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[Continued on next page]

(54) Title: FLUOROALCOHOL CONTAINING MOLECULAR PHOTORESIST MATERIALS AND PROCESSES OF USE

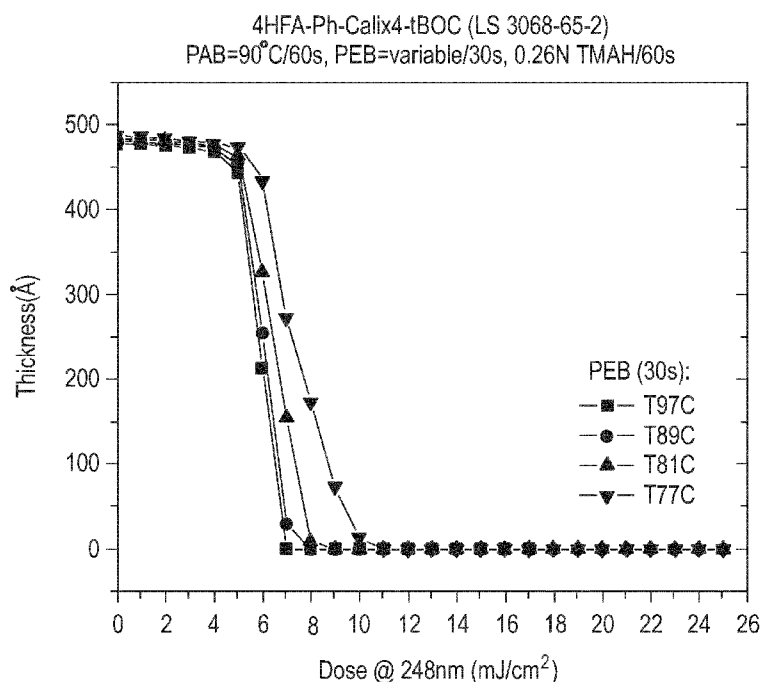


FIG. 1

(57) Abstract: Phenolic molecular glasses such as calixarenes include at least one fluoroalcohol containing unit. The fluoroalcohol containing molecular glasses can be used in photoresist compositions. Also disclosed are processes for generating a resist image on a substrate using the photoresist composition.



HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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## FLUOROALCOHOL CONTAINING MOLECULAR PHOTORESIST MATERIALS AND PROCESSES OF USE

### Field of the Invention

5

The present invention relates to molecular glass photoresists.

### Background of the Invention

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As the minimum critical dimension continues to shrink to less than 50 nm, it is becoming increasingly difficult to simultaneously meet critical performance criteria, sensitivity, resolution, and line edge roughness (LER). The size of polymers typically employed in chemical amplification photoresists is beginning to influence performance at these dimensions. For example, it is believed that the magnitude of line edge roughness is directly correlated to the molecular weight of the base polymer in the photoresist. As a result, a number of photoresists based on low molecular weight polymers or non-polymers have been proposed to address the performance issues needed for these advanced design rules.

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Molecular glass resists have gained attention as a potential candidate for next generation resist materials. Such small molecules termed “molecular glasses” (MGs) possess structural features that inhibit crystallization and display relatively high glass transition temperatures (T<sub>g</sub>) despite their modest size. MGs combine characteristic properties of small molecules such as high purity and well defined structure with beneficial aspects of polymers such as high thermal stability and thin film forming properties. The small molecular size of 1 to 2 nm is expected to facilitate high-resolution patterning due to the possibility of reducing the “pixel” size of the basic imaging unit.

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30

This new class of resist materials has shown progress in terms of resolution, sensitivity and LER. However, although MGs offer potential advantages over polymeric resists in terms of molecular size, there are many challenges with the synthesis and processing of these materials. One of the main issues with these materials is the poor solubility in a casting solvent that prevents the formation of good quality thin films. Another challenge is the

ability to synthesize monodisperse materials. In previously published systems, a molecular glass resist consisted of a matrix with a core structure that is functionalized with an average number of acid labile protecting groups. These resist materials have a distribution of protecting groups. Chromatography based purification methods were used to obtain monodisperse units which showed superior performance compared to the disperse matrix. In order to obtain a monodisperse material that showed improved performance required very tedious synthetic and purification processes. Another issue is that several MG systems require diluted developer due to their high dissolution rates and therefore incompatible with 0.26N tetramethylammonium hydroxide (TMAH), the conventional developer.

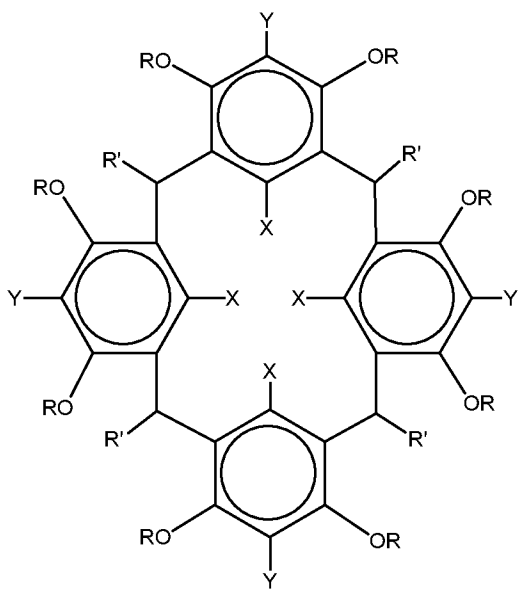
Therefore to advance this resist platform, there is a need to develop molecular glass materials that are monodisperse, readily soluble in casting solvents, compatible with 0.26N TMAH developer, and easy to synthesize.

#### Disclosure of the Invention

Disclosed herein is a phenolic molecular glass having at least one fluoroalcohol containing unit, a photoresist composition including the phenolic molecular glass having at least one fluoroalcohol containing unit and a photoacid generator, and a process for generating a resist image on a substrate.

Accordingly, the present invention provides, viewed from a first aspect, a phenolic molecular glass having at least one fluoroalcohol containing unit.

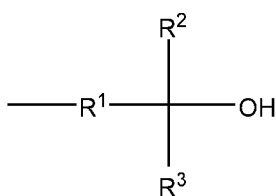
The phenolic molecular glass is preferably a calixarene, preferably a calix[4]resorcinarene of structural formula (I):



wherein R' comprises the at least one fluoroalcohol containing unit and R is independently selected from the group consisting of hydrogen and an acid labile functional group.

- 5 The X and Y moieties may be the same or different and are preferably selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, alkoxy, aryl, aralkyl, alkaryl, halo, cyano, nitro and carboxylate.

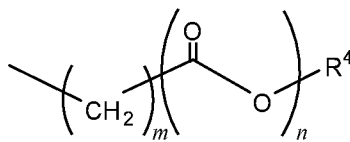
10 Preferably, the phenolic molecular glass comprises at least one fluoroalcohol containing unit of the structural formula (II):



(II),

15 wherein R<sup>1</sup> is a linear or branched alkylene group, a substituted or unsubstituted alicyclic group, a substituted or unsubstituted arylene group, a substituted or unsubstituted heteroarylene group, a substituted or unsubstituted heterocyclic group; R<sup>2</sup> and R<sup>3</sup> are each independently fluorinated alkyl group.

Preferably, in the phenolic molecular glass, R is an acid-labile functional group that has a structural formula (III):



(III),

wherein m is 0 to 4, n is 0 or 1, and  $\text{R}^4$  is  $\text{CR}^5\text{R}^6\text{R}^7$ , or  $\text{SiR}^8\text{R}^9\text{R}^{10}$ , wherein  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  are independently hydrogen, alkyl, alkoxy, aryl, or aryloxy, or are linked to form a cycloalkyl or cyclooxyalkyl ring, and  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are each an alkyl substituent.

5

Preferably, in the phenolic molecular glass, R is hydrogen.

10

According to a second aspect of the present invention, there is provided a photoresist composition, comprising a phenolic molecular glass having at least one fluoroalcohol containing unit of the first aspect, and a photoacid generator.

Preferably, in the photoresist composition, R is hydrogen and the photoresist composition further comprises a crosslinking agent.

15

Preferably, the photoresist composition further comprises a pigment, a sensitizer, a preservative, an acid-diffusion controlling agent, an adhesion promoter, a coating aid, a plasticizer, a surface modifying agent, and/or a dissolution inhibitor.

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According to a third aspect of the present invention, there is provided a process for generating a resist image on a substrate, comprising: coating a substrate with a film comprising a photoresist composition comprising a phenolic molecular glass having at least one fluoroalcohol functionality of the first aspect, a photoacid generator, and a solvent; imagewise exposing the film to radiation to form latent image therein; and developing the resist image with an aqueous base developer.

25

Preferably in the process, R is hydrogen and the photoresist composition further comprises a crosslinker.

30

Preferably in the process, subsequent to imagewise exposing the film to radiation and prior to developing, the film is heated to a temperature within a range of 25°C to 150°C.

