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(54) Title: SPIN-ON-GLASS ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY

(57) Abstract: Anti-reflective coating materials for ultraviolet photolithography include at least one organic light-absorbing compound incorporated into spin-on-glass materials. Suitable absorbing compounds are strongly absorbing over wavelength ranges around wavelengths such as 365 nm, 248 nm, 193 nm and 157 nm that may be used in photolithography. A method of making absorbing spin-on-glass materials includes combining at least one organic absorbing compound with alkoxysilane or halosilane reactants during synthesis of the spin-on-glass materials.

S P I N - O N - G L A S S   A N T I - R E F L E C T I V E  
C O A T I N G S

F O R   P H O T O L I T H O G R A P H Y

5    This application is a continuation-in-part of U.S. Patent 6,268,457 issued to Kennedy et al. (July 31, 2001), of U.S. Patent Application Serial No. 09/698,883 filed October 27, 2000, and of U.S. Patent Application Serial No. 09/491,166 filed January 26, 2000, which are all incorporated herein in their entirety by reference.

10    F i e l d   o f   t h e   I n v e n t i o n

        The present invention relates generally to spin-on glass materials and more specifically to light-absorbing spin-on glass materials for use as anti-reflective layers in photolithography and methods of producing the materials.

15    B a c k g r o u n d   o f   t h e   I n v e n t i o n

        To meet the requirements for faster performance, the characteristic dimensions of features of integrated circuit devices have continued to be decreased. Manufacturing of devices with smaller feature sizes introduces new challenges in many of the processes conventionally used in semiconductor fabrication. One of the most important of these  
20    fabrication processes is photolithography.

        It has long been recognized that linewidth variations in patterns produced by photolithography can result from optical interference from light reflecting off an underlying layer on a semiconductor wafer. Variations in photoresist thickness due to the topography of the underlying layer also induce linewidth variations. Anti-reflective coatings (ARC) applied  
25    under a photoresist layer have been used to prevent interference from reflection of the irradiating beam. In addition, anti-reflective coatings partially planarize the wafer

topography, helping to improve linewidth variation over steps because the photoresist thickness is more uniform.

Organic polymer films, particularly those that absorb at the i-line (365 nm) and g-line (436 nm) wavelengths conventionally used to expose photoresists, and at the recently used  
5 248 nm wavelength, have been employed as anti-reflective coatings. However, the fact that the organic ARC's share many chemical properties with the organic photoresists can limit usable process sequences. Furthermore ARC's may intermix with photoresist layers. One solution to avoid intermixing, is to introduce thermosetting binders as additional components of organic ARC's, as described, for example in U.S. Patent No. 5,693,691 to Flaim et al.

10 Dyes may also be incorporated in organic ARC's, as well as, optionally, additional additives such as wetting agents, adhesions promoters, preservatives, and plasticizers, as described in U. S. Patent No. 4,910,122 to Arnold et al.

Silicon oxynitride is another material that has been used as an anti-reflective coating. However, silicon oxynitride works as an ARC by a destructive interference process rather  
15 than by absorption, which means that very tight control of the oxynitride thickness is necessary and that the material may not work well as an ARC over highly variable topography. Furthermore, silicon oxynitride is typically deposited by chemical vapor deposition, while photoresist layers are typically applied using a spin-coater. The additional chemical vapor deposition process can add to processing complexity.

20 Another class of materials that can be used as an anti-reflective layer is spin-on-glass (SOG) compositions containing a dye. Yau et al., U.S. Patent No. 4,587,138, disclose a dye such as basic yellow #11 mixed with a spin-on-glass in an amount approximately 1% by weight. Allman et al. U. S. Patent No. 5,100,503 disclose a cross-linked polyorganosiloxane containing an inorganic dye such as  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_7$ ,  $\text{MoO}_4$ ,  $\text{MnO}_4$ , or  $\text{ScO}_4$ , and an adhesion  
25 promoter. Allman additionally teaches that the spin-on-glass compositions also serve as a planarizing layer. However, the spin-on-glass, dye combinations that have been disclosed to date are not optimal for exposure to the deep ultraviolet, particularly 248 and 193 nm, light sources that are coming into use to produce devices with small feature sizes. Furthermore, not all dyes can be readily incorporated into an arbitrary spin-on-glass composition.

Therefore, an absorbing spin-on-glass anti-reflective coating and lithography material that absorbs strongly and uniformly in the ultraviolet spectral region and a method of producing the spin-on glass anti-reflective coating would be desirable. It would also be desirable for the ARC layer to be impervious to photoresist developers.

## 5 S u m m a r y o f t h e I n v e n t i o n

An anti-reflective coating material for deep ultraviolet photolithography comprises one or more organic absorbing compounds incorporated into a spin-on-glass (SOG) material. The spin-on-glass materials comprise silicon-based compounds, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane,  
10 methylphenylsilsesquioxane, silicate polymers and mixtures thereof. As used herein, the group known as "spin-on-glass materials" also comprises siloxane polymers, hydrogensiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_x$  and hydrogensilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about four. Also included are copolymers of hydrogensilsesquioxane and  
15 alkoxyhydridosiloxane or hydroxyhydridosiloxane. Spin-on-glass materials additionally include organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ , where m is greater than zero and the sum of n and m is greater than about four and R is alkyl or aryl.

20 Absorbing compounds suitable for incorporation into the spin-on-glass materials are strongly absorbing at wavelengths less than 375 nm or less than about 260 nm. In particular, suitable absorbing compounds absorb light around wavelengths such as 248 nm, 193 nm, 157 nm or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. The chromophores of suitable compounds typically have at least one benzene ring, and in  
25 those instances where there are two or more benzene rings, those rings may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, wherein the reactive groups can include hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three alkoxy group or halogen atom substituents. The reactive groups may be directly bonded to

the chromophore or the reactive groups may be attached to the chromophore through a hydrocarbon bridge or an oxygen linkage. The chromophores may also comprise silicon-based compounds or polymers similar to those used to formulate the spin-on glass materials.

Examples of suitable incorporatable organic absorbing compounds include those compounds with one benzene ring, such as phenyltrialkoxysilane (phenyltriethoxysilane, phenyltrimethoxysilane, phenyltripropoxysilane); those compounds with two or more benzene rings that are not fused, such as 2-hydroxy-4-(3-trialkoxysilylpropoxy)-diphenylketone, 3-hydroxy-4-(3-trialkoxysilylpropoxy)-diphenylketone, rosolic acid, 4-phenylazophenol, and 4-alkoxyphenylazobenzene-4-carboxy-alkyl triethoxysilane, primuline; and those with two or more benzene rings that are fused, such as trialkoxysilylpropyl-1,8-naphthalimide, anthraflavic acid, alizarin, quinizarin, 9-anthracene carboxy-alkyl triethoxysilanes (9-anthracene carboxy-methyl triethoxysilane, 9-anthracene carboxy-ethyl triethoxysilane, 9-anthracene carboxy-butyl triethoxysilane, 9-anthracene carboxy-propyl triethoxysilane, 9-anthracene carboxy-pentyl triethoxysilane), 9-anthracene carboxylic acid, 9-anthracene methanol and mixtures thereof.

According to another aspect of the present invention, methods for synthesizing absorbing spin-on-glass compositions are provided. Spin-on-glass materials are conventionally synthesized from silane and silicon-based reactants such as triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane, and diphenyldimethoxysilane. Halosilanes, particularly chlorosilanes, for example, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants.

A method of making an absorbing spin-on-glass composition includes combining one or more alkoxysilanes, or, one or more halosilanes, one or more incorporatable organic absorbing compounds, an acid/water mixture, such as a nitric acid/water mixture, and one or

more solvents to form a reaction mixture; and refluxing the reaction mixture to form the absorbing spin-on-glass composition. The spin-on-glass composition so formed is diluted with one or more solvents to provide coating solutions that produce films of various thicknesses. Alternative methods of making an absorbing spin-on-glass composition, including methods using halosilanes and a phase transfer catalyst, are also provided.

In yet another aspect of the present invention, an absorbing spin on composition is produced comprising a silicon-based compound and an incorporatable organic absorbing compound that strongly absorbs light at wavelengths less than about 375 nm. Further provided are absorbing spin on compositions, wherein at least one of the silicon-based compound or the incorporatable organic absorbing compound comprises at least one alkyl group, alkoxy group, ketone group or azo group.

According to yet another aspect of the invention, the absorbing compounds of the chemical class comprising 9-anthracene carboxy-alkyl trialkoxysilane is provided. A method of synthesizing any one of the 9-anthracene carboxy-alkyl trialkoxysilanes includes combining 9-anthracene carboxylic acid, chloroalkyltrialkoxysilane, triethylamine, and a solvent to form a reaction mixture; refluxing the reaction mixture; cooling the refluxed reaction mixture to form a precipitate and a remaining solution; and filtering the remaining solution to produce liquid 9-anthracene carboxy-alkyl trialkoxysilane.

## B r i e f   D e s c r i p t i o n   o f   t h e   F i g u r e s

Figs. 1a – 1f show chemical formulas of absorbing compounds incorporated into spin-on-glass compositions.

Figs. 2a - 2h illustrate the use of absorbing spin-on-glass compositions as anti-reflective coating layers in a photolithography process.

Detailed Description

An anti-reflective coating material for ultraviolet photolithography includes at least one organic absorbing compound incorporated into a spin-on-glass (SOG) material. The absorbing spin-on-glass compositions are dissolved in appropriate solvents to form coating solutions and applied to various layers of materials in fabricating semiconductor devices. The absorbing spin-on-glass anti-reflective coatings are designed to be readily integrated into existing semiconductor fabrication processes. Some properties that facilitate integration include a) developer resistance, b) thermal stability during standard photoresist processing, and c) selective removal with respect to underlying layers.

