

SEMICONDUCTOR OPTOELECTRONICS DEVICES

Background of the Invention

5 Field of the Invention

The present invention relates to a process for making semiconductor devices by utilizing novel polymers. In particular, the invention provides novel semiconductors in which at least one layer optical or electrical of CMOS image sensors is made utilizing a polymer or polymer
10 compositions of functionalized silane monomers. Further, the invention concerns integrated circuit and optoelectronic devices and methods of processing novel polymer materials in manufacturing them.

Description of Related Art

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The commercial use of electronic image sensors in electronics has increased dramatically over the last few years. They are found in cameras, cell phones, and are used for new safety features in automobiles e.g. for estimating distances between vehicles, detecting blind spots not exposed by mirrors etc. Many semiconductor manufacturers are converting production
20 lines to CMOS sensor production to meet this demand. CMOS sensor manufacturing uses many of the processes currently used in standard IC manufacturing and does not require a large capital investment to produce state of the art devices.

Processing from the bottom up, a photodiode is built in the silicon layer. Standard dielectrics
25 and metal circuitry are built above the diode to transfer the current. Directly above the diode is an optically transparent material to transfer light from the device surface and through a color filter to the active photo-diode. Transparent protection and planarization material is typically placed over the color filters and device. The micro-lenses are built over the planarized layer above the color filters in order to improve device performance. Finally a passivation layer
30 maybe placed over the lens or alternatively a glass slide is placed over the lens array leaving an air gap between the lens and the cover. Most CMOS sensors are built using subtractive aluminum/ CVD oxide metallization with one or more levels of metal. For the manufacturing

of planarizing layer or micro-lenses are also used organic polymers such as polyimide or novolac materials or maybe sometimes siloxane polymers.

Organic polymers can be divided into two different groups with respect to the behavior of their dielectric constant. Non-polar polymers contain molecules with almost purely covalent bonds. Since they mainly consist of non-polar C–C bonds, the dielectric constant can be estimated using only density and chemical composition. Polar polymers do not have low loss, but rather contain atoms of different electronegativity, which give rise to an asymmetric charge distribution. Thus polar polymers have higher dielectric loss and a dielectric constant, which depends on the frequency and temperature at which they are evaluated. Several organic polymers have been developed for dielectric purposes. However, applicability of these films is limited because of their low thermal stability, softness, and incompatibility with traditional technological processes developed for SiO₂ based dielectrics. For example, organic polymer cannot be chemical mechanical polished or etched back by dry processing without damaging the film.

Therefore some of recent focus has been on SSQ (silsesquioxane or siloxane) or silica based dielectric and optical materials. For SSQ based materials, silsesquioxane (siloxane) is the elementary unit. Silsesquioxanes, or T-resins, are organic-inorganic hybrid polymers with the empirical formula (R-SiO_{3/2})_n. The most common representative of these materials comprise a ladder-type structure, and a cage structure containing eight silicon atoms placed at the vertices of a cube (T₈ cube) on silicon can include hydrogen, alkyl, alkenyl, alkoxy, and aryl. Many silsesquioxanes have reasonably good solubility in common organic solvents due to their organic substitution on Si. The organic substitutes provide low density and low dielectric constant matrix material. The lower dielectric constant of the matrix material is also attributed to a low polarizability of the Si–R bond in comparison with the Si–O bond in SiO₂. The silsesquioxane based materials for microelectronic application are mainly hydrogen-silsesquioxane, HSQ, and methyl-silsesquioxane, (CH₃-SiO_{3/2})_n (MSQ). MSQ materials have a lower dielectric constant as compared to HSQ because of the larger size of the CH₃ group ~2.8 and 3.0–3.2, respectively and lower polarizability of the Si–CH₃ bond as compared to Si–H. However, these films index of refraction at visible range typically around 1.4 to 1.5 and always less than 1.6.

The silica-based materials have the tetrahedral basic structure of SiO_2 . Silica has a molecular structure in which each Si atom is bonded to four oxygen atoms. Each silicon atom is at the center of a regular tetrahedron of oxygen atoms, i.e., it forms bridging crosslinks. All pure of silica have dense structures and high chemical and excellent thermal stability. For example, amorphous silica films, used in microelectronics, have a density of 2.1 to 2.2 g/cm^3 . However, their dielectric constant is also high ranging from 4.0 to 4.2 due to high frequency dispersion of the dielectric constant which is related to the high polarizability of the Si-O bonds. Therefore, it is necessary to replace one or more Si-O-Si bridging groups with C-containing organic groups, such as CH_3 groups, which lowers the k -value. However, these organic units reduce the degrees of bridging crosslinks as well increases the free volume between the molecules due to steric hindrance. Therefore, their mechanic strength (Young's modulus < 6 GPa) and chemical resistance is reduced compared to tetrahedral silicon dioxide. Also, these methyl-based silicate and SSQ (i.e., MSQ) polymers have relatively low cracking threshold, typically on the order of 1 μm or less.

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Summary of the Invention

In one embodiment of the present invention, there is provided a novel high index of refraction siloxane polymer compatible with traditional Integrated Circuit (IC) processing and CMOS image sensor applications.

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In a second embodiment of the present invention, there is provided a method of modifying the monomer so as to form a novel organo-functionalized molecule.

In a third embodiment of the present invention, there is provided methods of producing poly(organo siloxane) compositions, which are suitable for the preparation of thin films having excellent dielectric properties and optical properties.

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In a fourth embodiment of the present invention, there is provided novel thin films, having low dielectric constant, excellent mechanical and thermal properties, said films being formed by the above-mentioned polymer.

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In a fifth embodiment of the present invention, there is provided dielectric layers on silicon and glass wafers.

5 These and other embodiments, together with the advantages thereof over the known dielectric thin films and methods for the preparation thereof, which shall become apparent from specification which follows, are accomplished by the invention as hereinafter described and claimed.

10 In order to achieve these objectives in the present invention, novel polyorgano silsesquioxane materials, which are based on multisilane molecules, and useful as interlayer insulating films for semiconductor or optoelectronic devices, are introduced.

15 Generally, the monomer of the novel materials comprises at least two metal atoms, which are interconnected by a bridging hydrocarbyl radical and which exhibit hydrolysable substituents on both of the metal atoms along with at least one organic group which is capable of reducing the polarizability of the polymer, further cross-linking the polymer, forming nanometer size porosity to the polymer or combination of all previous properties formed from the monomer.

20 In particular, the metal atoms are silicon atoms, and the bridging radical is a linear or branched (bivalent) hydrocarbyl group which links the two silicon atoms together. Furthermore, typically one of the silicon atoms contains three hydrolysable groups and the other silicon atom contains two hydrolysable groups and an organic cross-linking group, reactive cleaving group or polarizability reducing organic group, such as an alkyl, alkenyl, alkynyl, aryl, polycyclic group or organic containing silicon group. The latter group may also be fully or
25 partially fluorinated.