Preferably in the process, the radiation is ultraviolet radiation, x-ray, EUV, or electron beam.

Preferably, the process further comprises a pigment, a sensitizer, a preservative, an acid-diffusion controlling agent, an adhesion promoter, a coating aid, a plasticizer, a surface  
5 modifying agent, and/or a dissolution inhibitor.

Additional features and advantages are realized through the techniques of the present invention. Other embodiments and aspects of the invention are described in detail herein and are considered a part of the claimed invention. For a better understanding of the  
10 invention with the advantages and the features, refer to the description and to the drawings.

#### Brief Description of the Drawings

The subject matter, which is regarded as the invention, is particularly pointed out and  
15 distinctly claimed in the claims at the conclusion of the specification. The foregoing and other features and advantages of embodiments of the invention are apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 graphically illustrates contrast curves at 248 nm as a function of post exposure bake  
20 (PEB) temperature in 0.26 N TMAH developer for a hexafluoroalcohol containing molecular glass resist in accordance with a preferred embodiment of the present invention;

FIG. 2 graphically illustrates e-beam contrast curves as a function of post exposure bake  
25 (PEB) temperature in 0.26 N TMAH developer for a hexafluoroalcohol containing molecular glass resist in accordance with a preferred embodiment of the present invention;

FIG. 3. pictorially illustrates scanning electron micrographs of 130 nm 1:1 line space  
30 patterns printed from a hexafluoroalcohol containing molecular glass resist in accordance with a preferred embodiment of the present invention on a 0.6 NA 248 nm stepper;

FIG. 4 pictorially illustrates scanning electron micrographs of 60 nm 1:1 line space patterns printed from a hexafluoroalcohol containing molecular glass photoresist of a preferred embodiment of the present invention on a 100 KeV e-beam exposure tool;

5 FIG. 5 pictorially illustrates scanning electron micrographs of 30/45 nm line space patterns printed from a hexafluoroalcohol containing molecular glass photoresist of a preferred embodiment of the present invention on a 100 KeV e-beam exposure tool; and

10 FIG. 6 pictorially illustrates scanning electron micrographs of 50 nm line space patterns printed from a hexafluoroalcohol containing molecular glass photoresist of a preferred embodiment of the present invention on an extreme ultraviolet (EUV) micro exposure tool.

#### Detailed Description of the Preferred Embodiment

15 The present invention relates to fluoroalcohol containing molecular glass resist materials for high resolution lithographic applications. The fluoroalcohol containing molecular glass resist materials are monodisperse; readily soluble in casting solvents; compatible with 0.26N TMAH developer; and easy to synthesize.

20 In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below.

25 The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. The term "lower alkyl" intends an alkyl group of one to six carbon atoms, preferably one to four carbon atoms, and the term "lower alkyl ester" refers to an ester functionality--C(O)O--R wherein R is a lower alkyl.

30 The term "alkenyl" as used herein refers to a branched or unbranched hydrocarbon group of 2 to 24 carbon atoms containing at least one double bond, typically containing one to six



double bonds, more typically one or two double bonds, e.g., ethenyl, n-propenyl, n-butenyl, octenyl, decenyl, and the like, as well as cycloalkenyl groups such as cyclopentenyl, cyclohexenyl and the like. The term "lower alkenyl" intends an alkenyl group of two to six carbon atoms, preferably two to four carbon atoms.

5

The term "alkynyl" as used herein refers to a branched or unbranched hydrocarbon group of 2 to 24 carbon atoms containing at least one triple bond, e.g., ethynyl, n-propynyl, n-butylnyl, octynyl, decynyl, and the like, as well as cycloalkynyl groups such as and the like. The term "lower alkynyl" intends an alkynyl group of two to six carbon atoms, preferably two to four carbon atoms.

10

The term "alkoxy" as used herein refers to a substituent--O--R wherein R is alkyl as defined above. The term "lower alkoxy" refers to such a group wherein R is lower alkyl.

15

The term "aryl" as used herein, and unless otherwise specified, refers to an aromatic moiety containing one to five aromatic rings. For aryl groups containing more than one aromatic ring, the rings may be fused or linked. Preferred monocyclic aromatic substituents are phenyl and substituted phenyl, optionally substituted with one to five, typically one to four, halo, alkyl, alkenyl, alkynyl, alkoxy, nitro or other substituents.

20

The term "halo" is used in its conventional sense to refer to a chloro, bromo, fluoro or iodo substituent. The terms "haloalkyl," "haloaryl" (or "halogenated alkyl" or "halogenated aryl") refers to an alkyl or aryl group, respectively, in which at least one of the hydrogen atoms in the group has been replaced with a halogen atom.

25

The term "alkaryl" refers to an aryl group with an alkyl substituent, wherein "aryl" and "alkyl" are as defined above.

30

The term "aralkyl" refers to an alkyl group that has an aryl substituent, wherein "alkyl" and "aryl" are as defined above.

The term "fluorinated" refers to replacement of a hydrogen atom in a molecule or molecular segment with a fluorine atom, and includes perfluorinated moieties. The term "perfluorinated" is also used in its conventional sense to refer to a molecule or molecular segment wherein all hydrogen atoms are replaced with fluorine atoms. Thus, a "fluorinated" methyl group encompasses  $\text{—CH}_2\text{F}$  and  $\text{—CHF}_2$  as well as the "perfluorinated" methyl group, i.e.,  $\text{—CF}_3$  (trifluoromethyl). The term "fluoroalkyl" refers to a fluorinated alkyl group, the term "fluoroalkylene" refers to a fluorinated alkylene linkage, the term "fluoroalicyclic" refers to a fluorinated alicyclic moiety, and the like.

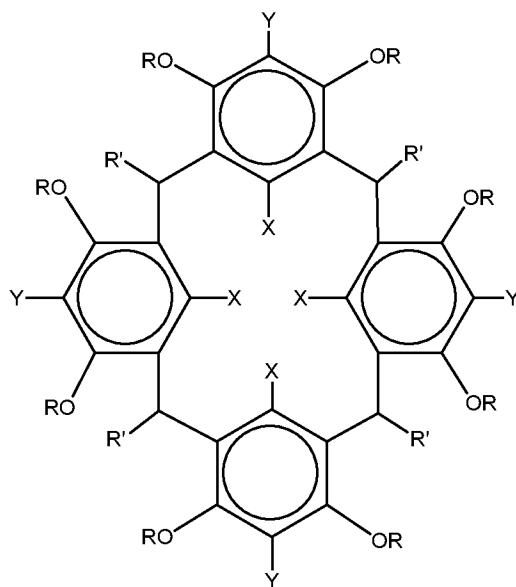
The terms "photogenerated acid" and "photoacid" are used interchangeably herein to refer to the acid that is created upon exposure of the present compositions to radiation, i.e., as a result of the radiation-sensitive acid generator in the compositions.

The terms "acid-labile" or "acid-cleavable" are used interchangeably herein to refer to a molecular moiety that undergoes a change in structure upon contact with a strong acid, e.g., a carboxylic ester that, upon contact with a sulfonic acid is converted to a carboxylic acid, a carbonate ester that, upon contact with acid is converted to a hydroxyl group, or the like. The groups that are "acid-labile" or "acid-cleavable" in the context of the present invention are also referred to as "acid-labile functionalities".

"Optional" or "optionally" means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" means that a non-hydrogen substituent may or may not be present, and, thus, the description includes structures wherein a non-hydrogen substituent is present and structures wherein a non-hydrogen substituent is not present.

For additional information concerning terms used in the field of lithography and lithographic compositions, reference may be had to Introduction to Microlithography, 2<sup>nd</sup> Edition, Eds. L. Thompson et al. (Washington, D.C.: American Chemical Society, 1994).

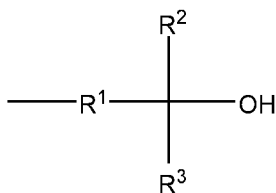
In one embodiment, the fluoroalcohol containing molecular glass resist materials are calixarenes. By way of example, the calixarenes can be fluoroalcohol containing calix[4]resorcinarenes having the structure of formula (I) below.



(I)

In one embodiment, at least one of the R' moieties contain a fluoroalcohol functionality and the R moieties represent hydrogen and/or acid-labile functional groups. The various fluoroalcohol containing calix[4]resorcinarenes are condensation products of resorcinols and fluoroalcohol containing aldehydes. It will be appreciated that the symmetric location of the -OR moieties in the calix[4]resorcinarene of formula (I) corresponds to the positioning of the -OR moieties on the resorcinol starting material used to make these compounds.