Contemplated spin-on-glass materials comprise silicon-based compounds, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, silazane polymers, silicate polymers and mixtures thereof. A contemplated silazane polymer is perhydrosilazane, which has a “transparent” polymer backbone where chromophores can be attached. As used herein, the phrase “spin-on-glass materials” also includes siloxane polymers and blockpolymers, hydrogensiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_x$  and hydrogensilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about four. Also included are copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane. Spin-on-glass materials additionally include organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ , where m is greater than zero and the sum of n and m is greater than about four and R is alkyl or aryl. Some useful organohydridosiloxane polymers have the sum of n and m from about four to about 5000 where R is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>6</sub>-C<sub>12</sub> aryl group. The organohydridosiloxane and organohydridosilsesquioxane polymers are alternatively denoted spin-on-polymers. Some specific examples include alkylhydridosiloxanes, such as methylhydridosiloxanes, ethylhydridosiloxanes, propylhydridosiloxanes, t-butylhydridosiloxanes, phenylhydridosiloxanes; and alkylhydridosilsesquioxanes, such as

methylhydrosilsequioxanes, ethylhydrosilsequioxanes, propylhydrosilsequioxanes, t-butylhydrosilsequioxanes, phenylhydrosilsequioxanes, and combinations thereof.

Many naphthalene- and anthracene-based compounds have significant absorption at 248 nm and below. Benzene-based, equivalently termed here phenyl-based, compounds have significant absorption at wavelengths shorter than 200 nm. While these naphthalene-, anthracene-, and phenyl-based compounds are frequently referred to as dyes, the term absorbing compound is used here because the absorptions of these compounds are not limited to wavelengths in the visible region of the spectrum. However, not all such absorbing compounds can be incorporated into spin-on-glasses for use as ARC materials. Absorbing compounds suitable for use with the present invention absorb light at a wavelength range that is centered around wavelengths such as 248 nm, 193 nm, or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography.

The chromophores of suitable absorbing compounds typically have at least one benzene ring, and where there are two or more benzene rings, the rings may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, wherein the reactive groups include hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three "leaving groups," such as alkoxy groups or halogen atoms. Ethoxy or methoxy groups or chlorine atoms are frequently used as leaving groups. Reactive groups that include these frequently used leaving groups include siliconalkoxy, silcondialkoxy, and silicontrialkoxy compounds, such as siliconethoxy, silcondiethoxy, silcontriethoxy, siliconmethoxy, silcondimethoxy, silicontrimethoxy, chlorosilyl, dichlorosilyl, and trichlorosilyl groups. The reactive groups may be directly bonded to the chromophore, as, for example, in phenyltriethoxysilane, or the reactive groups may be attached to the chromophore through an oxygen linkage or a hydrocarbon bridge, as, for example, in 9-anthracene carboxy-alkyl triethoxysilane. The inclusion of silicontrialkoxy groups on chromophores, for example, has been found to be advantageous, especially for promoting stability of the absorbing SOG films. Other useful absorbing compounds are those that contain an azo group, -N=N-, and an accessible reactive group, particularly those containing an azo group linking benzene rings, especially when absorption around 365 nm is desired for the particular application.



In the absorbing spin-on-glass compositions or materials, the absorbing compounds may be incorporated interstitially in the spin-on-glass matrix. Alternatively, the absorbing compounds can be chemically bonded to the spin-on-glass polymer. In some contemplated embodiments, the incorporatable absorbing compounds form bonds with the spin-on-glass polymer backbone via the accessible reactive groups.

In some contemplated embodiments, absorbing spin on compositions comprise a silicon-based compound and an incorporatable organic absorbing compound that absorbs light over wavelengths less than about 375 nm. In other contemplated embodiments, the absorbing spin-on composition absorbs light over a wavelength range greater than 2 nm. In yet other contemplated embodiments, the absorbing spin-on composition absorbs light over a wavelength range greater than 10 nm.

Further, at least one of the silicon-based compound or the incorporatable organic absorbing compound comprises at least one alkyl group, alkoxy group, ketone group or azo group.

Examples of absorbing compounds suitable for use with the present invention include anthraflavic acid (1), 9-anthracene carboxylic acid (2), 9-anthracene methanol (3), 9-anthracene ethanol (4), 9-anthracene propanol (5), 9-anthracene butanol (6), alizarin (7), quinizarin (8), primuline (9), 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone (10), 2-hydroxy-4-(3-trimethoxysilylpropoxy)-diphenylketone (11), 2-hydroxy-4-(3-tributoxysilylpropoxy)-diphenylketone (12), 2-hydroxy-4-(3-tripropoxysilylpropoxy)-diphenylketone (13), rosolic acid (14), triethoxysilylpropyl-1,8-naphthalimide (15), trimethoxysilylpropyl-1,8-naphthalimide (16), tripropoxysilylpropyl-1,8-naphthalimide (17), 9-anthracene carboxy-methyl triethoxysilane (18), 9-anthracene carboxy-ethyl triethoxysilane (19), 9-anthracene carboxy-butyl triethoxysilane (20), 9-anthracene carboxy-propyl triethoxysilane (21), 9-anthracene carboxy-methyl trimethoxysilane (22), 9-anthracene carboxy-ethyl tributoxysilane (23), 9-anthracene carboxy-methyl tripropoxysilane (24), 9-anthracene carboxy-propyl trimethoxysilane (25), phenyltriethoxysilane (26), phenyltrimethoxysilane (27), phenyltripropoxysilane (28), 4-phenylazophenol, (29), 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (30), 4-

methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (31), 4-ethoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (32), 4-butoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (33), 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (34), 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (35), 4-methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (36), 4-methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (37), and combinations, thereof. Chemical formulas of absorbing compounds 1 - 37 are illustrated in Figs. 1a - 1f. Advantageous results have been obtained, for example, with 9-anthracene carboxy-methyl triethoxysilane (18) with combinations of 9-anthracene methanol (3), 2-hydroxy-4-(3-triethoxysilyloxy)-diphenylketone (10), and rosolic acid (14), and with phenyltriethoxysilane (26). It should be appreciated, however, that this list of specific compounds is not an exhaustive list, and that contemplated and preferred compounds can be selected from the chemical compound classes that comprise these specific compounds.

Most of these absorbing compounds are available commercially, for example, from Aldrich Chemical Company (Milwaukee, WI). 9-anthracene carboxy-alkyl trialkoxysilanes are synthesized using esterification methods, as described immediately below. Examples of phenyl-based absorbing compounds in addition to the above absorbing compounds include alkoxybenzoic acid compounds, such as methoxybenzoic acid; structures with silicon-based reactive groups attached to phenyl rings or to substituted phenyls, such as methylphenyl, chlorophenyl, and chloromethylphenyl. Specific phenyl-based absorbing compounds include phenyltrimethoxysilane, benzyltrichlorosilane, chloromethylphenyltrimethoxysilane, phenyltrifluorosilane, to name only a few examples. Diphenyl silanes including one or two "leaving groups," such as diphenylmethylethoxysilane, diphenyldiethoxysilane, and diphenyldichlorosilane, to again name only a few examples, are also suitable incorporatable absorbing compounds.

A general method of synthesizing 9-anthracene carboxy-alkyl trialkoxysilane compounds comprises using 9-anthracene carboxylic acid and a chloromethyl trialkoxysilane compound as reactants. Specifically, a method of synthesizing 9-anthracene carboxy-methyl triethoxysilane (18) uses 9-anthracene carboxylic acid (2) and chloromethyl triethoxysilane as reactants. The reactants are combined with triethylamine and methylisobutylketone (MIBK),

previously dried over 4 Å molecular sieves, to form a reaction mixture that is heated to reflux and refluxed for from approximately 6 to 10 hours. After reflux, the reaction mixture is cooled overnight leading to a large quantity of solid precipitate. The remaining solution is roto-evaporated, filtered through a silica gel column, and roto-evaporated a second time, to produce 9-anthracene carboxy-methyl triethoxysilane (**18**) as a dark amber oily liquid, which may be purified. This method is significant because it is suitable to use to produce any compound in the class of 9-anthracene carboxy-alkyl trialkoxysilanes, including 9-anthracene carboxy-ethyl triethoxysilane (TESAC), 9-anthracene carboxy-propyl trimethoxysilane, and 9-anthracene carboxy-propyl triethoxysilane (ACTEP).

According to another aspect of the present invention, methods for synthesizing absorbing spin-on-glass compositions are provided. Spin-on-glass materials are typically synthesized from a variety of silane reactants including, for example, triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane (PTEOS), phenyltrimethoxysilane (PTMOS), diphenyldiethoxysilane, and diphenyldimethoxysilane. Halosilanes, including chlorosilanes, such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants. To produce the absorbing spin-on-glass compositions, the absorbing compounds, such as absorbing compounds **1 - 37**, or combinations thereof, are combined with the silane reactants during the synthesis of the SOG materials.

In a first method, a reaction mixture including silane reactants, for example HTEOS, or TEOS and MTEOS, or, TMOS and MTMOS; or, alternatively, tetrachlorosilane and methyltrichlorosilane, one or more absorbing compounds, such as absorbing compounds **1 - 37**; a solvent or combination of solvents; and an acid/water mixture, is formed in a reaction vessel. Appropriate solvents include acetone, 2-propanol, and other simple alcohols, ketones

and esters such as 1-propanol, MIBK, propoxypropanol, and propyl acetate. The acid/water mixture is, for example nitric acid and water. Other protic acids or acid anhydrides, such as acetic acid, formic acid, phosphoric acid, hydrochloric acid or acetic anhydride are alternatively used in the acid mixture. The resulting mixture is refluxed for between  
5 approximately 1 and 24 hours to produce the absorbing SOG polymer solution.

The absorbing SOG can be diluted with appropriate solvents to achieve coating solutions that produce films of various thicknesses. Suitable dilutant solvents include acetone, 2-propanol, ethanol, butanol, methanol, propylacetate, ethyl lactate, and propylene glycol propyl ether, referred to commercially as Propasol-P. Dilutant solvents with high  
10 boiling points such as ethyl lactate and propylene glycol propyl ether have been found beneficial. It is believed high boiling point solvents decrease the probability of formation of bubble film defects. In contrast, lower boiling point solvents may become entrapped below a crosslinked top layer of a film and subsequently produce voids when driven off during a baking process step. Additional solvents useful in the invention include ethylene glycol  
15 dimethyl ether, alternatively termed glyme, anisole, dibutyl ether, dipropyl ether, propylene glycol methyl ether acetate, and pentanol. Optionally, surfactants, such as the product FC430, provided by 3M (Minneapolis, MN), or the product Megaface R08, provided by DIC (Japan), are also added to the coating solution. The coating solution is typically between about 0.5 and 20 % polymer by weight. Prior to use, the coating solution is filtered by standard  
20 filtration techniques.