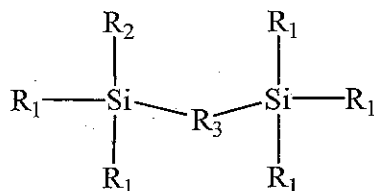
In one aspect of the present invention, there is provided a semiconductor device comprising:

- a semiconductor substrate;

- a plurality of photo-diodes arranged on the semiconductor substrate;
- metal lines and dielectric materials as interconnect layers on the substrate, said interconnect layers defining apertures at the photo-diodes;
- a first polymer which fills the gaps such as to cover the photo-diode;
- 5 - layers of color filters arranged on top the gap filling polymer layer opposite to the photo-diodes;
- a second polymer arranged on the interconnect layers for covering and for planarizing and passivating the color filter layers;
- a plurality of micro-lenses arranged on top of the planarizing polymer opposite to
- 10 the color filters; and
- a third polymer layer arranged on top of the micro-lenses for passivating the micro-lenses;

wherein at least one of the polymer materials is comprised of a siloxane polymer and

wherein at least one of the polymers comprises the general chemical structure (I):



wherein:

- R_1 is a hydrolysable group, such as hydrogen, a halide, an alkoxy or an acyloxy group,
 R_2 is hydrogen, an organic crosslinking group, a reactive cleaving group or a polarizability reducing organic group, and
 R_3 is a bridging linear or branched bivalent hydrocarbyl group,

wherein the first polymer has an at least 1% higher, or more preferably at least 5 % higher, index of refraction than the material defining the aperture.

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In another aspect of the invention, formula I covers two slightly different kinds of precursors, viz. a first initial precursor corresponds to formula I wherein R_2 stand for hydrogen. The second kind of precursor have formula I wherein R_2 stands for an organic cross-linking group, a reactive cleaving group or a polarizability reducing organic group, or combinations thereof.

- 15 These groups are represented by alkyl, alkenyl, alkynyl, aryl, polycyclic groups and organic-containing silicon groups.

Compounds according to the formula wherein R_2 group is hydrogen can be formed by a hydrosilylation reaction wherein a trihalosilane and a dihalosilane are reacted in the presence of cobalt octacarbonyl so as to form a 1,1,1,4,4-pentahalo-1,4-disilabutane intermediate at good yield. This intermediate can be converted by, e.g. hydrosilylation, to replace hydrogen at position R_2 so as to form an organo- functionalized silane. If R_2 group is a reactive group, the group may decompose during the film curing procedure and leave behind a cross-linking group or polarizability reducing group or a combination thereof.

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In another embodiment of the present invention, the polymer is produced by hydrolysing the hydrolysable groups of the multisilane monomer or a combination of the polymer described in the invention or a combination of molecules of the invention and molecules known in the art and then further polymerising it by a condensation polymerisation process.

The new material can be used as an optical dielectric film in an object comprising e.g. a (silicon) wafer.

- 5 In a further embodiment of the present invention, there is provided a method of forming a thin film having a dielectric constant of 4.0 or less or more preferably 3.5 or less and index of refraction more than 1.58 or preferably more than 1.60 at 632.8nm wavelength range, comprising a monomer having the formula I, to form a siloxane material, depositing the siloxane material in the form of a thin layer; and curing the thin layer to form a film.
- 10 Considerable advantages are obtained by the present novel materials and by the methods of manufacturing them. Thus, embodiments of the present invention presents a solution for existing problems related to optical dielectric polymers, more specifically index of refraction, CMP compatibility, mechanical properties (modulus and hardness), cracking threshold and thermal properties, also applicable to IC integration temperatures. The film is also particularly
- 15 applicable to light or radiation (preferably UV wavelength or e-beam) enhanced curing, optionally carried out simultaneously with the thermal curing process.

The novel organo-functionalized molecule can be built into such a form that it is capable of further reacting in the matrix. This means, for example, that the organic function of the

20 molecule can undergo cross-linking, cleaving or combination of both, i.e., subsequent cleaving and cross-linking reactions.

Embodiments of the present invention provide excellent chemical resistance and very low chemical adsorption behavior due to high cross-linking bridging group density.

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If R_2 group is a cleaving group still very small pore size is resulted in, i.e., typically 1.5 nm or less. However, the polymer formed according to innovation is also compatible with traditional type porogens such as cyclodextrin, which can be used to form micro-porosity into the polymer and thus reduce the dielectric constant of the polymer.

Another important advantages can be that the novel optical dielectric materials have excellent properties of planarization resulting in excellent local and global planarity on top a semiconductor substrate topography, which reduces or even fully eliminates the need for chemical mechanical planarization after dielectric and oxide liner deposition.

Furthermore, the novel materials can have excellent gap fill properties.

By incorporating nanoparticles into the materials comprising a disilane structure having optionally functional groups the refractive index which is already high compared with conventional siloxane materials (about 1.65 compared to <1.5) can be even improved and values in the range of up to 1.75 or even higher can be attained which makes the novel materials particularly attractive for CMOS camera applications.

In summary, embodiments of the present invention provides an optical dielectric siloxane polymer applicable to forming thermally and mechanically stable, high index of refraction, dense dielectric films exhibiting high-cracking threshold, low pore volume and pore size. The polymer will give a non-aqueous and silanol free film with excellent local and global planarization as well as gap fill after subjected to thermal treatment with having excellent electrical and optical properties. A film made out of the novel polymer remains structurally, mechanically and electrically unchanged after final cure even if subjected to temperatures higher than the final cure temperature. All these properties, as they are superior over conventional optical dielectric polymers, are crucial to overcome existing problems as well as in order to improve device performance in optical dielectric film integration to a optical semiconductor device.

Next, the invention will be examined more closely by means of the following detailed description and with reference to a number of working examples.

Brief Description of the Drawings

Figure 1 shows a schematic cross-section of CMOS image sensor device;

Figure 2 shows the thermogravimetric diagram of high index of refraction Polymer 3;

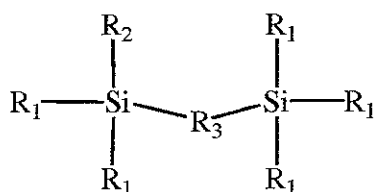
Figure 3 shows a thermogravimetric diagram of high index of refraction Polymer 4; and Figure 4 shows an FTIR spectrogramme of refraction Polymer 5.