The R' moieties including the fluoroalcohol functionality are of the general formula (II):

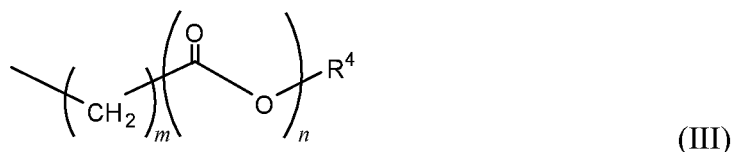


(II)

wherein R<sup>1</sup> is a linear or branched alkylene group, a substituted or unsubstituted alicyclic group, a substituted or unsubstituted arylene group, a substituted or unsubstituted heteroarylene group, a substituted or unsubstituted heterocyclic group; R<sup>2</sup> and R<sup>3</sup> are

each independently fluorinated alkyl group, wherein the fluorinated alkyl group may be the same or different.

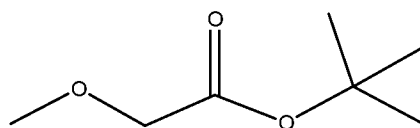
Suitable acid-labile functional groups include, but are not limited to, moieties having the structure of formula (III)



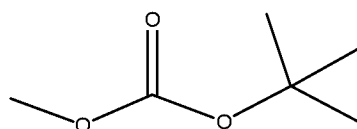
in which  $m$  is 0 to 4,  $n$  is 0 or 1, and  $\text{R}^4$  is  $\text{CR}^5\text{R}^6\text{R}^7$ , or  $\text{SiR}^8\text{R}^9\text{R}^{10}$ , wherein  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  are independently hydrogen, alkyl, alkoxy, aryl, or aryloxy, typically hydrogen, lower alkyl or lower alkoxy, or are linked to form a cycloalkyl or cyclooxyalkyl ring, typically a five- to twelve-membered ring, and  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are the same or different and are each an alkyl, typically a lower alkyl, substituent.

Thus,  $\text{R}^4$  may be, for example, methoxymethyl, ethoxymethyl, methoxyethoxymethyl, benzyloxymethyl, cyclopropylmethyl, diphenylmethyl, triphenylmethyl, 1-methoxyethyl, 1,1-dimethoxyethyl, 1-ethoxyethyl, 1-ethylthioethyl, 1,1-diethoxyethyl, 1-phenoxyethyl, 1,1-diphenoxyethyl, 1-cyclopropylethyl, 1-phenylethyl, 1,1-diphenylethyl, *t*-butyl, 1,1-dimethylpropyl, 1-methylbutyl, 1,1-dimethylbutyl, methylcyclopentyl, ethylcyclopentyl, methylcyclohexyl, ethylcyclohexyl, methylcyclooctyl, ethylcyclooctyl, methyladamantyl, ethyladamantyl, trimethylsilyl, ethyldimethylsilyl, diethylmethylsilyl, triethylsilyl, dimethylisopropylsilyl, *t*-butyldimethylsilyl, di-*t*-butylmethylsilyl, tri-*t*-butylsilyl, dimethylphenylsilyl, methyldiphenylsilyl, triphenylsilyl, trimethylgermyl, ethyldimethylgermyl, diethylmethylgermyl, triethylgermyl, dimethylisopropylgermyl, methyldiisopropylgermyl, triisopropylgermyl, *t*-butyldimethylgermyl, di-*t*-butylmethylgermyl, tri-*t*-butylgermyl, dimethylphenylgermyl, methyldiphenylgermyl, triphenylgermyl, and the like. Other suitable acid-labile protecting groups may be found in the pertinent literature and texts (e.g., Greene et al., *Protective Groups in Organic Synthesis*, 2<sup>nd</sup> Ed., John Wiley & Sons, 1991).

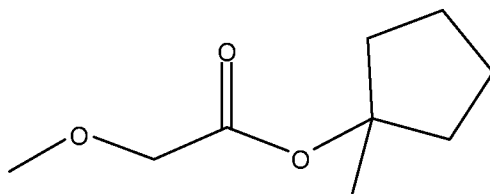
Representative--OR moieties are illustrated in formulas (IV)-(IX) below.



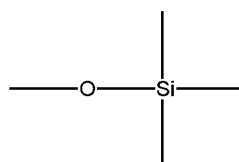
(IV)



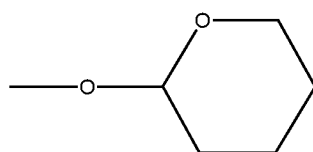
(V)



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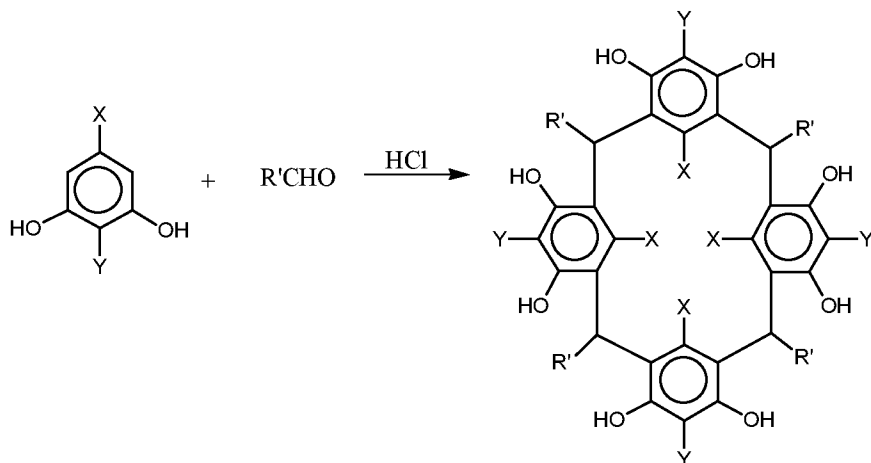


(IX)

The X and Y moieties may be the same or different and are selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, alkoxy, aryl, aralkyl, alkaryl, halo, cyano, nitro and carboxylate. In certain embodiments, the X moieties are all hydrogen, and the Y moieties are selected from the group consisting of hydrogen and lower alkyl.

The basic calix[4]resorcinarene molecule can exist in either of two isomeric forms, commonly referred to as the  $C_{2v}$  and the  $C_{4v}$  configurations (also sometimes referred to herein as the "ctt" and "ccc" isomers, respectively). These isomers can be separated by fractional crystallization using conventional techniques. In the context of the invention, the calix[4]resorcinarenes may be in either the  $C_{2v}$  or the  $C_{4v}$  configurations so as to provide structural monomodality. Alternatively, a mixture of isomers can be used in the blend.

The calix[4]resorcinarenes can generally be prepared by condensation reaction with resorcinol and a fluorocontaining aldehyde using hydrochloric acid as a catalyst in accordance with the following scheme.



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The acid labile moieties can then be introduced into the calix[4]resorcinarene molecule by reacting with the unprotected calix[4]resorcinarene with a desired moiety that will then provide an acid-labile functionality on the eight hydroxyl groups. The reaction may be conducted using conventional means known to those skilled in the art. For example, to provide a calix[4]resorcinarene with the t-butoxycarbonylmethyl (t-BuOOCCH<sub>2</sub>) groups, the calix[4]resorcinarene may be reacted with eight equivalents or a slight excess of t-butyl bromoacetate and potassium carbonate. Similarly, to provide a calix[4]resorcinarene fully protected with the t-butoxycarbonyl (tBuOOC) group, the calix[4]resorcinarene may be reacted with eight equivalents or a slight excess of di-t-butyl dicarbonate. Various reaction schemes to fabricate the calix[4]resorcinarenes are known in the art and are not intended to be limited to that shown above. By way of example, the calix[4]resorcinarenes can be prepared in accordance with Ito et al., Characterization and Lithographic Application of Calix[4]resorcinarene Derivatives, Chem. Mater. 20: 341-356 (2008).

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For positive tone applications, the photoresist compositions herein include fluoroalcohol containing calix[4]resorcinarenes, a photoacid generator, and a solvent. For negative tone applications, the photoresist may further include a crosslinker.