According to a second method of forming absorbing SOG materials, a reaction mixture including silane reactants, one or more of absorbing compounds, such as absorbing compounds 1 - 37, and a solvent or combination of solvents is formed in a reaction vessel. The reaction mixture is heated to reflux and refluxed for between approximately 1 and 24  
25 hours. The silane reactants and solvents are as described in the first method above. An acid/water mixture, as described above, is added to the reaction mixture while stirring. The resulting mixture is heated to reflux and refluxed for between approximately 1 and 24 hours to produce the absorbing SOG polymer. The absorbing SOG is diluted and filtered as described above to form a coating solution.

A method of forming an absorbing organohydridosiloxane material includes forming a mixture of a dual phase solvent which includes both a non-polar solvent and a polar solvent and a phase transfer catalyst; adding one or more organotrihalosilane, hydridotrihalosilane, and one or more of absorbing compounds, such as absorbing compounds 1 - 37, to provide a dual phase reaction mixture; and reacting the dual phase reaction mixture for between 1 and 24 hours to produce the absorbing organohydridosiloxane polymer. The phase transfer catalyst includes but is not limited to tetrabutylammonium chloride and benzyltrimethylammonium chloride. Exemplary non-polar solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride and mixtures thereof. Useful polar solvents include water, alcohols, and alcohol and water mixtures. The absorbing polymer solution is diluted and filtered as described above to form a coating solution.

The absorbing SOG coating solutions are applied to various layers used in semiconductor processing, depending on the specific fabrication process, typically by conventional spin-on deposition techniques. These techniques include a dispense spin, a thickness spin, and thermal bake steps, to produce an absorbing SOG anti-reflective coating. Typical processes include a thickness spin of between 1000 and 4000 rpm for about 20 seconds and two or three bake steps at temperatures between 80°C and 300°C for about one minute each. The absorbing SOG anti-reflective coatings, according to the present invention exhibit refractive indices between about 1.3 and about 2.0 and extinction coefficients greater than 0.07. As reported below in the Examples Section, extinction coefficients greater than 0.4 have been obtained. In contrast, the extinction coefficient of dielectric materials such as silicon dioxide, silicate, and methylsiloxane, are about zero at wavelengths greater than 190 nm.

A general method of using an absorbing spin-on-glass material according to the present invention as an anti-reflective coating in a photolithographic process is illustrated in Figs. 2a-2h. As shown in Fig. 2a, a dielectric layer 22 is deposited on a silicon substrate 20. Dielectric layer 22 can be composed of a variety of dielectric materials including, for example, a silicon dioxide layer derived from TEOS, a silane based silicon dioxide layer, a thermally grown oxide, or a chemical-vapor-deposition-produced methylhydridosiloxane or

silicon dioxide incorporating other elements or compounds. Dielectric layer 22 is typically an optically transparent medium. An absorbing SOG anti-reflective coating layer 24 is applied above dielectric layer 22 (Fig. 2b) that is covered by a photoresist layer 26, of a conventional positive photoresist, to produce the stack shown in Fig. 2c. The stack of Fig. 2c is exposed to ultraviolet radiation 32 through mask 30, as shown in Fig. 2d. During the exposure, the absorbing SOG ARC layer 24 absorbs UV light 32 transmitted through the photoresist. Because the dielectric layer 22 is transparent in the UV wavelength range, if absorbing SOG ARC layer 24 were not present, the UV light 32 would reflect off the underlying silicon layer 20 degrading a critical dimension, for example critical dimension 27 of the exposed photoresist. In this example, a positive photoresist, which provides direct image transfer, is assumed.

The exposed stack is developed to produce the stack of Fig. 2e. The absorbing SOG ARC layer 24 is resistant to conventional photoresist developer solutions such as a 2.5% solution of tetramethylammoniumhydroxide (TMAH). In contrast, organic ARC layers, which have some of the chemical characteristics of the photoresist materials, are more sensitive to photoresist developers. Furthermore, it is anticipated that absorbing SOG ARC layers are resistant to reducing chemistry, gas-based, photoresist stripping processes, whereas organic ARC's are not resistant. Thus, use of absorbing SOG layers may facilitate photoresist rework, without the need to reapply the ARC layer.

Next, a pattern is etched in the absorbing SOG ARC layer 24 through the opening in photoresist layer 26 to produce the etched stack of Fig. 2f. A fluorocarbon etch, which has a high selectivity to photoresist, is used to etch the absorbing SOG ARC layer 24. The response of the absorbing SOG to a fluorocarbon etch provides an additional advantage of the absorbing SOG over organic ARC layers, which require an oxygen plasma etch. An oxygen plasma etch can degrade the critical dimension of the developed photoresist because the photoresist, being organic based, is also etched by an oxygen plasma. A fluorocarbon plasma consumes less photoresist than an oxygen plasma. At shorter UV wavelengths, depth of focus requirements will limit the thickness of photoresist layer 26 at the exposure step shown in Fig. 2d. For example, it is estimated that at 193 nm, the thickness of photoresist layer should be approximately 300 nm. Thus, as these short wavelengths start to be employed, it

will be important to have an ARC layer that can be etched selectively with respect to the photoresist.

The fluorocarbon etch is continued through the dielectric layer 22 to produce the stack of Fig. 2g. Photoresist layer 26 is partially consumed during the continued etch process.

- 5 Finally, the photoresist layer 26 is stripped using an oxygen plasma or a hydrogen reducing chemistry or wet chemistry and the SOG ARC layer 24 is stripped using either a buffered oxide etch, for example a standard hydrofluoric acid/water mixture, or an aqueous or non-aqueous organoamine or aqueous or non-aqueous fluorine-based chemistry. Advantageously, the SOG ARC layer can be stripped with solutions that show a good selectivity with respect
- 10 to the underlying dielectric layer. Thus, the general photolithographic method shown in Figs. 2a-2h illustrates the process advantages of absorbing SOG materials as anti-reflective coating layers and as sacrificial anti-reflective coating layers.

## Examples

The methods of synthesizing the absorbing SOG materials as well as the synthesis of absorbing compounds, such as 9-anthracene carboxy-alkyl trialkoxysilane and more specifically 9-anthracene carboxy-ethyl triethoxysilane and 9-anthracene carboxy-propyl triethoxysilane, are illustrated in the following examples.

### Example 1

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268. It should be appreciated, however, that higher purity starting materials and absorbing compounds, such as the 9-anthracene carboxy-methyl triethoxysilane in this example, would give higher extinction coefficients. The same spin and bake process parameters and measurement technique was used in all of the following examples.

25



**Synthesis of absorbing SOG containing  
9-anthracene carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 0.1 M nitric  
acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams  
of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-ethyl trimethoxysilane**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl trimethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours.  
To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329  
20 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis,  
MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000  
rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each.  
Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams  
5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
1487.1 Angstroms;  $k = 0.4315$ ;  $n=1.4986$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

15 In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 49 grams TEOS, 55 grams  
MTEOS, 48 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
20 ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
534.45 Angstroms;  $k = 0.45$ ;  $n=1.49$ .

25

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 13 grams TEOS, 110 grams  
5 MTEOS, 13 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
414.17 Angstroms;  $k = 0.3551$ ;  $n=1.5079$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

15  
In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 96 grams TEOS, 15 grams  
MTEOS, 13 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
20 solution, 15 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
25 494.77 Angstroms;  $k = 0.3354$ ;  $n=1.5243$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 56 grams TEOS, 64 grams  
5 MTEOS, 7.63 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
3629.76 Angstroms;  $k = 0.3559$ ;  $n = 1.4508$ . Second thickness = 1377.37 Angstroms;  $k =$   
0.358;  $n = 2.643$ , however,  $n$  values may vary according to the thickness and purity of the  
starting components and reactants.

15

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 86 grams TEOS, 25 grams  
20 MTEOS, 12.1 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
25 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
1455.93 Angstroms;  $k = 0.339$ ;  $n = 1.5895$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 21 grams TEOS, 101 grams  
5 MTEOS, 12 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
345.31 Angstroms;  $k = 0.3264$ ;  $n = 1.4614$ . Second thickness = 1021.18 Angstroms;  $k =$   
0.3215;  $n = 1.5059$ .

15

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 37 grams TEOS, 74 grams  
MTEOS, 36 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
20 and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
25 properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
6000 Angstroms;  $k = 0.3701$ ;  $n = 1.4486$ . Second thickness = 2851.52;  $k = 0.3912$ ;  $n =$   
1.4786.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 64 grams TEOS, 42 grams  
5 MTEOS, 36 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 0.1 M nitric acid  
and 40 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
10 thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer. Thickness is  
5988 Angstroms;  $k = 0.36$ ;  $n = 1.445$ . Second thickness = 2888.27 Angstroms;  $k = 0.3835$ ;  $n =$   
1.4856.

15

**Example 2**

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilyloxy)-diphenylketone, and rosolic acid**

20

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-  
triethoxysilyloxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
25 solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of  
ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. Thickness = 1436 Å,  $n = 1.479$ ,  $k = 0.1255$ .

**Synthesis of absorbing SOG containing 9-anthracene ethanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 25 grams 9-anthracene ethanol, 10 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of  
ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, and rosolic acid**

5           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-  
trimethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
10 solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of  
ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing SOG containing 9-anthracene ethanol,  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, and rosolic acid**

15           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene ethanol, 10 grams 2-hydroxy-4-(3-  
trimethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
20 solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of  
ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.



**Example 3****Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, and rosolic acid**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 71.90 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57  
10 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Example 4**

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
20 triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

25

**Example 5****Synthesis of absorbing SOG containing  
2-hydroxy-4-(3-triethoxysilyloxy)-diphenylketone**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilyloxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
10 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3592 Å, n= 1.563, k = 0.067.

**Synthesis of absorbing SOG containing****· 2-hydroxy-4-(3-trimethoxysilyloxy)-diphenylketone**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilyloxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
20 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Example 6**

25

**Synthesis of absorbing SOG containing 9-anthracene methanol**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

#### **Synthesis of absorbing SOG containing 9-anthracene ethanol**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene ethanol, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

#### **Synthesis of absorbing SOG containing 9-anthracene propanol**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene propanol, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

#### **Example 7**

**Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic Acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3503 Å,  $n = 1.475$ ,  $k = 0.193$ .