Detailed Description of the Invention

5 The present invention provides an optical dielectric polymer comprising at least one multisilane monomer unit with at least one organic bridging group between silicon atoms. In addition, one of the silicon atoms also contains one organic cross-linking group, reactive cleaving group, index of refraction increasing group, UV blocking group, polarizability reducing organic group or a combination of all previous such as an alkyl, alkenyl, alkynyl, 10 aryl, polyaromatic, polycyclic group or organic containing silicon group.

One of the silicon atoms comprises two hydrolysable groups and the other three hydrolysable groups capable of forming a continuous siloxane backbone matrix once hydrolyzed and polymerized, such as hydrogen, halide, alkoxy or acyloxy groups, but most preferably 15 chlorine, methoxide or ethoxide groups or any of their combination.

The general formula I of the precursor used for polymerization in the present invention is the following:



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wherein:

R₁ is a hydrolysable group

R₂ is an organic crosslinking group, reactive cleaving group, polarizability reducing organic group or combination of all previous, such as an alkyl, 25 alkenyl, alkynyl, aryl, polycyclic group or organic containing silicon group, and

R_3 is a bridging linear or branched bivalent hydrocarbyl group.

R_1 is preferably selected from the group of halides, alkoxy groups, acyloxy groups and hydrogen, R_2 is preferably selected from alkyl groups, alkenyl groups, alkynyl and aryl groups, polycyclic group or organic containing silicon group, and R_3 is preferably selected from linear and branched alkylene groups, alkenylene groups and alkynylene groups, and bivalent alicyclic groups (polycyclic groups) and bivalent aromatic groups which all are included in the definition of a bivalent hydrocarbyl group.

- 10 The cured composition obtained by essentially homopolymerizing monomers of the above formula, with subsequent curing to achieve cross-linking, comprises a cross-linked organosiloxane polymer, i.e. poly(organosiloxane). It can be formed into a thin film.

15 “Alkenyl” as used herein includes straight-chained and branched alkenyl groups, such as vinyl and allyl groups. The term “alkynyl” as used herein includes straight-chained and branched alkynyl groups, suitably acetylene. “Aryl” means a mono-, bi-, or more cyclic aromatic carbocyclic group, substituted or non-substituted; examples of aryl are phenyl, naphthyl, or pentafluorophenyl propyl. “Polycyclic” group used herein includes for example adamantyl, dimethyl adamantyl propyl, norbornyl or norbornene. More specifically, the alkyl, alkenyl or 20 alkynyl may be linear or branched.

Alkyl contains preferably 1 to 18, more preferably 1 to 14 and particularly preferred 1 to 12 carbon atoms. The alkyl is preferably branched at the alpha or beta position with one and more, preferably two, C_1 to C_6 alkyl groups, especially preferred halogenated, in particular 25 partially or fully fluorinated or per-fluorinated alkyl, alkenyl or alkynyl groups. Some examples are non-fluorinated, partially fluorinated and per-fluorinated i-propyl, t-butyl, but-2-yl, 2-methylbut-2-yl, and 1,2-dimethylbut-2-yl. In particular, the alkyl group is a lower alkyl containing 1 to 6 carbon atoms, which optionally bears 1 to 3 substituents selected from methyl and halogen. Methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl and t-butyl are 30 particularly preferred.

Alkenyl contains preferably 2 to 18, more preferably 2 to 14 and particularly preferred 2 to 12 carbon atoms. The ethylenic, i.e. two carbon atoms bonded with double bond, group is preferably located at the position 2 or higher, related to the Si or M atom in the molecule.

- 5 Branched alkenyl is preferably branched at the alpha or beta position with one and more, preferably two, C₁ to C₆ alkyl, alkenyl or alkynyl groups, particularly preferred fluorinated or per-fluorinated alkyl, alkenyl or alkynyl groups.

- 10 Alkynyl contains preferably 3 to 18, more preferably 3 to 14 and particularly preferred 3 to 12 carbon atoms. The ethylinic group, i.e. two carbon atoms bonded with triple bond, group is preferably located at the position 2 or higher, related to the Si or M atom in the molecule. Branched alkynyl is preferably branched at the alpha or beta position with one and more, preferably two, C₁ to C₆ alkyl, alkenyl or alkynyl groups, particularly preferred per-fluorinated alkyl, alkenyl or alkynyl groups.

- 15 The bivalent alicyclic groups may be polycyclic aliphatic groups including residues derived from ring structures having 5 to 20 carbon atoms, such as norbornene (norbornenyl) and adamantyl (adamantylene). "Arylene" stands for bivalent aryls comprising 1 to 6 rings, preferably 1 to 6, and in particular 1 to 5, fused rings, such as phenylene, naphthylene and anthracenyl.

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The aryl group is preferably phenyl, which optionally bears 1 to 5 substituents selected from halogen, alkyl or alkenyl on the ring, or naphthyl, which optionally bear 1 to 11 substituents selected from halogen alkyl or alkenyl on the ring structure, the substituents being optionally fluorinated (including per-fluorinated or partially fluorinated)

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The polycyclic group is for example adamantyl, dimethyl adamantyl propyl, norbornyl or norbornene, which optionally bear 1-8 substituents or can be also optionally 'spaced' from the silicon atom by alkyl, alkenyl, alkynyl or aryl groups containing 1-12 carbons.

- 30 "Hydrolysable group" stands for halogen (chlorine, fluorine, bromine), alkoxy (in particular C₁₋₁₀ alkoxy, such as methoxy, ethoxy, propoxy, or butoxy), acyloxy, hydrogen or any other

group that can easily be cleaved off the monomer during polymerization, e.g. condensation polymerization.

5 The alkoxy groups stand generally for a group having the formula R_4O- , wherein R_4 stands for an alkyl as defined above. The alkyl residue of the alkoxy groups can be linear or branched. Typically, the alkoxy groups are comprised of lower alkoxy groups having 1 to 6 carbon atoms, such as methoxy, ethoxy and t-butoxy groups.

10 The acyloxy groups have the general formula R_5O_2- , wherein R_5 stands for an alkyl as defined above. In particular, the alkyl residue of the acyloxy group can have the same meanings as the corresponding residue in the alkoxy group.

15 In the context of the disclosure the organic group substituent halogen may be a F, Cl, Br or I atom and is preferably F or Cl. Generally, term 'halogen' herein means a fluorine, chlorine, bromine or iodine atom.

In the monomer of formula I, the silicon atoms are linked to each other via a linker group. Typically, the linker comprises 1 to 20, preferably about 1 to 10, carbon atoms. Examples of suitable linker groups R_3 include alkylene, alkenylene and alkynylene groups. "Alkylene" groups generally have the formula $-(CH_2)_r-$ in which r is an integer 1 to 10. One or both of the hydrogens of at least one unit $-CH_2-$ can be substituted by any of the substituents mentioned below. The "alkenylene" groups correspond to alkylene residues, which contain at least one double bond in the hydrocarbon backbone. If there are several double bonds, they are preferably conjugated. "Alkynylene" groups, by contrast, contain at least one triple bond in the hydrocarbon backbone corresponding to the alkylene residues.