25

Upon exposure to radiation, the photoacid generator generates an acid that is used to cleave the acid labile groups as in the case of a positive tone resist or effect a crosslinking reaction

as in the case of a negative tone resist. A variety of photoacid generators (also referred to herein as "PAGs") can be used in the composition of the present invention. Generally, suitable acid generators have a high thermal stability (preferably to temperatures greater than 140° C) so they are not degraded during pre-exposure processing. Any suitable photoacid generator can be used in the photoresist compositions of the invention. Typical photoacid generators include, without limitation: sulfonium salts, such as triphenylsulfonium perfluoromethanesulfonate (triphenylsulfonium triflate), triphenylsulfonium perfluorobutanesulfonate, triphenylsulfonium perfluoropentanesulfonate, triphenylsulfonium perfluorooctanesulfonate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium bromide, triphenylsulfonium chloride, triphenylsulfonium iodide, 2,4,6-trimethylphenyldiphenylsulfonium perfluorobutanesulfonate, 2,4,6-trimethylphenyldiphenylsulfonium benzenesulfonate, tris(t-butylphenyl)sulfonium perfluorooctanesulfonate, diphenylethylsulfonium chloride, and phenacyldimethylsulfonium chloride; halonium salts, particularly iodonium salts, including diphenyliodonium perfluoromethanesulfonate (diphenyliodonium triflate), diphenyliodonium perfluorobutanesulfonate, diphenyliodonium perfluoropentanesulfonate, diphenyliodonium perfluorooctanesulfonate, diphenyliodonium hexafluoroantimonate, diphenyliodonium hexafluoroarsenate, diphenyliodonium bis-(t-butylphenyl)iodonium triflate, and bis-(di-t-butylphenyl)-iodonium camphanylsulfonate;  $\alpha,\alpha'$ -bis-sulfonyl-diazomethanes such as bis(p-toluenesulfonyl)diazomethane, methylsulfonyl p-toluenesulfonyldiazomethane, 1-cyclohexylsulfonyl-1-(1,1-dimethylethylsulfonyl) diazomethane, and bis(cyclohexylsulfonyl) diazomethane; trifluoromethanesulfonate esters of imides and hydroxyimides, e.g.,  $\alpha$ -(trifluoromethylsulfonyloxy)-bicyclo[2.2.1] hept-5-ene-2,3-dicarboximide (MDT); nitrobenzyl sulfonate esters such as 2-nitrobenzyl p-toluenesulfonate, 2,6-dinitrobenzyl p-toluenesulfonate, and 2,4-dinitrobenzyl p-trifluoromethylbenzenesulfonate; sulfonyloxynaphthalimides such as N-camphorsulfonyloxynaphthalimide and N-pentafluorophenylsulfonyloxynaphthalimide; pyrogallol derivatives (e.g., trimesylate of pyrogallol); naphthoquinone-4-diazides; alkyl disulfones; s-triazine derivatives, as described in U.S. Pat. No. 4,189,323; and miscellaneous sulfonic acid generators including t-butylphenyl- $\alpha$ -(p-toluenesulfonyloxy)-acetate, t-butyl- $\alpha$ -

(p-toluenesulfonyloxy)acetate, and N-hydroxy-naphthalimide dodecanesulfonate (DDSN), and benzoin tosylate.

Other suitable photoacid generators are disclosed in Reichmanis et al. (1991), *Chemistry of Materials* 3:395, and in U.S. Pat. No. 5,679,495 to Yamachika et al. Additional suitable acid generators useful in conjunction with the compositions and methods provided herein will be known to those skilled in the art and/or are described in the pertinent literature.

The photoresist composition herein preferably comprises approximately 0.5-10 wt. % of the photoacid generator, and up to about 94.5 wt. % of the fluoroalcohol containing calix[4]resorcinarenes. If crosslinking agents are present, they will typically be present in the range of about 1 wt. % to 40 wt. %, preferably about 5 wt. % to 30 wt. %, of the total solids.

The crosslinking agent used in the photoresist compositions of the invention may be any suitable crosslinking agent known in the negative photoresist art, which is otherwise compatible with the other selected components of the photoresist composition. The crosslinking agents preferably act to crosslink the polymer component in the presence of a generated acid. Preferred crosslinking agents are glycoluril compounds such as tetramethoxymethyl glycoluril, methylpropyltetramethoxymethyl glycoluril, and methylphenyltetramethoxymethyl glycoluril, available under the POWDERLINK trademark from American Cyanamid Company. Other suitable crosslinking agents can also be found in Japanese Laid-Open Patent Application (Kokai) No. 1-293339, as well as etherified amino resins (for example, methylated or butylated melamine resins (N-methoxymethyl- or N-butoxymethyl-melamine, respectively)), or methylated/butylated glycolurils (for example as can be found in Canadian Patent No. 1 204 547). Combinations of crosslinking agents may be used.

Other customary additives may also be present in the photoresist composition, including pigments, sensitizers, preservatives, acid-diffusion controlling agents, coating aids such as surfactants or anti-foaming agents, adhesion promoters, plasticizers, and dissolution inhibitors, surface modifying agents, among others. Typically, the sum of all customary



additives will comprise less than 20 percent of the solids included in the resist formulation, preferably, less than 5 percent.

Pigments may be used to adjust the optical density of the formulated resist and sensitizer, which can enhance the activity of photoacid generators by absorbing radiation and transferring it to the photoacid generator. Examples include aromatics such as functionalized benzenes, pyridines, pyrimidines, biphenylenes, indenenes, naphthalenes, coumarins, anthraquinones, and other aromatic ketones.

A wide variety of compounds with varying basicity may be used as preservatives and acid-diffusion controlling additives. They may include nitrogenous compounds such as aliphatic primary, secondary, and tertiary amines, cyclic amines such as piperidines, pyrimidines, morpholines, aromatic heterocycles such as pyridines, pyrimidines, purines, imines such as diazabicycloundecene (DBU), guanidines, imides, amides, and others. Ammonium salts of basic anions may also be used, including ammonium, primary, secondary, tertiary, and quaternary alkyl- and arylammonium salts of alkoxides including hydroxide, phenolates, carboxylates, aryl and alkyl sulfonates, sulfonamides, and others. Other cationic nitrogenous compounds including pyridinium salts and salts of other heterocyclic nitrogenous compounds with anions such as alkoxides including hydroxide, phenolates, carboxylates, aryl and alkyl sulfonates, sulfonamides, and the like may also be employed. Surfactants may be used to improve coating uniformity, and include a wide variety of ionic and non-ionic, monomeric, oligomeric, and polymeric species. Likewise, a wide variety of anti-foaming agents may be employed to suppress coating defects. Adhesion promoters may be used as well; again, a wide variety of compounds may be employed to serve this function. A wide variety of monomeric, oligomeric, and polymeric plasticizers such as oligo- and polyethyleneglycol ethers, cycloaliphatic esters, and non-acid reactive steroidally derived materials may be used as plasticizers, if desired. However, neither the classes of compounds nor the specific compounds mentioned above are intended to be comprehensive and/or limiting. One versed in the art will recognize the wide spectrum of commercially available products that may be used to carry out the types of functions that these customary additives perform.

The remainder of the photoresist composition is composed of a solvent. The choice of solvent is governed by many factors not limited to the solubility and miscibility of resist components, the coating process, and safety and environmental regulations. Additionally, inertness to other resist components is desirable. It is also desirable that the solvent possess the appropriate volatility to allow uniform coating of films yet also allow significant reduction or complete removal of residual solvent during the post-application bake process. See, e.g., Introduction to Microlithography, Eds. Thompson et al., cited previously. Solvents may generally be chosen from ether-, ester-, hydroxyl-, and ketone-containing compounds, or mixtures of these compounds. Examples of appropriate solvents include cyclopentanone, cyclohexanone, lactate esters such as ethyl lactate, alkylene glycol alkyl ether esters such as propylene glycol methyl ether acetate, alkylene glycol monoalkyl esters such as methyl cellosolve, butyl acetate, 2-ethoxyethanol, and ethyl 3-ethoxypropionate. Preferred solvents include ethyl lactate, propylene glycol methyl ether acetate, and mixtures of ethyl lactate and ethyl 3-ethoxypropionate. The above list of solvents is for illustrative purposes only and should not be viewed as being comprehensive nor should the choice of solvent be viewed as limiting the invention in any way. Those skilled in the art will recognize that any number of solvents or solvent mixtures may be used.

Greater than 50% of the total mass of the resist formulation is typically composed of the solvent, preferably greater than 80%.

The present invention also relates to a process for generating a resist image on a substrate comprising the steps of: (a) coating a substrate with a film comprising the resist composition of the invention; (b) imagewise exposing the film to radiation; and (c) developing the image. The first step involves coating the substrate with a film comprising the resist composition dissolved in a suitable solvent. Suitable substrates are silicon-containing, and include, for example, silicon dioxide, silicon nitride, silicon oxynitride, and chrome-coated quartz or glass. The substrate may or may not be coated with an organic anti-reflective layer prior to deposition of the resist composition. Preferably, the surface of the substrate is cleaned by standard procedures before the film is deposited thereon. Suitable solvents for the composition are as described in the preceding section, and include, for example, cyclohexanone, ethyl lactate, and propylene glycol methyl ether acetate. The film can be

coated on the substrate using art-known techniques such as spin or spray coating, or doctor blading. Preferably, before the film has been exposed to radiation, the film is heated to a temperature of about 25-150°C for a short period of time, typically on the order of about 1 minute. The dried film has a thickness of about 20-5000 nm, preferably about 50-1200 nm.

In the second step of the process, the film is imagewise exposed to activating energy such as may be provided by x-ray, electron beam (e-beam), ultraviolet radiation or extreme ultraviolet (EUV) radiation (13.4 nm). The radiation is absorbed by the radiation-sensitive photoacid generator to generate free acid, which, in the case of a positive tone resist, with heating causes cleavage of the acid-cleavable ester substituent and formation of the corresponding acid, or as in the case of a negative tone resist crosslinking. Preferably, after the film has been exposed to radiation, the film is again heated to a temperature of about 25-150°C for a short period of time, on the order of about 1 minute.