### **Example 8**

10

#### **Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic Acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3119 Å,  $n = 1.454$ ,  $k = 0.175$ .

### **Example 9**

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, quinizarin,  
and alizarin**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 2 grams of quinizarin, 2 grams alizarin, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was  
5 refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3554 Å,  $n = 1.489$ ,  $k = 0.193$ .

### **Example 10**

10

#### **Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and alizarin**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51.5  
15 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, 5 grams of rosolic acid, and 2 grams alizarin, 0.5599 grams 0.1 M nitric acid and 71.90 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 56.68 grams of butanol, 87.99 grams 2-propanol, 44.10 grams of acetone, 59.31 grams of ethanol, 9.55 grams deionized water and 3.75 grams of 10% FC 430  
20 (3M, Minneapolis, MN) were added. Thickness= 3109 Å,  $n = 1.454$ ,  $k = 0.193$ .

### **Example 11**

25

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M

nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3010 Å,  $n= 1.377$ ,  $k = 0.163$ .

5

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
10 grams MTEOS, 30 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-propyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
20 grams MTEOS, 30 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

25

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-pentyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 30 grams 9-anthracene carboxy-pentyl triethoxysilane, 0.6 grams 0.1 M nitric  
acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

10

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-methyl trimethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
15 grams MTEOS, 30 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours.  
To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

20

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-ethyl trimethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 30 grams 9-anthracene carboxy-ethyl trimethoxysilane, 0.6 grams 0.1 M  
25 nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours.  
To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-propyl trimethoxysilane**

5            In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 30 grams 9-anthracene carboxy-propyl trimethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours.  
To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN)  
10        were added.

**Example 12**

**Synthesis of absorbing SOG containing 9-anthracene methanol**

15            In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, and 10 grams 9-anthracene methanol are combined. The solution is refluxed  
for 6 hours. A mixture of 0.6 grams 0.1 M nitric acid and 72 grams deionized water are  
added to the flask. The flask is refluxed for 4 hours. To the solution, 57 grams of butanol, 88  
20        grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and  
3.75 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

**Synthesis of absorbing SOG containing 9-anthracene ethanol**

25            In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, and 10 grams 9-anthracene ethanol are combined. The solution is refluxed



for 6 hours. A mixture of 0.6 grams 0.1 M nitric acid and 72 grams deionized water are added to the flask. The flask is refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

**Synthesis of absorbing SOG containing 9-anthracene propanol**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, and 10 grams 9-anthracene propanol are combined. The solution is refluxed  
for 6 hours. A mixture of 0.6 grams 0.1 M nitric acid and 72 grams deionized water are  
added to the flask. The flask is refluxed for 4 hours. To the solution, 57 grams of butanol, 88  
grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and  
3.75 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

10

**Example 13****Synthesis of absorbing SOG containing 9-anthracene  
carboxy-methyl triethoxysilane**

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In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
grams MTMOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To  
the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams  
20 of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
are added.

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-ethyl triethoxysilane**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
grams MTMOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 0.1 M nitric

acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

5

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-methyl trimethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
10 grams MTMOS, 60 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To  
the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams  
of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
are added.

15

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-propyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
20 grams MTMOS, 60 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To  
the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams  
of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
are added.

25

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-methyl tripropoxysilane**

5            In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
grams MTMOS, 60 grams 9-anthracene carboxy-methyl tripropoxysilane, 0.6 grams 0.1 M  
nitric acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To  
the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams  
of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 are added.

**Synthesis of absorbing SOG containing 9-anthracene  
carboxy-ethyl tributoxysilane**

15            In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
grams MTMOS, 60 grams 9-anthracene carboxy-ethyl tributoxysilane, 0.6 grams 0.1 M nitric  
acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To the  
solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are  
20 added.

**Example 14**

**Synthesis of 9-anthracene carboxy-methyl triethoxysilane**

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In a 2 L flask, 90.0g 9-anthracenecarboxylic acid, 86.0 ml  
chloromethyltriethoxysilane, 66 ml triethylamine, and 1.25 L methylisobutylketone (MIBK)  
that had been dried over 4 Å molecular sieves were stirred, heated slowly to reflux and

refluxed for 8.5 hours. The solution was transferred to a 2L Teflon bottle and left overnight. A large quantity of solid precipitate formed. The MIBK solution was decanted and roto-evaporated to about 200 g. An equal weight of hexane was added and mixed. A precipitate formed. A 1.75 inch diameter by 2 inch high column of silica gel slurried with 20% ethylacetate / 80% hexane was prepared. The MIBK/hexane solution was passed through the column under pressure and the column washed with 800 ml of 20% ethylacetate / 80% hexane. The solution was filtered to 0.2  $\mu\text{m}$  and roto-evaporated. When the solvent stopped coming off, the temperature was raised to 35°C for 60 minutes. A dark amber oily liquid product was obtained (85g).

10

#### **Synthesis of 9-anthracene carboxy-ethyl triethoxysilane**

In a 2 L flask, 90.0g 9-anthracenecarboxylic acid, 86.0 ml chloroethyltriethoxysilane, 66 ml triethylamine, and 1.25 L methylisobutylketone (MIBK) that had been dried over 4 Å molecular sieves were stirred, heated slowly to reflux and refluxed for 8.5 hours. The solution was transferred to a 2L Teflon bottle and left overnight. A large quantity of solid precipitate formed. The MIBK solution was decanted and roto-evaporated to about 200 g. An equal weight of hexane was added and mixed. A precipitate formed. A 1.75 inch diameter by 2 inch high column of silica gel slurried with 20% ethylacetate / 80% hexane was prepared. The MIBK/hexane solution was passed through the column under pressure and the column washed with 800 ml of 20% ethylacetate / 80% hexane. The solution was filtered to 0.2  $\mu\text{m}$  and roto-evaporated. When the solvent stopped coming off, the temperature was raised to 35°C for 60 minutes.

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20

#### **Synthesis of 9-anthracene carboxy-propyl triethoxysilane**

In a 2 L flask, 90.0g 9-anthracenecarboxylic acid, 86.0 ml chloropropyltriethoxysilane, 66 ml triethylamine, and 1.25 L methylisobutylketone (MIBK) that had been dried over 4 Å

25

molecular sieves were stirred, heated slowly to reflux and refluxed for 8.5 hours. The solution was transferred to a 2L Teflon bottle and left overnight. A large quantity of solid precipitate formed. The MIBK solution was decanted and roto-evaporated to about 200 g. An equal weight of hexane was added and mixed. A precipitate formed. A 1.75 inch diameter by 2 inch high column of silica gel slurried with 20% ethylacetate / 80% hexane was prepared. The MIBK/hexane solution was passed through the column under pressure and the column washed with 800 ml of 20% ethylacetate / 80% hexane. The solution was filtered to 0.2  $\mu\text{m}$  and roto-evaporated. When the solvent stopped coming off, the temperature was raised to 35°C for 60 minutes.

10

#### **Synthesis of 9-anthracene carboxy-methyl trimethoxysilane**

In a 2 L flask, 90.0g 9-anthracenecarboxylic acid, 86.0 ml chloromethyltrimethoxysilane, 66 ml triethylamine, and 1.25 L methylisobutylketone (MIBK) that had been dried over 4 Å molecular sieves were stirred, heated slowly to reflux and refluxed for 8.5 hours. The solution was transferred to a 2L Teflon bottle and left overnight. A large quantity of solid precipitate formed. The MIBK solution was decanted and roto-evaporated to about 200 g. An equal weight of hexane was added and mixed. A precipitate formed. A 1.75 inch diameter by 2 inch high column of silica gel slurried with 20% ethylacetate / 80% hexane was prepared. The MIBK/hexane solution was passed through the column under pressure and the column washed with 800 ml of 20% ethylacetate / 80% hexane. The solution was filtered to 0.2  $\mu\text{m}$  and roto-evaporated. When the solvent stopped coming off, the temperature was raised to 35°C for 60 minutes.

15  
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**Example 15****Synthesis of absorbing SOG containing  
9-anthracene carboxy-methyl triethoxysilane**

5

In a 1-liter flask 297 grams (4.798 moles), 2-Propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
10 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 43 grams (0.590 moles) of butanol and 1260 grams (8.344 moles) of ethyl lactate were added. Thickness=1156 Å,  $n = 1.502$ ,  $k = 0.446$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

15

In a 1-liter flask 297 grams (4.798 moles), 2-Propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
20 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 43 grams (0.590 moles) of butanol and 1260 grams (8.344 moles) of ethyl lactate were added.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-ethyl triethoxysilane**

25

In a 1-liter flask 297 grams (4.798 moles), 2-Propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
5 the solution, 43 grams (0.590 moles) of butanol and 1260 grams (8.344 moles) of ethyl lactate were added.



**Synthesis of absorbing SOG containing  
9-anthracene carboxy-methyl trimethoxysilane**

5            In a 1-liter flask 297 grams (4.798 moles), 2-Propanol, 148 grams (2.558 moles)  
acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 43 grams (0.590 moles) of butanol and 1260 grams (8.344 moles) of ethyl lactate  
10        were added.

**Example 16**

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-methyl triethoxysilane**

15            In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)  
acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
20        grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44  
grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles)  
deionized water and 3.7 grams of 10% FC 430 were added.

25            **Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water and 3.7 grams of 10% FC 430 were added.

### **Synthesis of absorbing SOG containing**

#### **9-anthracene carboxy-ethyl trimethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water and 3.7 grams of 10% FC 430 were added.

### **Synthesis of absorbing SOG containing**

#### **9-anthracene carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44

grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water and 3.7 grams of 10% FC 430 were added.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-butyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)  
5 acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44  
grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles)  
10 deionized water and 3.7 grams of 10% FC 430 were added.

**Example 17**

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-methyl triethoxysilane**

15 In a 1-liter flask 297 grams (4.798 moles), 2-propanol, 148 grams (2.558 moles)  
acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
20 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 43 grams (0.590 moles) of butanol and 981 grams (8.301 moles) of propasol-p  
were added. Thickness=1407 Å,  $n = 1.334$ ,  $k = 0.551$ .

