the resist film, thereby forming a patterned resist film (not shown); and developing (not shown) the formed patterned resist film to form a developed patterned resist film 17a. Etching 18b the resist underlayer functional film 16 according to a pattern of the patterned resist film 17a (forms a patterned resist underlayer functional film 16a); and processing 18c, such as etching 18c according to a pattern of the patterned resist underlayer functional film 16a and developing (not shown) forms a patterned organic or inorganic film 14a, followed by one or more processing (18d), such as etching 18d according to the patterned organic or inorganic film 14a and developing (not shown) forms a patterned spin-on carbon hardmask 12b followed by etching 18e according to the patterned spin-on carbon hardmask 12b followed and developing (not shown) forms a patterned substrate.

Subsequent pattern transfer etch processes can be applied to transfer the pattern formed on the photoresist to the substrate (Figure 1).

The radiation sensitive coating material can also be used as negative radiation patterning coating. In the negative patterning, exposure to radiation converts the irradiated coating material into a material that is more resistant to removal with a developer composition relative to the non-irradiated coating material. Selectively removal of at least a portion of the coating material leaves a pattern where regions have been removed to expose the underlying substrate.

The formation of integrated electronic devices and the like generally involves the patterning of the materials to form individual elements or components within the structures. This patterning can involve different compositions covering selected portions of stacked layers that interface with each other vertically and/or horizontally to induce desired functionality.

The various materials can comprise semiconductors, which can have selected dopants, dielectrics, electrical conductors and/or other types of materials.

To form high resolution patterns, radiation sensitive organic compositions can be used to introduce patterns, and the compositions can be referred to as resists since portions of the composition are processed to be resistant to development/etching such that selective material removal can be used to introduce a selected pattern.

Radiation with the selected pattern or the negative of the pattern can be used to expose the resist and to form a pattern or latent image with developer resistant regions and developer dissolvable regions. The radiation sensitive metal can be used for the direct formation of desired inorganic material structures within the device and/or as a radiation patternable inorganic resist that is a replacement for an organic resist. In either case, significant processing improvements can be exploited, and the structure of the patterned material can be also improved.

The following non-limiting examples illustrate embodiments.

EXAMPLES

Methods

Molecular weight averages (Mz, Mw and Mn), Molecular weight distribution (MWD) and its broadness, described by polydispersity index, PDI = Mw/Mn (wherein Mn is the number average molecular weight and Mw is the weight average molecular weight) were determined by Gel Permeation Chromatography (GPC). A GPC instrument, equipped with differential refractometer (RI) from Agilent Technologies, equipped with 3 x Shodex KF separation columns (KF-801, KF-802, KF-803L) and Shodex KF-G 4A Guard columns was used. As the solvent and mobile phase tetrahydrofuran (THF) was used. The chromatographic system was operated at 40 °C and at a constant flow rate of 1 mL/min. 200 µL of sample solution was injected per analysis. The column set was calibrated using 12 narrow MWD polystyrene (PS) standards in the range of 0.16 kg/mol to 50.0 kg/mol. The PS standards were dissolved at room temperature over several hours. A third order polynomial fit was used to fit the calibration data. All samples were prepared in the concentration range of 0.5 – 1 mg/mL, dissolved at 20 °C for 5 min in THF under continuous gentle shaking and filtered through 0.22 µm Nylon filter.

Post-coating retardation (PCD) test: The polymer solutions from the examples were diluted with PGMEA to 6.5% solution, which was filtrated through a 0.22 µm nylon filter. Film samples were prepared by spin-coating the polymer solution onto 4" silicon wafers at 1500 rpm for 20 seconds. Then, a soft bake was performed on a hot plate at 250 °C for 90 seconds under N_2. Film thickness measurement was carried out using J.A. Woollam M2000D-ESM-200AXY spectroscopic ellipsometer.

The Thermal Gravimetric Analysis (TGA), used for testing, was made using TG 209 F3 Tarsus manufactured by NETZSCH. After the coating film was removed from the wafers, the obtained powder was tested by the TGA device. The following conditions were used: N_2 flow of 20 mL/min, temperature ramp from 30 °C to 600 °C, the heating rate of 10 ℃/min. The temperature at which the mass loss was 5% was recorded as a heat resistance value. The higher the 5% heat loss temperature was, the better the heat resistance of the coating film was.