The third step involves development of the image with a suitable solvent. Suitable solvents include an aqueous base, preferably an aqueous base without metal ions such as the industry standard developer tetramethyl ammonium hydroxide or choline. The resist composition of the invention has high radiation sensitivity and provides images exhibiting high contrast and straight walls. The composition can also be readily developed in industry standard developer. Development is without unacceptable thinning or swelling. The resist has suitable thermal properties ( $T_g$ ), good adhesion, and planarization. In addition, the presence of the fluoroalcohol functionalities significantly improved the solubility characteristics of the composition of the present invention.

The composition of the present invention may be used to make an integrated circuit assembly, such as an integrated circuit chip, multichip module, circuit board, quartz mask, or imprint template. The integrated circuit assembly comprises a circuit formed on a substrate by the steps of (a) coating a substrate with a film comprising the resist composition of the present invention, (b) imagewise exposing the film to radiation to form a latent image therein, (c) developing the image to expose the substrate, and (d) forming the circuit in the developed film on the substrate by art-known techniques. After the substrate has been exposed, circuit patterns can be formed in the exposed areas by coating the substrate with a

conductive material such as conductive metals by art-known dry techniques such as evaporation, sputtering, plating, chemical vapor deposition, or laser-induced deposition. The surface of the film can be milled to remove any excess conductive material. Dielectric materials may also be deposited by similar means during the process of making circuits.

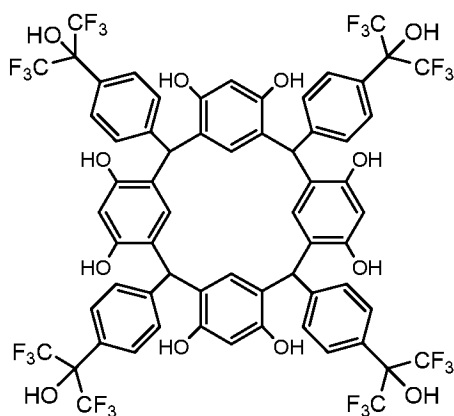
5 Inorganic ions such as boron, phosphorous, or arsenic can be implanted in the substrate in the process for making p-doped or n-doped circuit transistors. Other means for forming circuits are well known to those skilled in the art. The composition of the present invention may also be used to fabricate photomasks, imprint templates and the like.

10 It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, that the foregoing description as well as the examples that follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

### 15 Examples

Example 1. In this example, 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene (Structure 1 as shown below) was synthesized through an acid catalyzed condensation reaction between a hexafluoroalcohol containing aldehyde and resorcinol.

Structure 1.

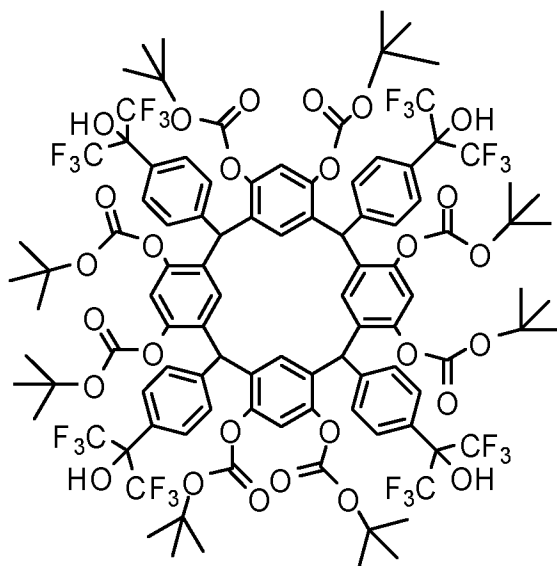


25 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)benzaldehyde (5g, 0.018mol), resorcinol (2g, 0.018mol) and methanol (20ml) were placed in a round bottom flask equipped with a stirrer. 5ml of concentrated hydrochloric acid was added to the mixture at room temperature and

then the reaction mixture was refluxed at 70°C for 18hrs. The completion of the reaction was determined by the disappearance of the carbonyl peak of the aldehyde starting material through NMR or IR spectrum. The reaction solvent, methanol, was evaporated by the rotary evaporator and the resulting material was precipitated in deionized water several times. The product was confirmed by NMR spectroscopy. Yield: 4.5g (68%). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): (ppm) 5.62 (s, CH, 4H), 6.16 (s, ArH, 4H), 6.21 (broad s, ArH, 2H), 6.69 (broad s, ArH, 2H), 6.81 (d, ArH, 8H), 7.39 (d, ArH, 8H), 8.38 (s, HFA-OH, 4H), 8.74 (d, Ar-OH, 8H).

Example 2. In this example, the 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene of example 1 was selectively functionalized at the phenolic hydroxyl units with tert-butoxy carbonyl (t-BOC) groups through a base catalyzed reaction to produce t-BOC protected 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene (structure 2 as shown below).

Structure 2



4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene (2g, 0.0014mol) and 4-dimethylaminopyridine (0.06 g, 0.0005 mol) were dissolved in 25ml of acetone in a round bottom flask equipped with a stirrer. The di-tert-butyl dicarbonate (2.39 g, 0.011 mol) was added slowly using a dropping funnel and stirred at a steady pace. The evolution of CO<sub>2</sub> gas occurred immediately indicating the progress of the reaction and the reaction mixture was stirred at room temperature for 8hrs. The solvent was reduced through evaporation and

the product was purified by column chromatography with acetone as the eluent. Yellow solid was obtained. The product was confirmed by NMR spectroscopy. Yield: 2.4g (80%). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): (ppm) 1.14 (s, CH<sub>3</sub>, 36H), 1.42 (s, CH<sub>3</sub>, 36H), 5.56 (s, CH, 4H), 6.33 (s, ArH, 4H), 6.78 (broad s, ArH, 8H), 7.07 (d, ArH, 2H), 7.12 (d, ArH, 2H), 7.25 (d, ArH, 8H), 8.6 (s, HFA-OH, 4H). Polydispersity: 1.02.

Example 3. In this example, a photoresist composition including the t-BOC protected 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene of Example 2 was lithographically evaluated. The resist was formulated with 0.25 g of the t-BOC protected 4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)phenylcalix[4]resorcinarene (Structure 2), 25 mg of triphenylsulfonium perfluoro-1-butanesulfonate (photoacid generator), and 0.75 mg of an organic base, which were dissolved in 5 g of propylene glycol monomethyl ether acetate (PGMEA). This solution was filtered through a 0.2 micron syringe filter.

The photoresist solution was spin coated onto blank silicon wafers at a thickness of about 500 angstroms (50 nm) using a post apply bake temperature of 90°C for 60 seconds. Figure 1 graphically illustrates contrast curves at 248 nm in 0.26N TMAH developer as a function of post exposure bake temperatures for 30 seconds that were generated using an ASML stepper. As shown, the resist exhibited good contrast when post exposure baked at 77°C or higher.

Figure 2 graphically illustrates e-beam contrast curves using a 100 keV Leica e-beam exposure system in 0.26N TMAH developer as a function of post exposure bake temperature for 30 seconds. In this example, the resist was coated to a thickness of about 750 angstroms (75 nm) using a post apply bake temperature of 94°C for 60 seconds.

Scanning electron micrographs (SEM) of 130 nm line/space patterns printed using the photoresist of example 2 on an ASML 248 nm 0.6 NA stepper are presented in Figure 3. The exposure conditions included a post apply bake of 90°C for 60 seconds, exposure at a dose of 14mJ/cm<sup>2</sup>, and post exposure baked at 90°C for 30 seconds.

Scanning electron micrographs (SEM) of 60 nm line/space patterns printed using the photoresist of example 2 on a 100keV Leica e-beam exposure system are presented in Figure 4. The exposure conditions included a post apply bake of 90°C for 60 seconds, exposure at a dose of 75  $\mu\text{C}/\text{cm}^2$ , and a post exposure bake at 90°C for 30 seconds.

Scanning electron micrographs (SEM) of 30/45 nm line/space patterns printed using the photoresist of example 2 on a 100keV Leica e-beam exposure system are presented in Figure 5. The exposure conditions included a post apply bake of 90°C for 60 seconds, exposure at a dose of 95  $\mu\text{C}/\text{cm}^2$ , and a post exposure bake at 90°C for 30 seconds.

Scanning electron micrographs (SEM) of 50nm line/space patterns printed using the photoresist of example 2 on an EUV Micro Exposure Tool (MET) system are presented in Figure 5. The exposure conditions included a post apply bake of 90°C for 60 seconds, exposure at a dose of 6  $\text{mJ}/\text{cm}^2$ , and a post exposure bake at 90°C for 30 seconds.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, element components, and/or groups thereof.