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles), 2-propanol, 148 grams (2.558 moles)  
5 acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 43 grams (0.590 moles) of butanol and 981 grams (8.301 moles) of propasol-p  
were added.

10

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles), 2-propanol, 148 grams (2.558 moles)  
15 acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To  
the solution, 43 grams (0.590 moles) of butanol and 981 grams (8.301 moles) of propasol-p  
were added.

20

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-methyl trimethoxysilane**

In a 1-liter flask 297 grams (4.798 moles), 2-propanol, 148 grams (2.558 moles)  
25 acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102  
moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To

the solution, 43 grams (0.590 moles) of butanol and 981 grams (8.301 moles) of propasol-p were added.

### **Example 18**

5

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-propyl triethoxysilane**

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a  
10 mechanical stirrer is charged with 5000mL hexanes 720mL ethanol, 65mL water and 120g of  
a 10% by weight tetrabutylammonium chloride hydrate solution in water. The mixture is  
equilibrated for 0.5hr with stirring at 25°C. A mixture of trichlorosilane (377.4g, 2.78Mol),  
methyltrichlorosilane (277.7g, 1.86Mol), and (203.8g, 0.46Mol) 9-anthracene carboxy-methyl  
triethoxysilane is added to the reactor using a peristaltic pump over a period of 70 minutes.  
15 Upon completion of the silane and absorbing compound addition, hexane is pumped through  
the lines for 10 minutes. The reaction is stirred for 2.3 hours, the ethanol/H<sub>2</sub>O layer is  
removed and then the remaining hexane solution filtered through a 3 micron (µm) filter,  
followed by a 1µm filter. To the solution, (3957g, 45.92Mol) hexane is added.

20

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-ethyl trimethoxysilane**

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a  
mechanical stirrer is charged with 5000mL hexanes 720mL ethanol, 65mL water and 120g of  
25 a 10% by weight tetrabutylammonium chloride hydrate solution in water. The mixture is  
equilibrated for 0.5hr with stirring at 25°C. A mixture of trichlorosilane (377.4g, 2.78Mol),  
methyltrichlorosilane (277.7g, 1.86Mol), and (203.8g, 0.46Mol) 9-anthracene carboxy-methyl  
triethoxysilane is added to the reactor using a peristaltic pump over a period of 70 minutes.

Upon completion of the silane and absorbing compound addition, hexane is pumped through the lines for 10 minutes. The reaction is stirred for 2.3 hours, the ethanol/H<sub>2</sub>O layer is removed and then the remaining hexane solution filtered through a 3 micron (µm) filter, followed by a 1µm filter. To the solution, (3957g, 45.92Mol) hexane is added.

5

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl trimethoxysilane**

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a mechanical stirrer is charged with 5000mL hexanes 720mL ethanol, 65mL water and 120g of a 10% by weight tetrabutylammonium chloride hydrate solution in water. The mixture is equilibrated for 0.5hr with stirring at 25°C. A mixture of trichlorosilane (377.4g, 2.78Mol), methyltrichlorosilane (277.7g, 1.86Mol), and (203.8g, 0.46Mol) 9-anthracene carboxy-methyl triethoxysilane is added to the reactor using a peristaltic pump over a period of 70 minutes.

15 Upon completion of the silane and absorbing compound addition, hexane is pumped through the lines for 10 minutes. The reaction is stirred for 2.3 hours, the ethanol/H<sub>2</sub>O layer is removed and then the remaining hexane solution filtered through a 3 micron (µm) filter, followed by a 1µm filter. To the solution, (3957g, 45.92Mol) hexane is added.

20

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-butyl tripropoxysilane**

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a mechanical stirrer is charged with 5000mL hexanes 720mL ethanol, 65mL water and 120g of a 10% by weight tetrabutylammonium chloride hydrate solution in water. The mixture is equilibrated for 0.5hr with stirring at 25°C. A mixture of trichlorosilane (377.4g, 2.78Mol), methyltrichlorosilane (277.7g, 1.86Mol), and (203.8g, 0.46Mol) 9-anthracene carboxy-methyl triethoxysilane is added to the reactor using a peristaltic pump over a period of 70 minutes.

Upon completion of the silane and absorbing compound addition, hexane is pumped through the lines for 10 minutes. The reaction is stirred for 2.3 hours, the ethanol/H<sub>2</sub>O layer is removed and then the remaining hexane solution filtered through a 3 micron (µm) filter, followed by a 1µm filter. To the solution, (3957g, 45.92Mol) hexane is added.

5

### **Example 19**

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

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In a 5 L flask, 508.8 grams (3.10 Mol) of triethoxysilane (HTEOS), 135.8 g (0.31Mol) 9-anthracene carboxy-methyl triethoxysilane, and 508.8 g (8.77 Mol) of acetone are mixed by magnetic stirring and cooled to below 20°C. A mixture of 508.8 g (8.77 Mol) of acetone, 46.69 g (2.59 Mol H<sub>2</sub>O, 0.0009 Mol HNO<sub>3</sub>) of 0.02N nitric acid, and 37.03 g (2.06 Mol) of  
15 deionized water are added slowly through a dropping funnel to the mixture in the 5 L flask over a 45 minute period, maintaining the temperature below 20°C. The solution is refluxed for 8 hours. To the solution, 4631g (30.67Mol) ethyl lactate is added.

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-propyl triethoxysilane**

20

In a 5 L flask, 508.8 grams (3.10 Mol) of triethoxysilane (HTEOS), 135.8 g (0.31Mol) 9-anthracene carboxy-methyl triethoxysilane, and 508.8 g (8.77 Mol) of acetone are mixed by magnetic stirring and cooled to below 20°C. A mixture of 508.8 g (8.77 Mol) of acetone,  
25 46.69 g (2.59 Mol H<sub>2</sub>O, 0.0009 Mol HNO<sub>3</sub>) of 0.02N nitric acid, and 37.03 g (2.06 Mol) of deionized water are added slowly through a dropping funnel to the mixture in the 5 L flask over a 45 minute period, maintaining the temperature below 20°C. The solution is refluxed for 8 hours. To the solution, 4631g (30.67Mol) ethyl lactate is added.



**Synthesis of absorbing SOG containing  
9-anthracene carboxy-ethyl trimethoxysilane**

5            In a 5 L flask, 508.8 grams (3.10 Mol) of triethoxysilane (HTEOS), 135.8 g (0.31Mol)  
9-anthracene carboxy-methyl triethoxysilane, and 508.8 g (8.77 Mol) of acetone are mixed by  
magnetic stirring and cooled to below 20°C. A mixture of 508.8 g (8.77 Mol) of acetone,  
46.69 g (2.59 Mol H<sub>2</sub>O, 0.0009 Mol HNO<sub>3</sub>) of 0.02N nitric acid, and 37.03 g (2.06 Mol) of  
10 deionized water are added slowly through a dropping funnel to the mixture in the 5 L flask  
over a 45 minute period, maintaining the temperature below 20°C. The solution is refluxed  
for 8 hours. To the solution, 4631g (30.67Mol) ethyl lactate is added.

**Synthesis of absorbing SOG containing  
9-anthracene carboxy-propyl tributoxysilane**

15            In a 5 L flask, 508.8 grams (3.10 Mol) of triethoxysilane (HTEOS), 135.8 g (0.31Mol)  
9-anthracene carboxy-methyl triethoxysilane, and 508.8 g (8.77 Mol) of acetone are mixed by  
magnetic stirring and cooled to below 20°C. A mixture of 508.8 g (8.77 Mol) of acetone,  
46.69 g (2.59 Mol H<sub>2</sub>O, 0.0009 Mol HNO<sub>3</sub>) of 0.02N nitric acid, and 37.03 g (2.06 Mol) of  
20 deionized water are added slowly through a dropping funnel to the mixture in the 5 L flask  
over a 45 minute period, maintaining the temperature below 20°C. The solution is refluxed  
for 8 hours. To the solution, 4631g (30.67Mol) ethyl lactate is added.

**Example 20**

25

**Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1727 Å,  $n = 1.957$ ,  $k = 0.384$ .

#### Synthesis of absorbing SOG containing phenyltrimethoxysilane

10

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

#### Synthesis of absorbing SOG containing phenyltripropoxysilane

20

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

25

### Synthesis of absorbing SOG containing phenyltributoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6  
5 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

### 10 Example 21

### Synthesis of absorbing SOG containing phenyltriethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)  
15 acetone, 93 grams (0.448 moles) TEOS, 37 grams (0.209 moles) MTEOS, 100 grams (0.418 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were  
20 added. Thickness=1325 Å,  $n=1.923$ ,  $k=0.364$ .

### Synthesis of absorbing SOG containing phenyltrimethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)  
25 acetone, 93 grams (0.448 moles) TEOS, 37 grams (0.209 moles) MTEOS, 100 grams (0.418 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57

grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

5                    **Synthesis of absorbing SOG containing phenyltripropoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 93 grams (0.448 moles) TEOS, 37 grams (0.209 moles) MTEOS, 100 grams (0.418 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

15                    **Example 22**

**Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 119 grams (0.573 moles) TEOS, 27 grams (0.153 moles) MTEOS 74 grams (0.306 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1286 Å, n= 1.889, k = 0.286.

**Synthesis of absorbing SOG containing phenyltrimethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 119 grams (0.573 moles) TEOS, 27 grams (0.153 moles) MTEOS 74 grams (0.306 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

10

**Synthesis of absorbing SOG containing phenyltripropoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 119 grams (0.573 moles) TEOS, 27 grams (0.153 moles) MTEOS 74 grams (0.306 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

20

**Example 23****Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS 121 grams (0.503 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles)

deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1047 Å, n= 1.993, k = 0.378.

5

#### **Synthesis of absorbing SOG containing phenyltrimethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS 121 grams (0.503 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

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#### **Synthesis of absorbing SOG containing phenyltripropoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS 121 grams (0.503 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

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#### **Synthesis of absorbing SOG containing phenyltributoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS 121 grams (0.503 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

#### **Example 24**

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#### **Synthesis of absorbing SOG containing phenyltriethoxysilane and 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS, 103 grams (0.428 moles) phenyltriethoxysilane, 12 grams (0.0298 moles) 2-hydroxy-4-(3-trieethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

#### **Example 25**

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#### **Synthesis of absorbing SOG containing 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.  $n = 1.499$ ,  $k = 0.162$  at 365 nm.