Refractive index (n) and extinction coefficient (k) were determined using a using J.A. Woollam M2000D-ESM-200AXY spectroscopic ellipsometer from a polymeric film sample having a thickness of 180 nm. The ellipsometer scans the film at wavelengths from 193 nm to 1000 nm and then modulate curves of changing optical parameters depending on wavelength.

Outgassing test: wafers coated with tested material were heated to 250 °C using Präzitherm PZ14ET hotplate, outgassing of the material was measured by electrochemical quartz crystal microbalance Gamry eQCM 10M.

Etch rate of the polymer was measured using Oxford RIE Plasmalab 80 Plus. The cured film was etched at oxygen plasma (O_2/5 sccm, Ar/20 sccm) at 30 mTorr for 30 seconds. Film thickness was measured before and after etching. The difference divided on etching time was the value of etch rate in nm/min.

Comparative example 1.

A reaction mixture of 9,9-bis(4-hydroxy-phenyl)fluorene (BPFL) (36.0 g, 102.7 mmol), formalin 37% aq. (15.0 g, 184.7 mmol), propylene glycol monomethyl ether acetate (PGMEA) (20.0 g, 151.2 mmol) and anhydrous oxalic acid (1.0 g, 11.1 mmol) was added to a two neck round bottom 100 mL flask, equipped with a magnetic stirred bar, distillation head with a condenser, a receiver flask, and a thermometer. The system was connected to N_2/vacuum manifold. Air was removed from the system via 3 degassing cycles of ca. 1 minute degassing in vacuum and ca. 1 minute degassing with nitrogen, before heating of the reaction mixture. The polymerization was done under a nitrogen atmosphere. Heating of the reaction mixture was initiated to dissolve the monomers in PGMEA. After that, the obtained reaction mixture was heated up to 100 °C (temperature was measured by thermocouple), oil bath temperature was ca. 140 °C. Byproducts were distilled off to a receiving flask. From time to time, a sample for GPC was taken from the reaction

mixture to monitor Mw and conversion. After 16 hours of heating at 100 °C, the reaction mixture was cooled to room temperature, the obtained solution was transferred to a 500 mL separatory funnel and then 80 mL of distilled *tert*-butyl methyl ether (MTBE) and 50 mL of PGMEA were added to the obtained solution. The obtained solution was sequentially washed with 3x100 mL of deionized water (DiW). The obtained organic phase was concentrated using a rotavapor with water bath of 60 °C and pressure of 30 mbar. A polymer solution (127.3 g, solid content 40.05 wt.%) having Mw/Mn=4293/1612 was obtained. A solution for spin-coating was prepared by diluting the obtained polymer mother batch to a 6.5 wt.% solution in PGMEA. 20 wt.% per polymer of cross-linker Resimene(R) 747 by INEOS Melamines GmbH and 0.1 wt.% per polymer of CXC-1612 by K-Pure King Industries, Inc, were added to the solution for spin-coating. The obtained solution was then filtered through a 0.22 µm Nylon filter and spin-coated on a silicon wafer. Thereafter, the obtained films were soft baked at 250 °C/60s.

Example 1.

A reaction mixture of 9,9-bis(4-hydroxy-phenyl)fluorene (BPFL) (27.31 g, 77.9 mmol), and propylene glycol monomethyl ether acetate (PGMEA) (67.24 g, 78.1 mmol) was added to a two neck round bottom 100 mL flask, equipped with a magnetic stirred bar, distillation head with a condenser, a receiver flask, and a thermometer. The system was connected to N_2/vacuum manifold. Air was removed from the system via 3 degassing cycles of ca. 1 minute degassing in vacuum and ca. 1 minute degassing with nitrogen, before the heating of the reaction mixture. The polymerization was done under a nitrogen atmosphere. Heating of the reaction mixture was initiated to dissolve the BPFL in the PGMEA. After that, concentrated sulfonic acid (0.24 mL, 4.6 mmol) was added to the reaction mixture. The obtained reaction mixture was heated up to 145 °C (temperature was measured by thermocouple), oil bath temperature was ca. 160 °C. Byproducts were distilled off to a receiving flask. The oil bath temperature was adjusted to control the evaporation rate so that vapor temperature was about 50 – 60 °C. From time to time, a sample for GPC was taken to monitor Mw and conversion. After 16 hours the reaction was cooled to room temperature, the obtained solution was transferred to a 1000 mL separatory funnel and then 100 mL of distilled MTBE was added to the obtained solution. The obtained solution was sequentially washed with pure 3 % (V/V) aq.