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The bivalent linker residue can be unsubstituted or substituted. The substituents are preferably selected from the group of fluoro, bromo, C_{1-10} -alkyl, C_{1-10} -alkenyl, C_{6-18} -aryl, acryl, epoxy, carboxyl and carbonyl groups. A particularly interesting alternative is comprised of methylene groups substituted with at least one alkyl group, preferably a lower alkyl group or 1 to 4 carbon atoms. As a result of the substitution, a branched linker chain is obtained. The

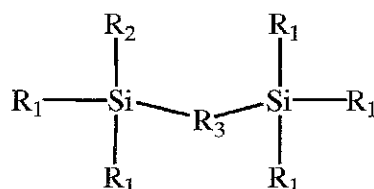
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branched linker chain, e.g. $-\text{CH}(\text{CH}_3)-$ can contain in total as many carbon atoms as the corresponding linear, e.g. $-\text{CH}_2\text{CH}_2-$, even if some of the carbon atoms are located in the side chain, as shown below in connection with the working examples. Such molecules can be considered “isomeric”, for the purpose of the present invention.

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As examples of a particularly preferred compounds according to formula I, 1-(trichlorosilyl)-2-(methyldichlorosilyl) ethane and 1-(methyldichlorosilyl)-1-(trichlorosilyl) ethane can be mentioned.

- 10 As mentioned above, in a first step of the method according to the present invention, a monomer is produced having the formula:



wherein:

- 15 R_1 is a hydrolysable group
 R_2 is hydrogen, and
 R_3 is a bridging linear or branched bivalent hydrocarbyl group.

- 20 This monomer and similar silane-based materials can be produced by hydrosilylation, which is carried out in the presence of cobalt octacarbonyl as a catalyst.

- In particular, the novel hydrosilylation reaction catalyzed in the presence of cobalt octacarbonyl or, generally, any similar transition metal octate catalyst, is using halosilanes as reactants. Thus, in order to produce, at high yield, a compound of the formula above, in which
 25 R_2 stands for hydrogen, a first trihalogenated silane compound can be reacted with a second dihalogenated silane compound in the present of cobalt octacarbonyl. The trihalosilane used

typically has a reactive organic group comprising an unsaturated bond for facilitating the hydrosilylation reaction.

This reaction is illustrated below in Example 1, wherein vinyltrichlorosilane is reacted with
5 dichlorosilane to form 1,1,1,4,4-pentachloro-1,4-disilabutane.

Surprisingly, by the method disclosed, the desired compound is obtained with high purity, which allows for the use of the monomer as a precursor for the following steps of the preparation of siloxane materials by incorporation of desired substituents at the R₂ position.

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The present invention provides an optical dielectric siloxane polymer applicable for forming thermally and mechanically stable, high index of refraction, optically transparent, high cracking threshold, dense and low pore volume and pore size dielectric film. The polymer results in water and silanol free film with excellent local and global planarization as well as
15 gap fill after subjected to thermal treatment with having excellent electrical properties. A film made out of the invented polymer remains structurally, mechanically and electrically unchanged after final cure even if subjected to temperatures higher than the final cure temperature. All these properties, as they are superior over conventional low dielectric constant polymers, are crucial to overcome existing problems in low dielectric constant film
20 integration to a semiconductor device.

The polymerization synthesis is based on hydrolysis and condensation chemistry synthesis technique. Polymerization can be carried out in melt phase or in liquid medium. The temperature is in the range of about 20 to 200 °C, typically about 25 to 160 °C, in particular
25 about 80 to 150 °C. Generally polymerization is carried out at ambient pressure and the maximum temperature is set by the boiling point of any solvent used. Polymerization can be carried out at refluxing conditions. It is possible to polymerize the instant monomers without catalysts or by using alkaline or, in particular, acidic catalysts.

30 The present organosiloxane materials have a (weight average) molecular weight of from 500 to 100,000 g/mol. The molecular weight can be in the lower end of this range (e.g., from 500

to 10,000 g/mol, or more preferably 500 to 8,000 g/mol) or the organosiloxane material can have a molecular weight in the upper end of this range (such as from 10,000 to 100,000 g/mol or more preferably from 15,000 to 50,000 g/mol). It may be desirable to mix a polymer organosiloxane material having a lower molecular weight with a organosiloxane material
5 having a higher molecular weight.

We have found that a suitable polymer composition can be obtained by homopolymerizing a monomer of formula I comprising either a linear or a branched linker group. However, it is also possible to provide a composition that is obtained by copolymerizing first monomers
10 having formula I, wherein R_3 stands for a linear bivalent hydrocarbyl residue, with second monomers having formula I, wherein R_3 stands for a branched bivalent hydrocarbyl residue, the molar ratio of the first monomers to the second monomers is 95:5 to 5:95, in particular 90:10 to 10:90, preferably 80:20 to 20:80. Furthermore, the monomers of formula I can be also co-polymerized with any know hydrolysable siloxane or organo-metallic (e.g. titanium
15 alkoxide, titanium chloride, zirconium alkoxide, zirconium chloride, tantalum alkoxide, tantalum chloride, aluminum alkoxide or aluminum chloride but not limited to these) monomer in any ratio.

According to one preferred embodiment, in order to modify the properties, the siloxane
20 material deposited on a substrate of a semiconductor device is heated to cause further cross-linking, whereby a film is obtained, having a shrinkage after heating of less than 10 %, preferably less than 5 %, in particular less than 2 %, and a thermal stability of more 425 °C.

According to a particular embodiment, the film is baked after spin coating at a temperature
25 below about 200°C and then cured by exposure to UV radiation simultaneously with a thermal treatment at a temperature below 450 °C for 0.1 to 20 minutes. The curing is carried out for a sufficient period of time for reacting the organic substituent at position R_2 of the unit derived from a monomer having the formula I above.

30 The polymer of the present invention is capable of forming low dielectric films having a dielectric constant of 4.0 or less, in particular 3.5 or less, index of refraction 1.58 or more, in

particular 1.60 or more at 632.8nm wavelength range, a Young's modulus of 5.0 GPa or more, a porosity of 5 % or less and cracking threshold of 1 um or more after subjected to thermal treatment. Also the film formed from the polymer using a multisilane component remains stable on a semiconductor structure at temperatures up to 400 °C or more.