#### Synthesis of absorbing SOG containing

##### 10                    **4-ethoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

#### 20                    **Synthesis of absorbing SOG containing**

##### **4-methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-



propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

### Synthesis of absorbing SOG containing

#### 5                   4-methoxyphenylazobenzene-4-carboxy-propyl trimethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 10 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

15                   Thus, specific embodiments and applications of compositions and methods to produce spin-on glass materials comprising absorbing compounds have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended 20 claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, com- 25 ponents, or steps that are not expressly referenced.

## C L A I M S

We claim:

1. An absorbing spin-on-glass composition comprising a silicon-based compound and an incorporatable organic absorbing compound that absorbs light at a wavelength less  
5 than 375 nm, wherein at least one of the silicon-based compound or the incorporatable organic absorbing compound comprises an alkyl group, an alkoxy group, a ketone group or an azo group.
2. The composition of claim 1, wherein the range is at wavelengths less than about 260 nm.
- 10 3. The composition of claim 1, wherein the organic absorbing compound comprises at least one benzene ring and a reactive group selected from the group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.
- 15 4. The composition of claim 3, wherein the organic absorbing compound comprises two or more benzene rings.
5. The composition of claim 4, wherein the two or more benzene rings are fused.
6. The composition of claim 3, wherein the organic absorbing compound comprises a reactive group selected from the group comprising a siliconalkoxy, a silicondialkoxy,  
20 and a silicontrialkoxy.
7. The composition of claim 6, wherein the siliconalkoxy, the silicondialkoxy and the silicontrialkoxy comprises siliconethoxy, silicondiethoxy, silicontriethoxy, siliconmethoxy, silicondimethoxy, and silicontrimethoxy groups.
8. The composition of claim 3, wherein the reactive group is directly bonded to a  
25 benzene ring.

9. The composition of claim 3, wherein the reactive group is attached to a benzene ring through a hydrocarbon bridge.
10. The composition of claim 3, wherein the organic absorbing compound comprises an  
5 absorbing compound selected from the group consisting of anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-  
10 methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, and mixtures thereof.
11. The composition of claim 10, wherein 9-anthracene carboxy-alkyl triethoxysilane comprises 9-anthracene carboxy-propyl triethoxysilane.
12. The composition of claim 10, wherein the organic absorbing compound comprises  
15 phenyltriethoxysilane.
13. The composition of claim 1, wherein the silicon-based compound comprises a polymer selected from the group comprising methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, silazane polymers, silicate polymers and mixtures  
20 thereof.
14. The composition of claim 1, wherein the silicon-based compound is a polymer selected from the group comprising hydrogensiloxane, hydrogensilsesquioxane, organohydridosiloxane, and organohydridosilsesquioxane polymers; and copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane.
- 25 15. The composition of claim 14, wherein the polymer is of a general formula selected from the group comprising  $(\text{H}_{0-1.0}\text{SiO}_{1.5-2.0})_x$ , where x is greater than about 8, and  $(\text{H}_{0-1.0}\text{SiO}_{1.5-2.0})_n(\text{R}_{0-1.0}\text{SiO}_{1.5-2.0})_m$ , where m is greater than 0, the sum of n and m is from about 8 to about 5000 and R is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>6</sub>-C<sub>12</sub> aryl group.

16. A coating solution comprising the absorbing spin-on-glass composition of claim 1 and a solvent or a solvent mixture.
17. The coating solution of claim 16, wherein the solution is between about 0.5% and about 20% by weight absorbing spin-on-glass composition.
- 5 18. The coating solution of claim 17, wherein the solvent is selected from the group comprising ethyl lactate and propylene glycol propyl ether.
19. A method of making an absorbing spin-on-glass composition comprising:  
combining at least one silane reactant selected from the group comprising  
alkoxysilanes and halosilanes, at least one incorporatable organic absorbing  
10 compound, an acid/water mixture, and at least one solvent to form a reaction mixture;  
and  
refluxing the reaction mixture to form the absorbing spin-on-glass composition,  
wherein the absorbing spin-on glass composition comprises at least one alkyl group,  
alkoxy group, ketone group or azo group.
- 15 20. The method of claim 19, wherein the at least one organic absorbing compound  
comprises at least one benzene ring and a reactive group comprising hydroxyl groups,  
amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded  
to at least one substituent comprising alkoxy groups and halogen atoms.
21. The method of claim 19, wherein the one or more organic absorbing compound  
20 comprises anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol,  
alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone,  
rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl  
triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, 4-  
ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-  
25 methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, and mixtures thereof.
22. The method of claim 21, wherein the 9-anthracene carboxy-alkyl triethoxysilane  
comprises 9-anthracene carboxy-propyl triethoxysilane.

23. The method of claim 19, wherein the at least one silane reactant comprises triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, 5 diphenyldiethoxysilane, and diphenyldimethoxysilane, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and 10 chlorophenyltrimethoxysilane.
24. The method of claim 23, wherein the at least one silane reactant comprises tetraethoxysilane and methyltriethoxysilane.
25. The method of claim 19, wherein the acid/water mixture is a nitric acid/water mixture.
26. A method of making a coating solution containing an absorbing spin-on-glass polymer 15 comprising:
- combining at least one alkoxysilane or halosilane; at least one incorporatable organic absorbing compound; an acid/water mixture; and at least one solvent to form a reaction mixture; and
- refluxing the reaction mixture to form an absorbing spin-on-glass polymer, wherein 20 the absorbing spin-on glass composition comprises at least one alkyl group, alkoxy group, ketone group or azo group.
27. The method of claim 26, further comprising adding one or more dilutant solvents to the absorbing spin-on-glass composition to produce a coating solution.
28. The method of claim 26, wherein the coating solution is between about 0.5 % and 25 about 20 % absorbing spin-on-glass polymer.
29. A process of making 9-anthracene carboxy-propyl triethoxysilane comprising:

combining 9-anthracene carboxylic acid, chloropropyltriethoxysilane, triethylamine, and a solvent to form a reaction mixture;

refluxing the reaction mixture;

cooling the refluxed reaction mixture to form a precipitate and a remaining solution;

5 and

filtering the remaining solution to produce liquid 9-anthracene carboxy-propyl triethoxysilane.

30. The process of claim 29, wherein filtering the remaining solution comprises:

roto-evaporating the remaining solution;

10 passing the roto-evaporated solution through a silica gel column; and

roto-evaporating the solution passed through the silica gel column.

## AMENDED CLAIMS

[Received by the International Bureau on 03 March 2003 (03.03.03)]

1. An absorbing spin-on-glass composition comprising a silicon-based compound and an incorporatable organic absorbing compound that absorbs light at a wavelength less than 375 nm, wherein at least one of the silicon-based compound or the incorporatable organic absorbing compound comprises at least one  $C_nH_{2n+1}$  group, where n is greater than 2, at least one alkoxy group, at least one ketone group or at least one azo group.
2. The composition of claim 1, wherein the range is at wavelengths less than about 260 nm.
3. The composition of claim 1, wherein the organic absorbing compound comprises at least one benzene ring and a reactive group selected from the group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.
4. The composition of claim 3, wherein the organic absorbing compound comprises two or more benzene rings.
5. The composition of claim 4, wherein the two or more benzene rings are fused.
6. The composition of claim 3, wherein the organic absorbing compound comprises a reactive group selected from the group comprising a siliconalkoxy, a silicondialkoxy, and a silicontrialkoxy.
7. The composition of claim 6, wherein the siliconalkoxy, the silicondialkoxy and the silicontrialkoxy comprises siliconethoxy, silicondiethoxy, silicontriethoxy, siliconmethoxy, silicondimethoxy, and silicontrimethoxy groups.
8. The composition of claim 3, wherein the reactive group is directly bonded to a benzene ring.
9. The composition of claim 3, wherein the reactive group is attached to a benzene ring through a hydrocarbon bridge.

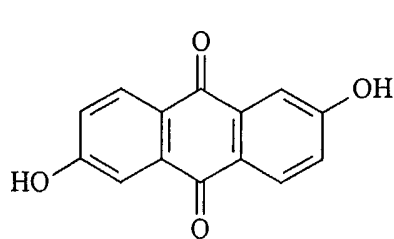
10. The composition of claim 3, wherein the organic absorbing compound comprises an absorbing compound selected from the group consisting of anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, and mixtures thereof.
11. The composition of claim 10, wherein 9-anthracene carboxy-alkyl triethoxysilane comprises 9-anthracene carboxy-propyl triethoxysilane.
12. The composition of claim 10, wherein the organic absorbing compound comprises phenyltriethoxysilane.
13. The composition of claim 1, wherein the silicon-based compound comprises a polymer selected from the group comprising methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, silazane polymers, silicate polymers and mixtures thereof.
14. The composition of claim 1, wherein the silicon-based compound is a polymer selected from the group comprising hydrogensiloxane, hydrogensilsesquioxane, organohydridosiloxane, and organohydridosilsesquioxane polymers; and copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane.
15. The composition of claim 14, wherein the polymer is of a general formula selected from the group comprising  $(\text{H}_{0.1-0.5}\text{SiO}_{1.5-2.0})_x$ , where x is greater than about 8, and  $(\text{H}_{0.1-0.5}\text{SiO}_{1.5-2.0})_n(\text{R}_{0.1-0.5}\text{SiO}_{1.5-2.0})_m$ , where m is greater than 0, the sum of n and m is from about 8 to about 5000 and R is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>6</sub>-C<sub>12</sub> aryl group.
16. A coating solution comprising the absorbing spin-on-glass composition of claim 1 and a solvent or a solvent mixture.
17. The coating solution of claim 16, wherein the solution is between about 0.5% and about 20% by weight absorbing spin-on-glass composition.