HNO_3 solution and deionized water (DiW), and the aq. phase was removed. The wash was repeated 3 times. After washing, the obtained organic phase was concentrated using a rotavapor with water bath of 60 °C and pressure of 30 mbar. A polymer solution (102 g, solid content 33.2 %) having Mw/Mn=1727/1127 was obtained. In addition to PGMEA, the polymer was found to be soluble in common solvents such as PGME, OK73, MEK, MIBK, MIBC, methyl 3-methoxypropionate, propiolactone and cyclopentanone. The theoretical carbon content is 86.8%. A solution for spin-coating was prepared by diluting the obtained polymer to a 6.5 wt.% solution in PGMEA. 20 wt.% per polymer of cross-linker Resimene(R) 747 by INEOS Melamines GmbH and 0.1 wt% per polymer of CXC-1612 by K-Pure King Industries, Inc, were added to the solution for spin-coating. The solution was then filtered through 40 nm Nylon and 5 nm HDPE filters and spin-coated on a silicon wafer. Thereafter, the obtained films were soft baked at 250 °C/60s.

Example 2.

4,4′-Dihydroxybiphenyl (22.0 g), PGMEA (127.5 g) and sulfuric acid (0.69 g) were used. Otherwise, the synthesis was made according to the procedure of example 1. The condensation reaction was allowed to proceed for 5 hours.

Example 3.

6,6′-(9H-fluoren-9,9-diyl)bis(naphthalen-2-ol) (30.0 g), PGMEA (70.0 g) and sulfuric acid (0.39 g) were used. Otherwise, the synthesis was made according to the procedure of example 1. The condensation reaction was allowed to proceed for 12 hours.

Example 4.

4,4′-Cyclohexylidenebisphenol (bisphenol Z) (30.0 g), PGMEA (70.0 g) and sulfuric acid (0.66 g) were used. Otherwise, the synthesis was made according to the procedure of example 1. The condensation reaction was allowed to proceed for 42 hours.

Example 5.

1,1-Bis(4-hydroxyphenyl)-1,1-diphenylmethane (bisphenol BP) (25 g), PGMEA (58.3 g) and sulfuric acid (0.42 g) were used. Otherwise, the synthesis was made

according to the procedure of example 1. The condensation reaction was allowed to proceed for 24 hours.

Example 6.

9,9-Bis(4-hydroxy-phenyl)fluorene (BPFL) (23.0 g, 66.0 mmol), hydrobenzoin (14.0 g, 66.0 mmol) and toluene (60.5 g, 656 mmol) were placed in a 100 mL rb flask, equipped with a magnetic stir bar. The flask was connected to a Dean-Stark adapter via one neck and to an N_2 flow via another neck. Before the heating air was removed from the system via 3 degassing cycles of ca. 1 minute degassing in vacuum and ca. 1 minute degassing with nitrogen. The polymerization was done under a nitrogen atmosphere. Heating of the mixture was initiated to dissolve monomers in toluene. After that, sulfuric acid (0.19 g, 2.0 mmol) was added. The obtained solution was heated up to 110-115 °C in the flask (temperature was measured by thermocouple), the oil bath was ca. 140 °C. Aqueous byproducts were collected by the Dean-Stark adapter. From time to time, a sample for GPC was taken to monitor Mw and conversion. After 12 hours the reaction was cooled to room temperature, the obtained solution was transferred to a 500 mL separatory funnel and then 90 mL of distilled MTBE was added. The obtained solution was sequentially washed with 3x100 ml of DiW. For solvent exchange, 80 mL of PGMEA was added to the solution. The obtained organic phase was concentrated using a rotavapor with water bath at 60 °C and pressure down to 20 mbar. A polymer solution (87.0 g, solid content 42.5 wt%) having Mw/Mn=730/635 was obtained. Theoretical carbon content is 88.8 %. A solution for spin-coating was prepared by diluting the polymer to a 6.5 % solution in PGMEA. 20 wt% per polymer of cross-linker Resimene(R) 747 by INEOS Melamines GmbH and 0.1 wt% per polymer of CXC-1612 by K-Pure King Industries, Inc were added. The solution was then filtered through 40 nm Nylon and 5 nm HDPE filters and spin-coated on a silicon wafer. The films were soft baked at 250 °C/60s.