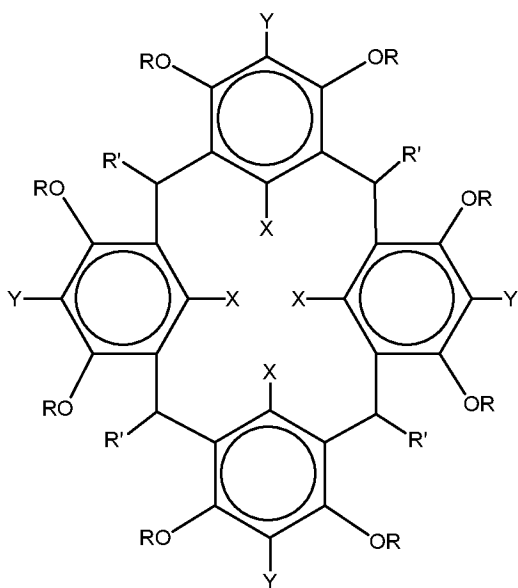
The corresponding structures, materials, and equivalents of all means or step plus function elements in the claims below are intended to include any structure, material, or for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope of the invention.

While the preferred embodiments to the invention have been described, it will be understood that those skilled in the art, both now and in the future, may make various improvements and enhancements which fall within the scope of the claims which follow. These claims should be construed to maintain the proper protection for the invention first described.



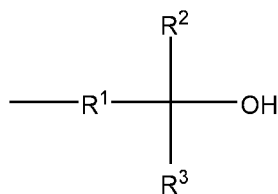
## CLAIMS

1. A phenolic molecular glass having at least one fluoroalcohol containing unit.
2. The phenolic molecular glass of claim 1, wherein the phenolic molecular glass is calixarene.
3. The phenolic molecular glass of claim 1 or 2, wherein the phenolic molecular glass is a calix[4]resorcinarene of structural formula (I):



wherein R' comprises the at least one fluoroalcohol containing unit, R is independently selected from the group consisting of hydrogen and an acid labile functional group, and X and Y are each independently selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, alkoxy, aryl, aralkyl, alkaryl, halo, cyano, nitro and carboxylate.

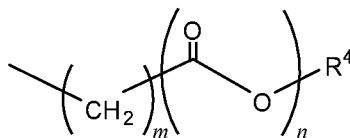
4. The phenolic molecular glass of any preceding claim, wherein at least one fluoroalcohol containing unit is of the structural formula (II):



(II),

wherein  $\text{R}^1$  is a linear or branched alkylene group, a substituted or unsubstituted alicyclic group, a substituted or unsubstituted arylene group, a substituted or unsubstituted heteroarylene group, a substituted or unsubstituted heterocyclic group;  $\text{R}^2$  and  $\text{R}^3$  are each independently fluorinated alkyl group.

5. The phenolic molecular glass of any preceding claim, wherein R is an acid-labile functional group that has a structural formula (III):



(III),

wherein m is 0 to 4, n is 0 or 1, and  $\text{R}^4$  is  $\text{CR}^5\text{R}^6\text{R}^7$ , or  $\text{SiR}^8\text{R}^9\text{R}^{10}$ , wherein  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  are independently hydrogen, alkyl, alkoxy, aryl, or aryloxy, or are linked to form a cycloalkyl or cyclooxyalkyl ring, and  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are each an alkyl substituent.

6. The phenolic molecular glass of any preceding claim, wherein R is hydrogen.

7. A photoresist composition, comprising a phenolic molecular glass having at least one fluoroalcohol containing unit, as claimed in any preceding claim, and a photoacid generator.

8. The photoresist composition of claim 7, wherein R is hydrogen and the photoresist composition further comprises a crosslinking agent.

9. The photoresist composition of claim 7 or 8, further comprising a pigment, a sensitizer, a preservative, an acid-diffusion controlling agent, an adhesion promoter, a coating aid, a plasticizer, a surface modifying agent, and/or a dissolution inhibitor.

10. A process for generating a resist image on a substrate, comprising:

coating a substrate with a film comprising a photoresist composition comprising a phenolic molecular glass having at least one fluoroalcohol functionality, as claimed in any of claims 1 to 6, a photoacid generator, and a solvent;

imagewise exposing the film to radiation to form latent image therein; and

developing the resist image with an aqueous base developer.

11. The process of claim 10, wherein R is hydrogen and the photoresist composition further comprises a crosslinker.

12. The process of claim 10 or 11, wherein subsequent to imagewise exposing the film to radiation and prior to developing, the film is heated to a temperature within a range of 25°C to 150°C.

13. The process of any of claims 10 to 12, wherein the radiation is ultraviolet radiation, x-ray, EUV, or electron beam.

14. The process of any of claims 10 to 13, further comprising a pigment, a sensitizer, a preservative, an acid-diffusion controlling agent, an adhesion promoter, a coating aid, a plasticizer, a surface modifying agent, and/or a dissolution inhibitor.