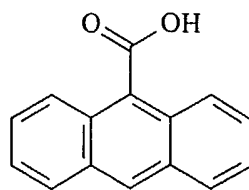
18. The coating solution of claim 17, wherein the solvent is selected from the group comprising ethyl lactate and propylene glycol propyl ether.
19. A method of making an absorbing spin-on-glass composition comprising:  
combining at least one silane reactant selected from the group comprising alkoxy silanes and halosilanes, at least one incorporatable organic absorbing compound, an acid/water mixture, and at least one solvent to form a reaction mixture;  
and  
refluxing the reaction mixture to form the absorbing spin-on-glass composition, wherein the absorbing spin-on glass composition comprises at least one alkyl group, alkoxy group, ketone group or azo group.
20. The method of claim 19, wherein the at least one organic absorbing compound comprises at least one benzene ring and a reactive group comprising hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent comprising alkoxy groups and halogen atoms.
21. The method of claim 19, wherein the one or more organic absorbing compound comprises anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, and mixtures thereof.
22. The method of claim 21, wherein the 9-anthracene carboxy-alkyl triethoxysilane comprises 9-anthracene carboxy-propyl triethoxysilane.
23. The method of claim 19, wherein the at least one silane reactant comprises triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane, and diphenyldimethoxysilane, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane,

chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane.

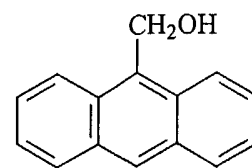
24. The method of claim 23, wherein the at least one silane reactant comprises tetraethoxysilane and methyltriethoxysilane.
25. The method of claim 19, wherein the acid/water mixture is a nitric acid/water mixture.
26. A method of making a coating solution containing an absorbing spin-on-glass polymer comprising:  
combining at least one alkoxy silane or halosilane; at least one incorporatable organic absorbing compound; an acid/water mixture; and at least one solvent to form a reaction mixture; and  
refluxing the reaction mixture to form an absorbing spin-on-glass polymer, wherein the absorbing spin-on glass composition comprises at least one alkyl group, alkoxy group, ketone group or azo group.
27. The method of claim 26, further comprising adding one or more dilutant solvents to the absorbing spin-on-glass composition to produce a coating solution.
28. The method of claim 26, wherein the coating solution is between about 0.5 % and about 20 % absorbing spin-on-glass polymer.
29. A process of making 9-anthracene carboxy-propyl triethoxysilane comprising:  
combining 9-anthracene carboxylic acid, chloropropyltriethoxysilane, triethylamine, and a solvent to form a reaction mixture;  
refluxing the reaction mixture;  
cooling the refluxed reaction mixture to form a precipitate and a remaining solution;  
and  
filtering the remaining solution to produce liquid 9-anthracene carboxy-propyl triethoxysilane.
30. The process of claim 29, wherein filtering the remaining solution comprises:  
roto-evaporating the remaining solution;  
passing the roto-evaporated solution through a silica gel column; and  
roto-evaporating the solution passed through the silica gel column.



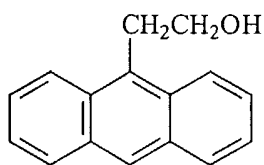
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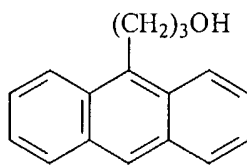
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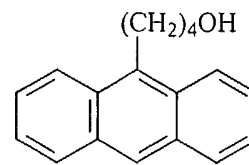
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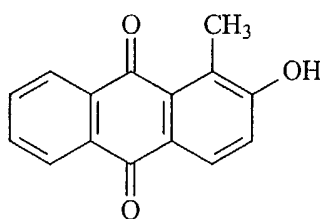
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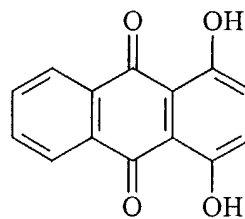
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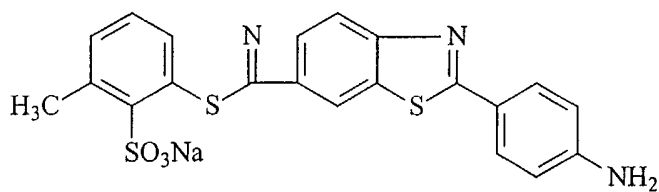
**9-anthracene butanol**  
6



**alizarin**  
7

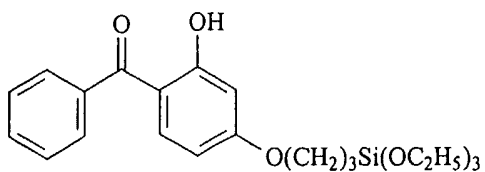


**quinizarin**  
8

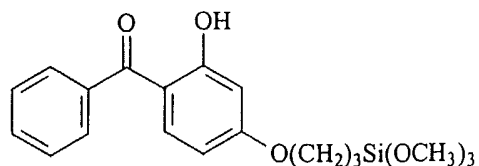


**primuline**  
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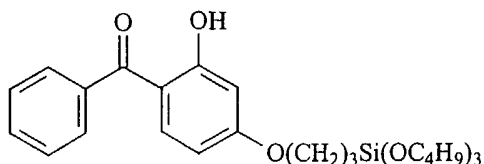
**FIGURE 1A**



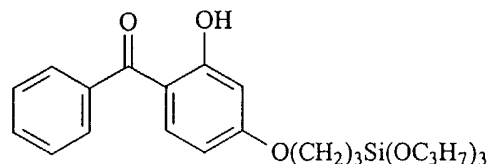
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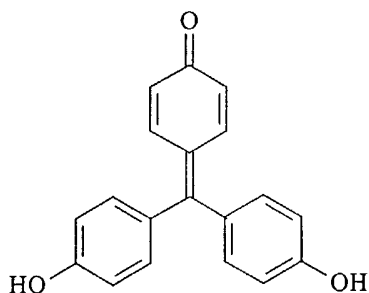
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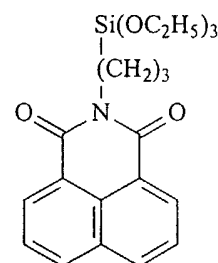
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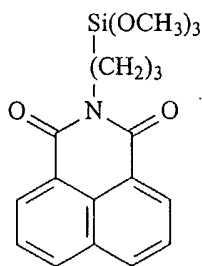
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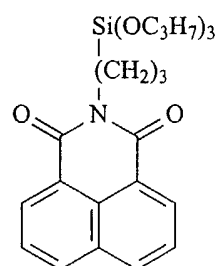
**rosolic acid**  
14