Summary of results obtained using a compound obtained from examples 1 – 6 are presented in Tables 1 – 2.

Table 1. Summary of the results from examples 1 – 6.

Example	**Monomer #1[1]**	**Monomer #2[2]**	**Mw[3]**	**n, 193 nm[4]**	**k, 193 nm[5]**
Comparative example 1	Bisphenol FL	Formalin	4293	1.374	0.623
Example #1	Bisphenol FL	PGMEA	2054	1.381	0.619
Example #2	4,4′-Dihydroxybiphenyl	PGMEA	1456	1.394	0,424
Example #3	6,6′-(9H-fluoren-9,9-diyl)bis(naphthalen-2-ol)	PGMEA	1712	1.453	0.746
Example #4	Bisphenol Z	PGMEA	846	1.447	0.473
Example #5	Bisphenol BP	PGMEA	1484	1.450	0.749
Example #6	Bisphenol FL	hydrobenzoin	790	1.453	0.725

[1] Monomer #1 refers to a compound of formula (IVa) or compound of formula (IVb) as disclosed in the present disclosure; [2] monomer #2 refers to a compound of formula (V) as disclosed in the present disclosure; [3] MW = molecular weight of formed compound of formula (I); [4] n, 193 nm is refractive index, which is measured at 193 nm wavelength; and [5] k, 193 is extinction coefficient, which is measured at 193 nm wavelength.

Table 2. Summary of the results obtained using a compound obtained from examples 1 – 6.

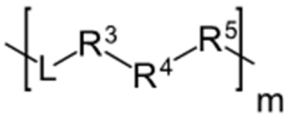
Example	**Etch rate, nm/min**	**TGA, °C (95%)**	**Avg. outgassing (µg)[1]**
Comparative example 1	181	346	2.05
Example #1	189	357	0.38
Example #2	198	346	n.a.
Example #3	161	355	n.a.
Example #4	214	353	n.a.

Example #5	185	355	n.a.
Example #6	179	333	1.84

[1] n.a. = not available

Claims:

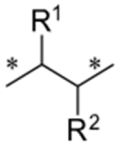
1. A compound of formula (I):



(I)

, wherein

L represent a moiety of formula (Ia):



(Ia)

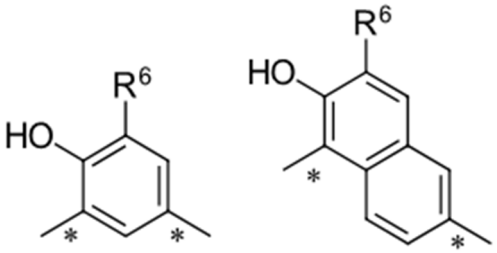
, wherein

R^1 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R';

R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and a 5-14 membered aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the saturated or unsaturated, linear, branched or cyclic C_{1-10} -hydrocarbyl, and the 5-14 membered aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R''; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

R^3 is selected from a moiety of formula (Ib) or a moiety of formula (Ic):

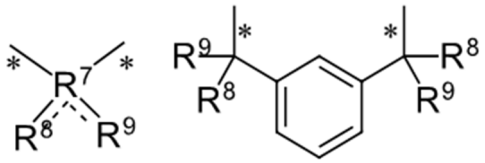


(Ib) , (Ic) , wherein

R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl; and

one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^5;