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The siloxane matrix can further be modified with nanoparticle doping. These nanoparticles include oxide, semiconductor and metal nanoparticles. It is beneficial to chemically dope siloxane matrices with nanoparticles in order to improve or change siloxane polymers' properties such as optical, electrical and mechanical properties. Nanoparticles can be modified on the surface by coupling chemical groups. These chemical coupling groups are typically so called silane-coupling groups but are not limited to those. Silane coupling elements are for example amino propyl trimethoxysilane, methacryloxy propyl trimethoxysilane or glysidoxy propyl trimethoxysilane and other similar groups having a silane residue which is coupled to functional groups. One advantage of using coupling treated nanoparticles is that it enhances the particles solubility to siloxane matrices and can also enable the particle covalent bonding to the siloxane matrix. The number of coupling elements can also vary at the surface of the nanoparticle. The relative amount of the linkers can be 1 or higher and typically it is preferable to have more than one linker molecule at the surface in order to secure sufficient bonding to the polymer matrix.

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Typically, the polymer or copolymer is combined with 1 to 500 parts by weight, preferably about 5 to 100 parts by weight, in particular about 10 to 50 parts by weight of nanoparticles with 100 parts by weight of the polymer or copolymer to form a nanoparticle containing composition.

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The polymer or copolymer can be combined with the nanoparticles by blending, in particular conventional mechanical blending.

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It is also possible to combine the polymer or copolymer with nanoparticles in such a way that some bonds, preferably chemical bonds, are formed between the polymers or copolymers and the nanoparticles. Thus, it is possible to use polymers or copolymers having reactive groups

capable of reacting with the nanoparticles and forming a bond between the polymer or copolymer and the nanoparticles. It is also possible to use nanoparticles having silane coupling elements or groups, as discussed above. Physical bonding between the components will also enhance the mechanical, optical and electrical properties of the composition.

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One embodiment comprises using chemically bonded nanoparticles and a blend of distinct polymers wherein the blend of distinct polymers comprises an ordered copolymer. The nanoparticles are bonded to at least one polymer component of the blend.

- 10 Nanoparticles suitable for use in the present invention can be manufactured, for example, by a method selected from the group of base or acid solution chemical methods, flame hydrolysis, laser densification and combinations of two or more of these methods. This list is, however, in no way limiting on the scope of the present invention. Any method that will yield particles having the desired particles sizes can be used. The particle size (average particle size) can be
- 15 from 1 nm range up to several micrometers, yet typically in optical and IC applications it is preferable to have a particle size of 20 nm or less, in particular about 0.5 to 18 nm. Also narrow particle size distribution is preferred but not required.

- Typical materials of the nanoparticles to be doped to the organo-siloxane matrix include, but is
- 20 not limited to, the following groups:

Metals: Fe, Ag, Ni, Co, Cu, Pt, Bi, Si and metal alloys.

Metal oxides: TiO_2 , ZnO , Ta_2O_5 , Nb_2O_5 , SnO_2 , ZrO_2 , MgO_2 , Er_2O_3 and SiO_2 .

Carbides: SiC .

- 25 Nitrides: Si_3N_4 , AlN and TiN .

Suitable nanoparticle materials are discussed in US Published Patent Application No. 2005/0170192, the content of which is herewith incorporated by reference.

- 30 Nanoparticles are typically used in the form of dispersions ("dispersion solutions"). Suitable dispersants include, for example, water, organic solvents, such as alcohols and hydrocarbons,

and combinations and mixtures thereof. The selection of preferred solvents generally depends on the properties of the nanoparticles. Thus, the dispersant and the nanoparticles should be selected so as to be compatible with the requirements for the formation of well dispersed particles. For example, gamma alumina particles are generally well dispersed at acidic pH values of about 3 – 4, silica particles generally are readily dispersed at basic pH values from 9 – 11, and titanium oxide particles generally disperse well at a pH near 7, although the preferred pH depends on the crystal structure and the surface structure. Generally, nanoparticles with little surface charge can be dispersed preferentially in less polar solvents. Thus, hydrophobic particles can be dispersed in nonaqueous (water-free) solvents or aqueous solutions with less polar cosolvents, and hydrophilic particles can be dispersed in aqueous solvent.

In these nanoparticle solvent dispersions the particle surfaces can also be treated with silane coupling agents. The hydrolysable part of such coupling groups reacts spontaneously with the surface of the nanoparticle especially in the presence water as a hydrolyzation catalyst.

As mentioned above, the present invention also provides methods of producing integrated circuit devices. Such methods typically comprise the steps of:

- forming a plurality of transistors on a semiconductor substrate;
 - forming multilayer interconnects by:
 - depositing a layer of metal;
 - patterning the metal layer;
 - depositing a first dielectric material having a first modulus and a first k value;
 - depositing a second dielectric material having a second modulus higher than the first modulus of the first material and with a k value lower than the first k value of the first material; and
 - patterning the first and second dielectric materials and depositing a via filling metal material into the patterned areas.
- The material according to the invention used for the first dielectric layer is preferably an organosiloxane material, which has a repeating -M-O-M-O- backbone having a first organic

substituent bound to the backbone, the material having a molecular weight of from 500 to 100,000 g/mol, where M is silicon and O is oxygen. The molecular weight is from 1500 to 30,000 g/mol, and it preferably exhibits one or several of the following properties:

- 5 a k value of 4.0 or less or even more preferably 3.5 or less,
 an index of refraction of 1.58 or more or even more preferably 1.6 or more
 a CTE 30 ppm or less, and
 Young's modulus 4 GPa or more.
- 10 Due to the excellent properties of planarization, the patterning step can be carried out without a preceding step of chemical mechanical planarization. Alternatively, 45 % or less of the total thickness of the second dielectric material is removed by performing chemical mechanical planarization on the second dielectric material.
- 15 The organosiloxane material can be deposited by polymerizing a monomer of formula I in a liquid medium formed by a first solvent to form a hydrolyzed product comprising a siloxane material; depositing the hydrolyzed product on the substrate as a thin layer; and curing the thin layer to form a thin film having a thickness of 0.01 to 10 μm .
- 20 Alternatively, the organosiloxane material can be deposited by polymerizing a monomer of formula I with any know hydrolysable siloxane or organo-metallic (e.g. titanium alkoxide, titanium chloride, zirconium alkoxide, zirconium chloride, tantalum alkoxide, tantalum chloride, aluminum alkoxide or aluminum chloride but not limited to these) monomer in a liquid medium formed by a first solvent to form a hydrolyzed product comprising a siloxane
- 25 material or hybrid siloxane-organo-metallic material; depositing the hydrolyzed product on the substrate as a thin layer; and curing the thin layer to form a thin film having a thickness of 0.01 to 10 μm .