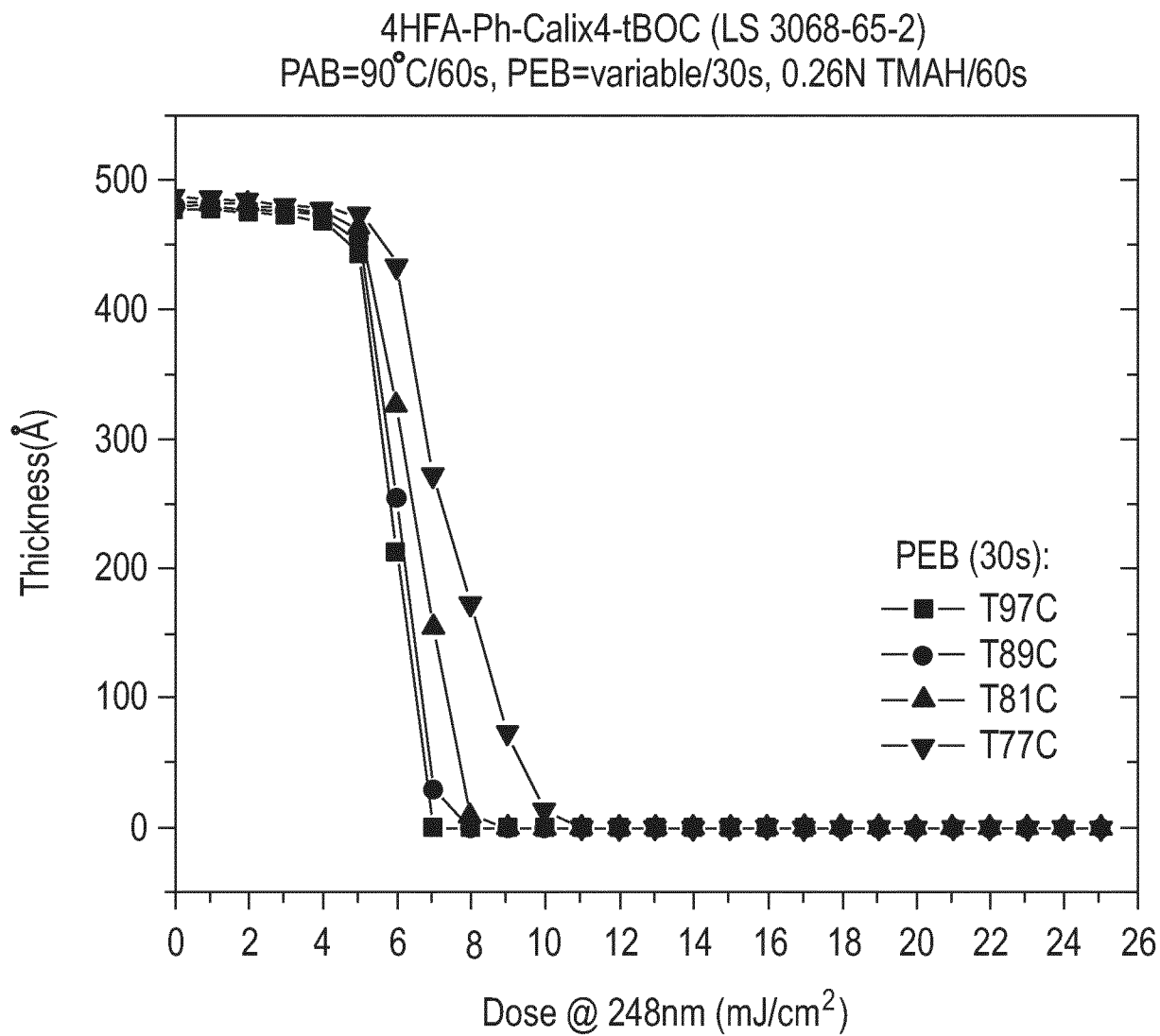


FIG. 1

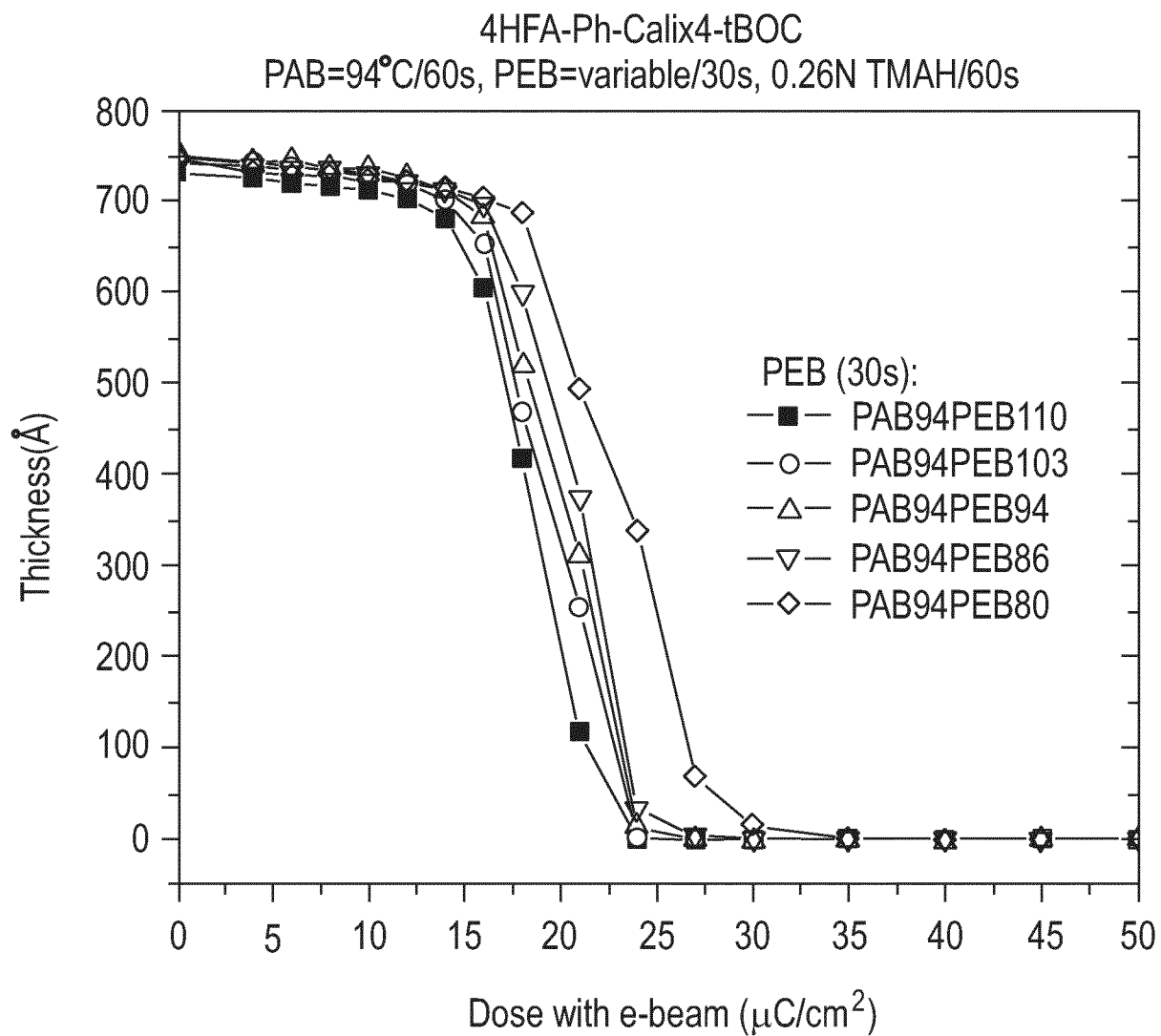
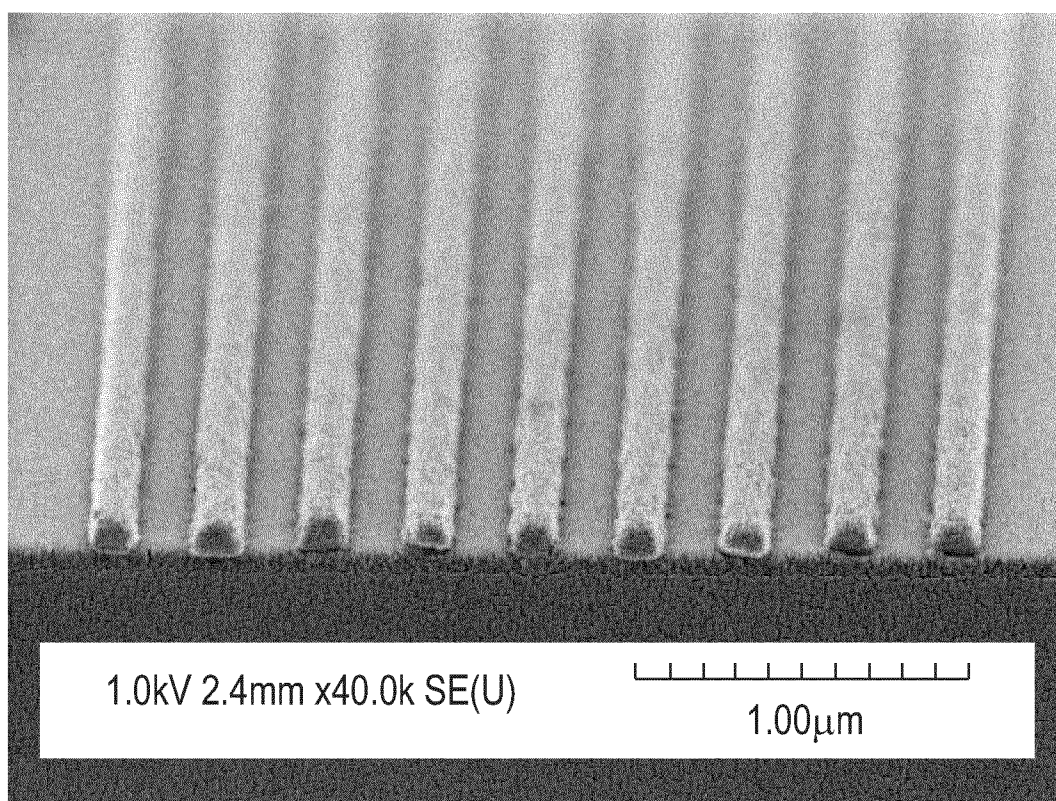