R^4 is absent, or is selected from a moiety of formula (If) or a moiety of formula (Ig):



(If) , (Ig) , wherein

each dotted line represents an optional bond;

R^7 is C or S;

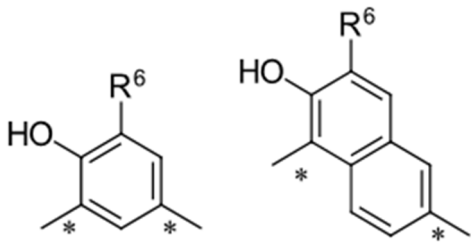
R^8 and R^9, provided that R^7 is C, together with the carbon they are attached to, form an aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the aliphatic or aromatic, 3-14 membered cyclic hydrocarbon group is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

R^8 and R^9 are selected from the group consisting of a 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-14 membered, cyclic, aliphatic or aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R'''; or

both R^8 and R^9 are O, provided that R^7 is S and the dotted lines represent bonds; and

one of the bonds marked with an asterisk is connected to R^3 and one of the bonds marked with an asterisk is connected to R^5;

R^5 is selected from a moiety of formula (Id) or a moiety of formula (Ie):



(Id) , (Ie) , wherein

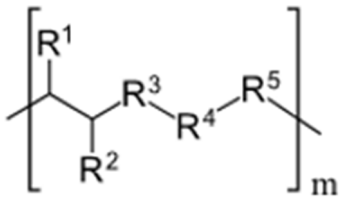
R^6 is H, or a linear, branched or cyclic C_{1-3} -hydrocarbyl; and

one of the bonds marked with an asterisk is connected to L and one of the bonds marked with an asterisk is connected to R^4 or, if R^4 is absent, to R^3;

wherein each R', R'' and R''' is independently selected from the group consisting of halogen, and C_{1-3} -alkyl; and

m is an integer selected from 1-100.

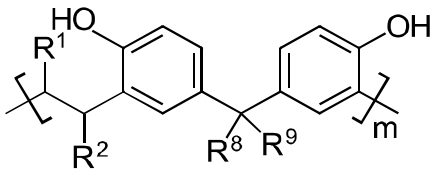
2. The compound as claimed in claim 1, wherein the compound has formula (Ih):



(Ih) , wherein

R^1, R^2, R^3, R^4, R^5, and m are as defined in claim 1.

3. The compound as claimed in claim 1 or 2, wherein the compound has formula (Ii):



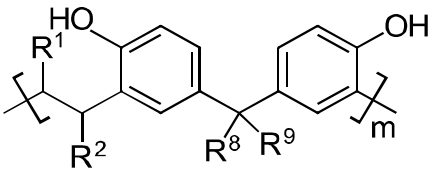
(Ii) , wherein

R^8 and R^9, together with the carbon they are attached to, form an aliphatic or aromatic, 5-14 membered cyclic hydrocarbon group optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 5-14

membered, cyclic, aliphatic or aromatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R'''; and

R^1, R^2, R''' and m are as defined in claim 1.

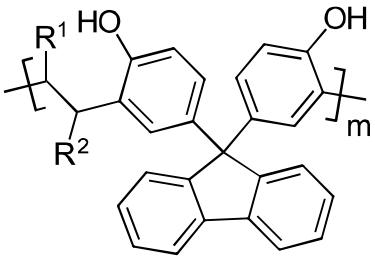
4. The compound as claimed in any of the preceding claims, wherein the compound has formula (Ii):



(Ii) , wherein

R^8 and R^9, together with the carbon they are attached to, form a group selected from 9H-fluorene, 9,10-dihydroanthracene, cyclopentan, and cyclohexan optionally substituted with 1-4 substituents each independently selected from the group represented by R''', and R''' is as defined in claim 1.