Whereas one of the dielectric materials comprises a material in accordance with the present

30 invention, the other material can be a known, organic, inorganic, or organic/inorganic material, e.g. of the kind discussed above in the introductory portion of the description.

Generally, the organosiloxane material is a spin coated material.

The organosiloxane material is an organic-inorganic and has a coefficient of thermal expansion of 12 to 30 ppm. It can have an index of refraction of 1.6 or less.

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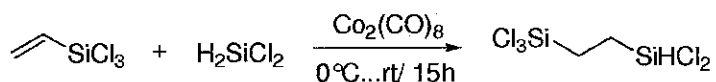
Further details of the invention will be discussed in connection with the following working examples:

EXAMPLES

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Example 1

1,1,1,4,4-Pentachloro-1,4-disilabutane (The Intermediate)



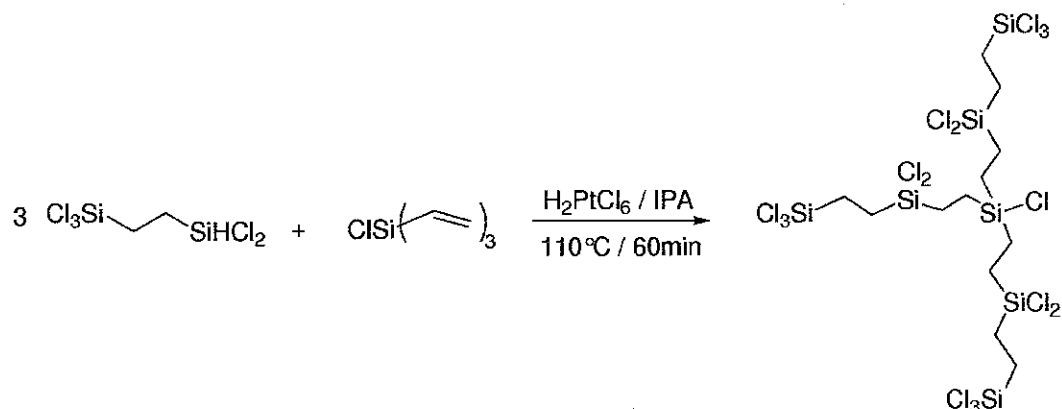
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Vinyltrichlorosilane (68.8 g, 426 mmol) and cobalt octacarbonyl (700 mg) were placed in a 100 mL rb flask and cooled in an ice bath to 0 °C. Dichlorosilane (bp. 8 °C, 44.3 g, 439 mmol) was then condensed into the flask, The system was allowed to warm up to room temperature during night. Distillation at 60...62 °C / 8 mbar gave 1,1,1,4,4-Pentachloro-1,4-disilabutane (120.8 g, 460 mmol) in 93% yield.

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Example 2

Tris(3,3,6,6,6-pentachloro-3,6-disilaheptyl)chlorosilane



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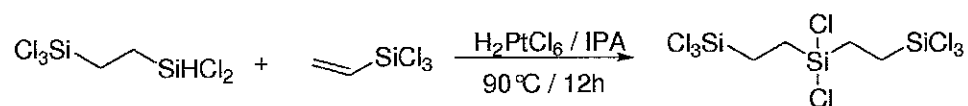
11.00 g (0.076 mol) trivinylchlorosilane was added to a 100 ml vessel followed by 2 ml 1,1,1,4,4-pentachloro-1,4-disilabutane. The solution was heated to 80 °C and 15 µL of a 10 % H₂PtCl₆ / IPA –solution was added. Strong exothermic reaction was observed and heat was switched off. Rest of 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min

10 keeping the temperature of the solution below 130 °C. The total amount of 1,1,1,4,4-pentachloro-1,4-disilabutane was 61.50 g (0.234 mol, 2.6 % excess). After addition heat was again switched on and solution was stirred for an hour at 110 °C. After that solution was distilled yielding 47.08 g (66 %) tris(3,3,6,6,6-pentachloro-3,6-disilaheptyl)chlorosilane. B.p. 264 °C / <0.5 mbar.

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Example 3

1,1,1,4,4,7,7,7-Octachloro-1,4,7-trisilaheptane



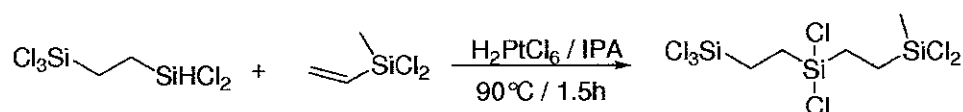
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Vinyltrichlorosilane (16.8 g, 104 mmol) was heated to 60 °C and 100 µL 10 % H₂PtCl₆ / IPA –solution was added. 1,1,1,4,4-pentachloro-1,4-disilabutane (20.4 g, 77.7 mmol) was added slowly during 20 min so that the temperature did not exceed 100 °C. The reaction was allowed

to proceed for 12 hours at 100 °C, after which it was distilled under vacuum at 115-130 °C / <1 mbar. The yield was 31.5 g (74.3 mmol, 96 %).

Example 4

5 1,1,1,4,4,7,7,7-Octachloro-1,4,7-trisilaoctane



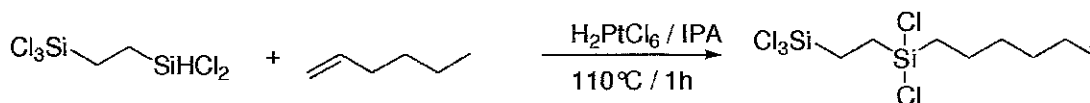
1,1,1,4,4-Pentachloro-1,4-disilabutane (51.6 g, 196 mmol) was heated to 80 °C and 20 µL 10
 10 % H_2PtCl_6 / IPA –solution was added. Vinylmethyldichlorosilane (29.7 g, 210 mmol) was
 added slowly during 20 min so that the temperature did not exceed 130 °C. The reaction was
 allowed to proceed for 1½ hours, after which it was distilled under vacuum at 90-102 °C / <1
 mbar. The yield was 70.2 g (174 mmol, 89 %).

15 Examples 5 to 7

1,1,1,4,4-Pentachloro-1,4-disiladecane

1,1,1,4,4-Pentachloro-1,4-disiladodecane

1,1,1,4,4-Pentachloro-1,4-disilatetrakaidecane



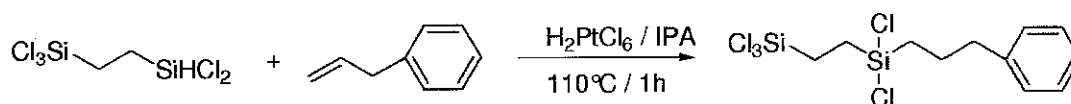
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32 ml (21.53 g, 0.256 mol) 1-hexene and 20 µl H_2PtCl_6 /IPA solution were added to a 100 ml
 vessel. Solution was heated up to 80 °C and 46.90 g (0.179 mol) 1,1,1,4,4-pentachloro-1,4-
 disilabutane was added slowly during 30 min. Heat was switched off when exothermic
 25 reaction was observed. Temperature during the addition was kept below 130 °C. After
 addition heat was again switched on and solution was stirred for an hour at 110 °C. After that
 product was purified by distillation. B.p. 100 °C / 0.8mbar. Yield 50.40 g (81.4 %).