**triethoxysilylpropyl-1,8-naphthalimide**  
15



**trimethoxysilylpropyl-1,8-naphthalimide**  
16



**tripropoxysilylpropyl-1,8-naphthalimide**  
17

**FIGURE 1B**

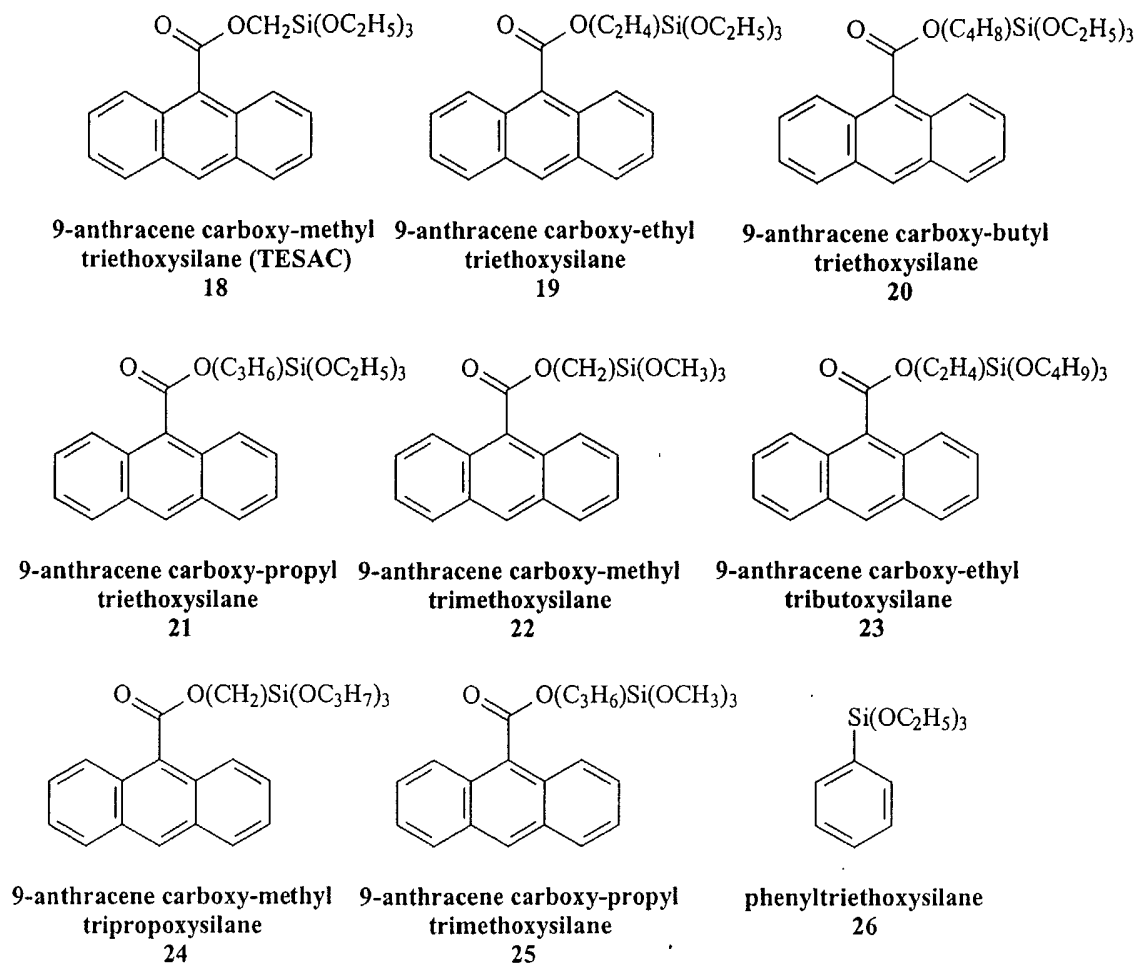


FIGURE 1c

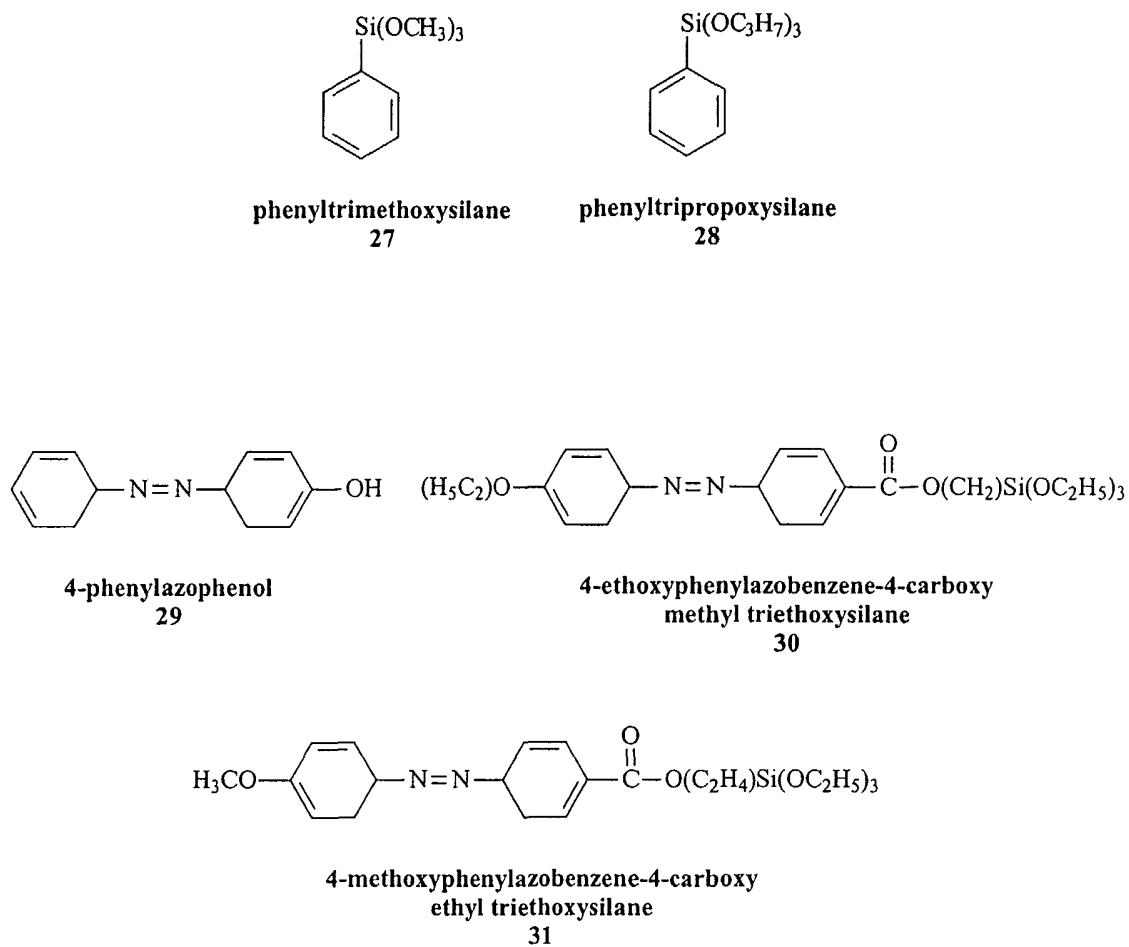
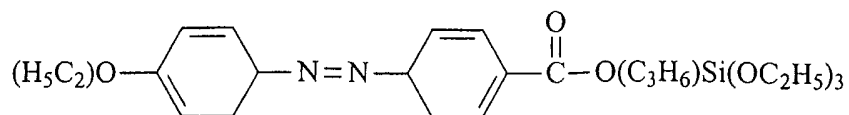
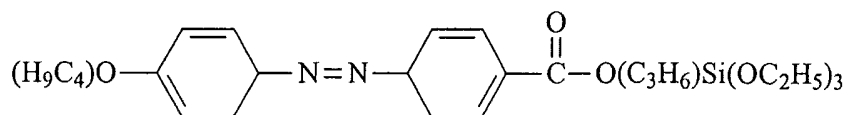


FIGURE 1d



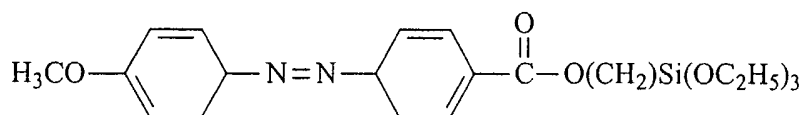
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propyl triethoxysilane**

32



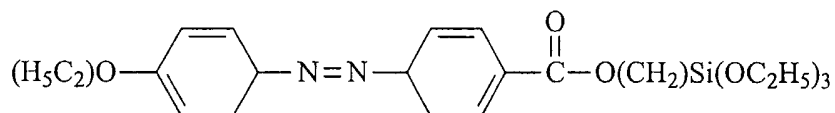
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33



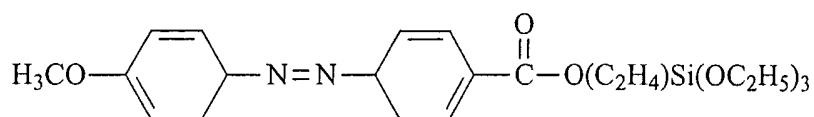
**4-methoxyphenylazobenzene-4-carboxy  
methyl triethoxysilane**

34



**4-ethoxyphenylazobenzene-4-carboxy  
methyl triethoxysilane**

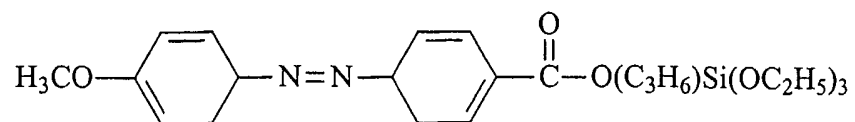
35



**4-methoxyphenylazobenzene-4-carboxy  
ethyl triethoxysilane**

36

**FIGURE 1e**



**4-methoxyphenylazobenzene-4-carboxy  
propyl triethoxysilane**  
37

**FIGURE 1f**



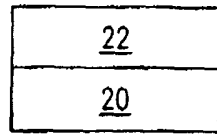


FIG. 2a

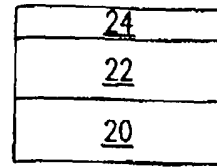


FIG. 2b

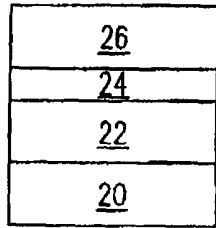


FIG. 2c

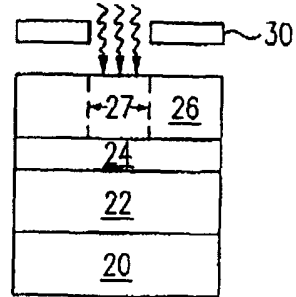


FIG. 2d

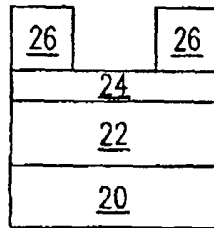


FIG. 2e

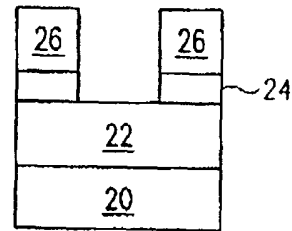


FIG. 2f

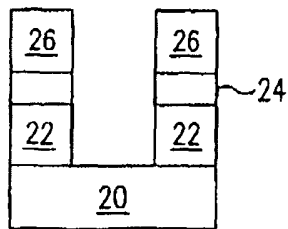


FIG. 2g

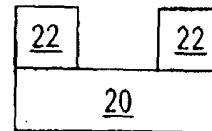


FIG. 2h

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US02/35101

<p><b>A. CLASSIFICATION OF SUBJECT MATTER</b>                  IPC(7) : C08G 77/12, 77/18; C07F 7/18                  US CL : 556/440; 528/39, 31                  According to International Patent Classification (IPC) or to both national classification and IPC</p>														
<p><b>B. FIELDS SEARCHED</b>                  Minimum documentation searched (classification system followed by classification symbols)                  U.S. : 556/440; 528/39, 31</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>														
<p><b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b></p> <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X --- Y</td> <td>US 6,174,631 A (FRENCH et al) 16 June 2001 (16.06.2001), see document starting at the bottom of column 6 through column 11.</td> <td>1- 8,13,16,17,19,20,23,2 4,26-28 ----- 9-12,18,21,22,25</td> </tr> <tr> <td>A,P</td> <td>US 6,365,765 A (BALDWIN et al) 02 April 2002 (04.02.2002), see entire document.</td> <td>29, 30</td> </tr> <tr> <td>X --- Y</td> <td>JP 06-56560 B (SONY CORP.) 01 March 1994 (01.03.1994), see structure 4 on column 4 and structure 1 on column 2.</td> <td>1-4,8, 13, ----- 16-18</td> </tr> </tbody> </table>			Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X --- Y	US 6,174,631 A (FRENCH et al) 16 June 2001 (16.06.2001), see document starting at the bottom of column 6 through column 11.	1- 8,13,16,17,19,20,23,2 4,26-28 ----- 9-12,18,21,22,25	A,P	US 6,365,765 A (BALDWIN et al) 02 April 2002 (04.02.2002), see entire document.	29, 30	X --- Y	JP 06-56560 B (SONY CORP.) 01 March 1994 (01.03.1994), see structure 4 on column 4 and structure 1 on column 2.	1-4,8, 13, ----- 16-18
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A,P	US 6,365,765 A (BALDWIN et al) 02 April 2002 (04.02.2002), see entire document.	29, 30												
X --- Y	JP 06-56560 B (SONY CORP.) 01 March 1994 (01.03.1994), see structure 4 on column 4 and structure 1 on column 2.	1-4,8, 13, ----- 16-18												
<p><input type="checkbox"/> Further documents are listed in the continuation of Box C.      <input type="checkbox"/> See patent family annex.</p>														
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"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</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent published on or after the international filing date	"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	"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)	"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	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed			
"A" document defining the general state of the art which is not considered to be of particular relevance	"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													
"E" earlier application or patent published on or after the international filing date	"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													
"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)	"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													
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family													
"P" document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search 03 January 2003 (03.01.2003)		Date of mailing of the international search report 14 JAN 2003												
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230		Authorized officer Robert Dawson Telephone No. 703-308-0661 <i>Dut</i>												