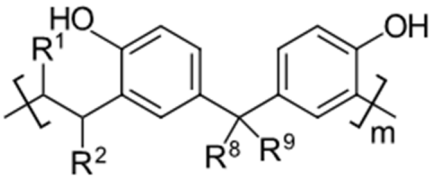
5. The compound as claimed in any of the preceding claims, wherein the compound has formula (II):



(II) , wherein

R^1 and R^2 are as defined in any of the preceding claims.

6. The compound as claimed in any of claims 1 – 3, wherein the compound has formula (Ii):

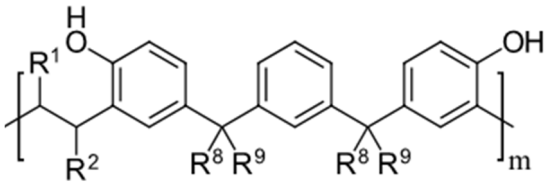


(Ii)

, wherein

R^8 and R^9 are each selected from a 1-10 membered aliphatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-10 membered aliphatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R’’’, preferably R^8 and R^9 are selected from phenyl, methyl, and trifluoromethyl, and R’’’ is as defined in claim 1.

7. The compound as claimed in any of claims 1 – 2, wherein the compound has formula (Ij):



(Ij)

, wherein

each R^8 and R^9 is independently selected from a 1-10 membered aliphatic hydrocarbyl optionally comprising 1-4 heteroatoms each selected from N, O, and S, wherein optionally the 1-10 membered aliphatic hydrocarbyl is substituted with 1-4 substituents each independently selected from the group represented by R’’’, preferably R^8 and R^9 are phenyl, methyl, or trifluoromethyl, and R’’’ is as defined in claim 1.

8. The compound as claimed in any of the preceding claims, wherein

R’, R’’ and R’’’ are each independently selected from the group consisting of Br, F, and methyl.

9. The compound as claimed in any of the preceding claims, wherein

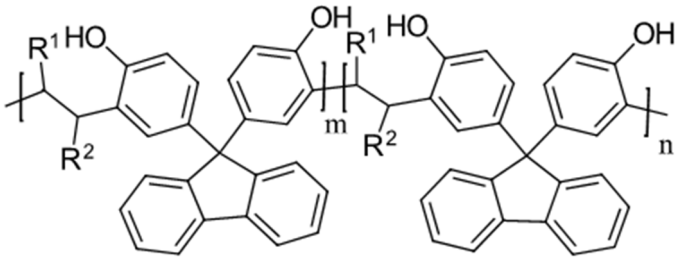
R^1 and R^2 are phenyl, optionally R^1 is substituted with 1-4 substituents each independently selected from the group represented by R’, and optionally R^2 is substituted with 1-4 substituents each independently selected from the group represented by R’’; and

R’ and R’’ are as defined in claim 1.

10. The compound as claimed in any of claims 1 – 8, wherein

one of R^1 and R^2 is H, and the other one of R^1 and R^2 is a saturated, linear, branched or cyclic $C_{1\text{-}10}$ -hydrocarbyl.

11. A compound of formula (III):



(III)

, wherein

each of R^1 and R^2 is as defined in any of the preceding claims, provided that the compound of formula (III) comprises at least two different R^1 and/or at least two different R^2;

m is as defined in any of the preceding claims; and

n is an integer selected from 1-100.

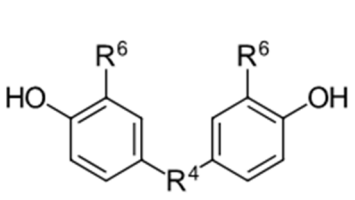
12. The compound as claimed in any of the preceding claims, wherein the compound has a number average molar mass (Mn) of 500 – 5000 g/mol.

13. A composition comprising a compound as defined in any of claims 1 – 12.

14. The composition as claimed in claim 13, wherein the composition further comprises a solvent, optionally the composition further comprises a crosslinking agent, optionally further a catalyst, such as a thermal acid generator, optionally the composition further comprises a surfactant.