1-hexene can be replaced by 1-octene or 1-decene to produce 1,1,1,4,4-pentachloro-1,4-disiladodecane (b.p.131 °C / 0.7 mbar, 88 % yield) and 1,1,1,4,4-pentachloro-1,4-disilatetradecane (b.p.138 °C / 0.8 mbar, 82 % yield), respectively.

5 Example 8

1,1,1,4,4-Pentachloro-7-phenyl-1,4-disilaheptane



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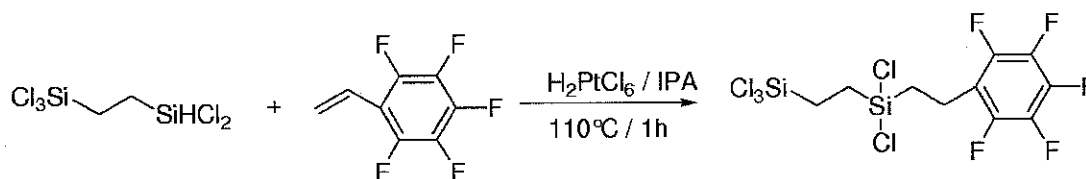
18.77 g (0.159 mol) allylbenzene and 50 µl H₂PtCl₆/IPA solution were added to a 100 ml vessel. Solution was heated up to 80 °C and 41.85 g (0.159 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min. Heat was switched off when exothermic reaction was observed. Temperature during the addition was kept below 130 °C. After addition heat was again switched on and solution was stirred for an hour at 110 °C. After that product was purified by distillation. B.p. 137 °C / 0.8mbar. Yield 35.10 g (58 %).

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Example 9

1,1,1,4,4-Pentachloro-6-pentafluorophenyl-1,4-disilaheptane

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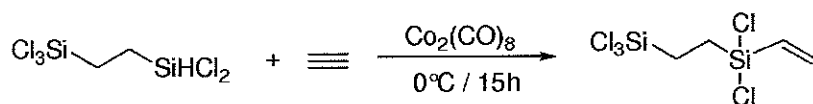


116.15g (0.442 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 250 ml vessel followed by 100 µl H₂PtCl₆ / IPA solution. Solution was heated up to 85 °C and 85.80 g (0.442mol) pentafluorostyrene was added slowly during 30min. After addition solution was stirred for an hour at 100 °C and then distilled. Bp. 122 °C / <1mbar, yield 158.50g (78%).

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Example 10

1,1,1,4,4-Pentachloro-1,4-disila-5-hexene



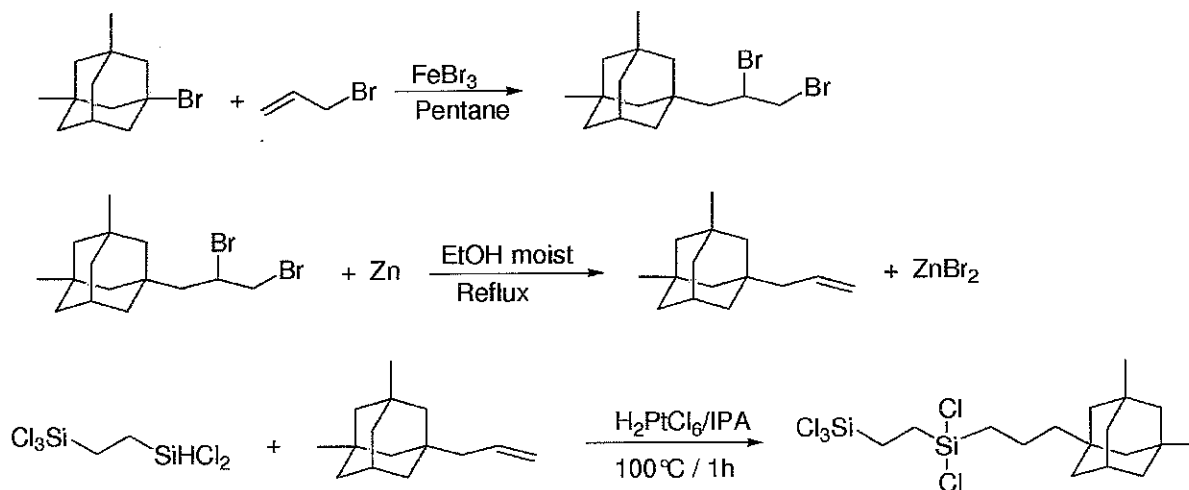
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40.00 g (0.152 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was dissolved in 1000 ml 1,4-dioxane in a 2000 ml vessel. The solution was cooled down to 0 °C and acetylene was bubbled to solution until it was saturated. The solution thus obtained was slowly warmed up to room temperature. 1,4-dioxane was evaporated and obtained crude 1,1,1,4,4-pentachloro-1,4-disila-5-hexene was purified by distillation.

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Example 11

1,1,1,4,4-Pentachloro-7-(3,5-dimethyladamantyl)-1,4-disilaheptane



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81.71 g (0.336 mol) 3,5-dimethyladamantylbromide was dissolved in 500 ml pentane. The solution was cooled to below -10 °C by ice/acetone bath. 51.40 g (0.425mol) allylbromide was added followed by 410 mg FeBr₃. The solution was then stirred for three hours at -20...10 °C after which analysis by GC-MS was carried out, indicating that some unreacted starting materials remained. 420 mg FeBr₃ was added and solution was stirred for an additional two hours after which GC-MS showed that all the dimethyladamantyl bromide had

20

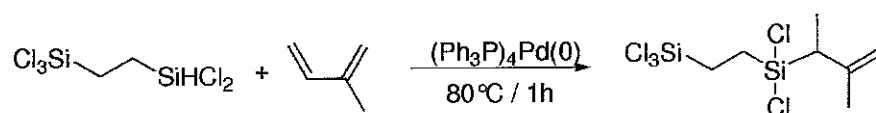
reacted. The solution was warmed up to room temperature and it was washed twice with 500 ml water. The organic layer was collected and pentane was evaporated. Remaining material was dissolved to 700 ml ethanol and a small amount of water was added followed by 25 g (0.382 mol) metallic zinc. The solution was then heated up to reflux and it was stirred for 15 h.