FIG. 2



**FIG. 3**

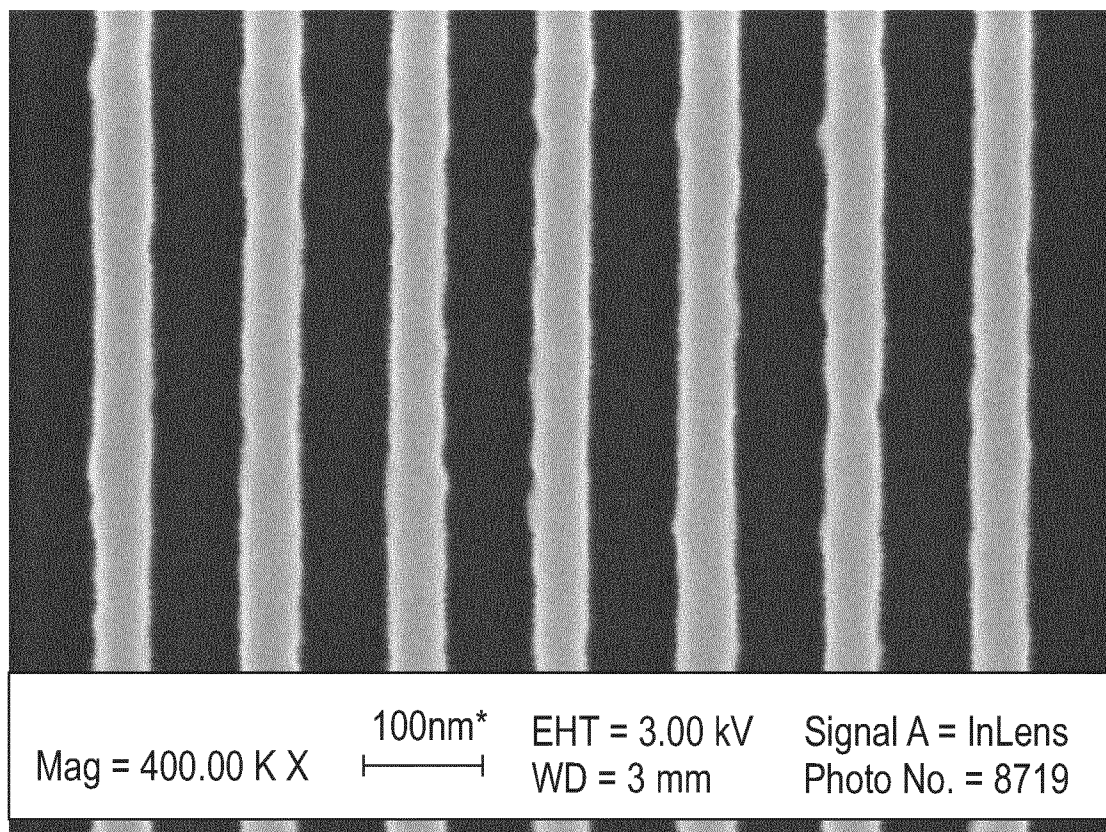
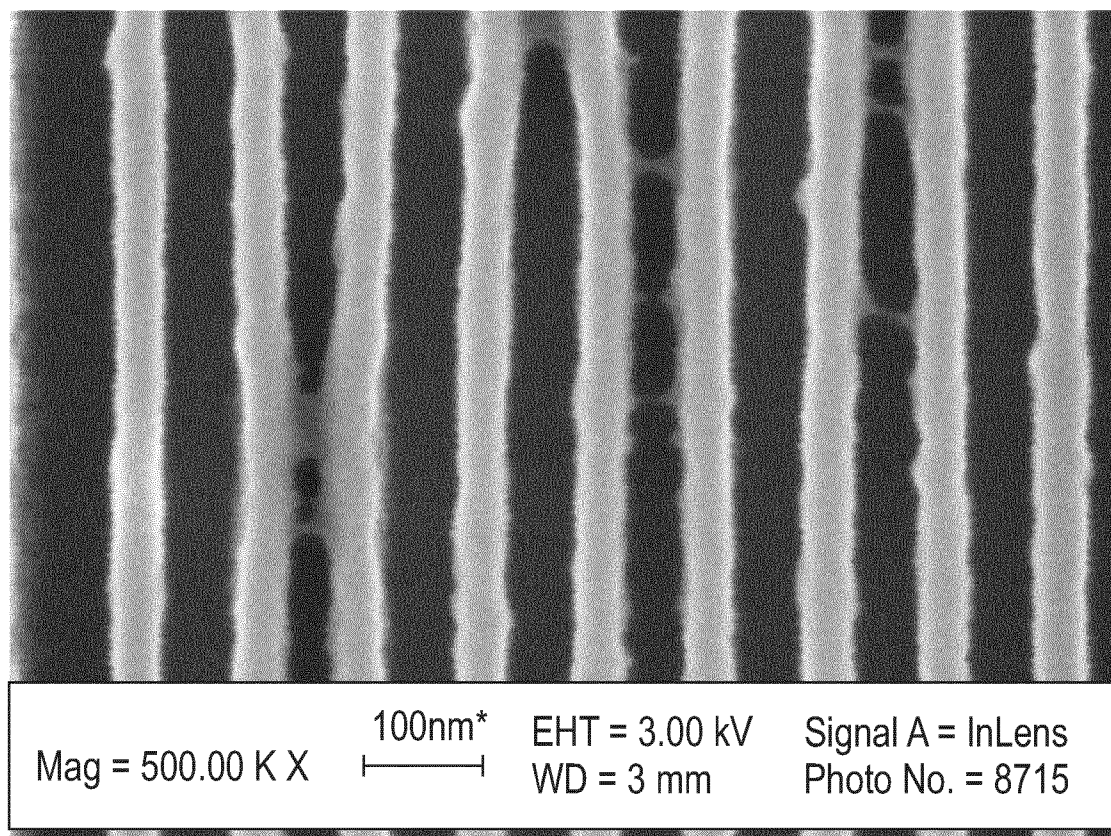
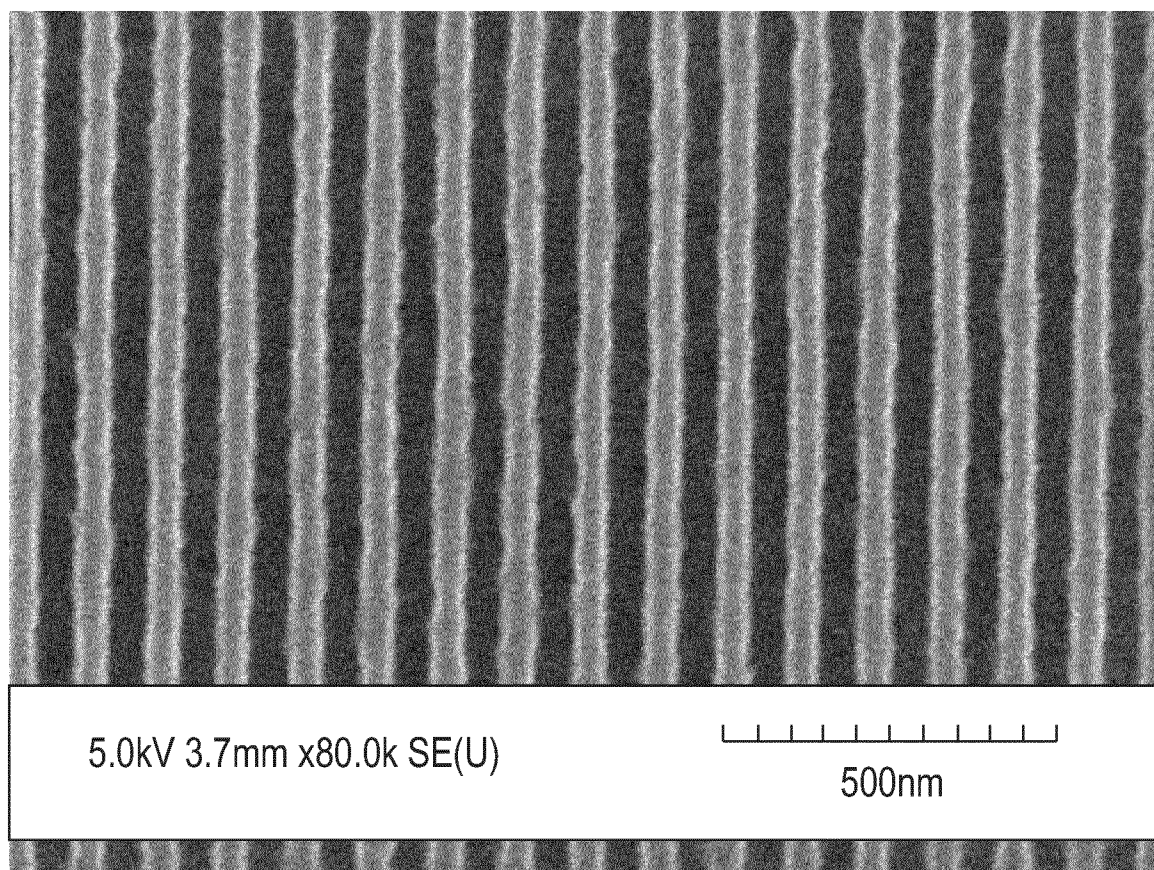


FIG. 4

**FIG. 5**





**FIG. 6**

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2011/070579

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C07C39/367 G03F7/004 G03F7/038 G03F7/039 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C07C G03F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X  Y    Y	US 2008/026317 A1 (BREYTA GREGORY [US] ET AL) 31 January 2008 (2008-01-31) paragraphs [0037], [0043]; claims 1,12,14 claims 4,5,11,13,20 examples 12-27 paragraphs [0043], [0052] ----- WO 2009/143357 A2 (UNIV CORNELL [US]; OBER CHRISTOPHER K [US]; MALLIARAS GEORGE [US]; LEE) 26 November 2009 (2009-11-26) paragraphs [0086], [0089] ----- <div style="text-align: center;">-/-</div>	1,2,4, 7-14 5,6       5,6
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</span> <span><input checked="" type="checkbox"/> See patent family annex.</span> </div>		
* Special categories of cited documents : <div style="display: flex;"> <div style="flex: 1;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search	Date of mailing of the international search report	
25 January 2012	22/02/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Beckert, Audrey	

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/070579

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DE SILVA ET AL: "Hexafluoroalcohol (HFA) containing molecular resist materials for high resolution lithographic applications", PROC. OF SPIE, vol. 7972, 15 April 2011 (2011-04-15), pages 79721Z-1-79721Z-10, XP002667904, the whole document -----	1-14
A	DATABASE WPI Week 200661 Thomson Scientific, London, GB; AN 2006-589091 XP002667905, -& JP 2006 208765 A (MATSUSHITA DENKI SANGYO KK) 10 August 2006 (2006-08-10) abstract -----	1-14
A	BJERRE JEANNETTE ET AL: "Synthesis of Some Trifluoromethylated Cyclodextrin Derivatives and Analysis of Their Properties as Artificial Glycosidases and Oxidases", EUROPEAN JOURNAL OF ORGANIC CHEMISTRY, vol. 2007, no. 4, February 2007 (2007-02), pages 704-710, XP002667906, ISSN: 1434-193X, DOI: 10.1002/ejoc.200600762 the whole document -----	1-6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/070579

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008026317 A1	31-01-2008	US 2008026317 A1	31-01-2008
		US 2010239985 A1	23-09-2010
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WO 2009143357 A2	26-11-2009	CN 102037409 A	27-04-2011
		EP 2297613 A2	23-03-2011
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