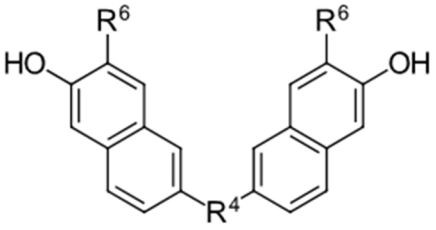
15. A method for the preparation of a compound as defined in any of claims 1 – 12, wherein the method comprises:

iii) providing a polymerization composition comprising a compound of formula (IVa) and/or formula (IVb):



(IVa)

,

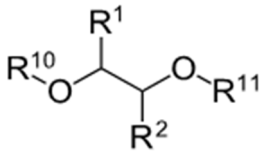


(IVb)

iv) , wherein

R^4 and R^6 are as defined in any of claims 1 – 12; and

a compound of formula (V):



(V)

, wherein

R^1 and R^2 are as defined in any of claims 1 – 12;

R^{10} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -hydrocarbyl; and

R^{11} is selected from the group consisting of H, and a $C_{1\text{-}10}$ -acyl; and

v) polymerizing the polymerization composition to form the compound as defined in any of claims 1 – 12.

16. The method for the preparation of a compound as claimed in claim 15, wherein R^1 and R^2 are phenyl; and R^{10} and R^{11} are H.

17. The method for the preparation of a compound as claimed in claim 15, wherein R^{10} is a $C_{1\text{-}10}$ -hydrocarbyl; and
R^{11} is a $C_{1\text{-}10}$ -acyl.

18. The method for the preparation of a compound as claimed in any of claims 15 – 17, wherein the polymerization composition comprises a solvent.

19. The method for the preparation of a compound as claimed in any of claims 15 – 18, wherein the polymerization composition comprises a catalyst.

20. The method for the preparation of a compound claimed in any of claims 15 – 19, wherein the polymerizing the polymerization composition comprises heating the polymerization composition to a temperature selected from 80 – 200 °C.

21. The method for the preparation of a compound as claimed in claim 20, wherein the polymerization composition is heated at the temperature for 2 – 48 h.

22. The method for the preparation of a compound as claimed in any of claims 15 – 21, wherein the weight ratio of the compound of formula (IVa) to the compound of formula (V) is 20:80 – 80:20 in the polymerization composition, or the weight ratio

of the compound of formula (IVb) to the compound of formula (V) is 20:80 – 80:20 in the polymerization composition.

23. Use of a compound or a composition as defined in any of claims 1 – 14 in a lithography method.

24. A lithography method comprising:

i) applying a compound or a composition as defined in any of claims 1 – 14 on a substrate, thereby forming a film on the substrate; and

ii) heating the formed film to form a spin-on carbon hardmask.

25. The lithography method as claimed in claim 24, wherein, in ii), heating the formed film at 200 – 400 °C.

26. The lithography method as claimed in any of claims 24 – 25, wherein, after ii) heating the formed film, the method further comprises:

iii) applying an organic or inorganic composition, such as a composition of high silicon content layer, silicon oxynitride, or metal oxide, on top of the formed spin-on carbon hardmask, thereby forming an additional layer, and baking the formed additional layer to form an organic or inorganic film;

iv) applying a composition for a functional coating layer, such as a composition comprising a poly(organosiloxane) on the formed organic or inorganic film, thereby forming a resist underlayer functional layer;

v) applying a composition for a resist onto the resist underlayer functional layer to form a resist film;

vi) exposing the formed resist film to light or electron beam radiation according to a predetermined pattern to form a photoresist pattern on the resist film, thereby forming a patterned resist film;

vii) developing the formed patterned resist film to form a developed patterned resist film;

viii) etching the resist underlayer functional film according to a pattern of the patterned resist film; and

ix) processing the substrate according to the pattern of the resist film and the resist underlayer functional film.

27. The lithography method as claimed in any of claims 24 – 26, wherein the substrate is a semiconductor substrate.

28. The lithography method as claimed in any of claims 24 – 27, wherein the substrate consists essential of or comprises TiO_2, Si, GaAs, SiO2, TiN, TaN, GaN, SiC, glass, Al_2O_3, or HfO_2.

29. An optical element, optically active device, optical device, or semiconductor device obtained by a method as defined in any claims 24 – 28.