- 5 After cooling down to room temperature the solution was filtered. 300 ml water was added and the product was extracted by washing twice with 500ml pentane. Pentane layers were collected and washed once with water. The organic layer were collected, dried with anhydrous magnesium sulfate and filtered. Pentane was evaporated and remaining crude 1-allyl-3,5-dimethyladamantane was purified by distillation, yield 45.90 g (67 %). 1-allyl-3,5-
- 10 dimethyladamantane was moved to a 100 ml vessel followed by 50 μ l H_2PtCl_6 / IPA solution. The solution was heated up to 85 °C and 59.50 g (0.227 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min. After addition, the solution was heated up to 100 °C and it was stirred for an hour. The product thus obtained was then purified by distillation yielding 53.54 g (51 %), bp. 157-158 °C / <0.5 mbar.

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Example 12

1,1,1,4,4-Pentachloro-5,6-dimethyl-1,4-disila-6-heptene



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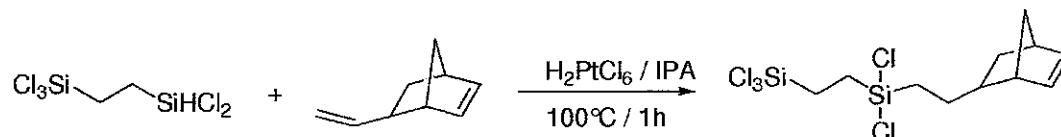
49.85 g (0.190 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 100 ml vessel followed by ~20-30 mg tetrakis(triphenylphosphine)palladium(0). The solution was heated to 80 °C and 13.10 g (0.192 mol) *iso*-prene was added slowly during 30 min. After addition, the solution was stirred for an hour at 100 °C and then distilled. Bp. 96 °C / <1 mbar, yield 58.50 g (93 %).

25

If the same reaction is carried out with a H_2PtCl_6 / IPA catalyst at 80 °C or with a $\text{Co}_2(\text{CO})_8$ catalyst at room temperature a 1:1 mixture of α and β substituted isomers is obtained.

Example 13

1,1,1,4,4-Pentachloro-6-(5-norborn-2-ene)-1,4-disilohexane



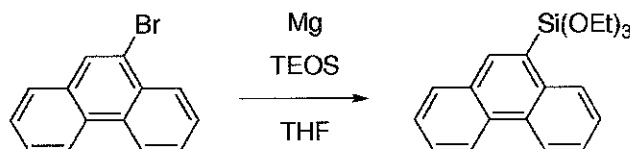
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22.63 g (0.086 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 100 ml vessel followed by 70 μ l of a H_2PtCl_6 / IPA solution. The solution obtained was heated to 85 $^\circ\text{C}$ and 10.81 g (0.090 mol) 5-vinyl-2-norbornene was then slowly added during 30 min. After addition, the solution was stirred for an hour at 100 $^\circ\text{C}$ and then distilled. Bp. 140 $^\circ\text{C}$ / <1 mbar, yield 20.05 g (61 %).

10

Example 14

9-Phenanthrenyl triethoxysilane



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5.33 g (0.0219 mol) magnesium and a small amount of iodine were added to a 1000 ml vessel followed by 56.38 g (0.219 mol) 9-bromophenanthrene. 196 ml (182.74 g, 0.877 mol) $\text{Si}(\text{OEt})_4$ was added to the vessel. 200 ml THF was added after which exothermic reaction occurred. After the solution had cooled down it was heated up to reflux and was stirred for over night.

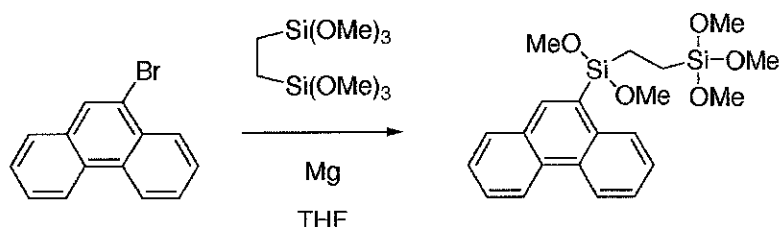
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Refluxing was stopped and 300 ml n-heptane was added. Solution was decanted to an another vessel and remaining solid was washed twice with 200 ml n-heptane. The washing solutions were added to reaction solution. THF and n-heptane were evaporated, and the remaining material was distilled. B.p. 175 $^\circ\text{C}$ / 0.7 mbar. Yield was 52.63 g = 70%.

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Example 15

1-(9-Phenanthrenyl)-1,1,4,4,4-pentamethoxy-1,4-disilabutane



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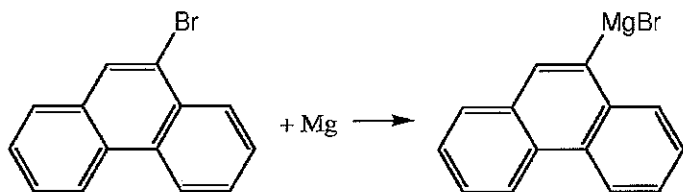
7.23 g (0.297 mol) magnesium and a small amount of iodine were added to a 1000 ml vessel followed by 56.38 g (0.219 mol) 9-bromophenanthrene. Bis(trimethoxysilyl)ethane (237 g, 0.876 mol) was added to the vessel, followed by 200ml THF. In a few minutes, an exothermic reaction occurred. After the solution had cooled down it was heated up to reflux and was stirred for over night.

Refluxing was stopped and 300 ml n-heptane was added. Solution was decanted to an another vessel and remaining solid was washed twice with 200 ml n-heptane. The washing solutions were added to reaction solution. THF and n-heptane were evaporated, and the remaining material was distilled. B.p. 190-205 °C/ <0.1 mbar. Yield was 59.23 g = 65%.

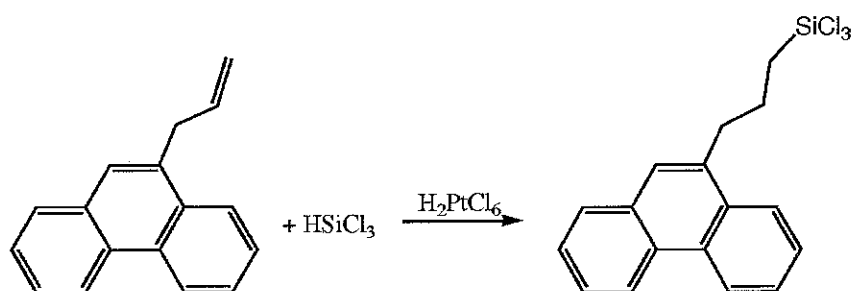
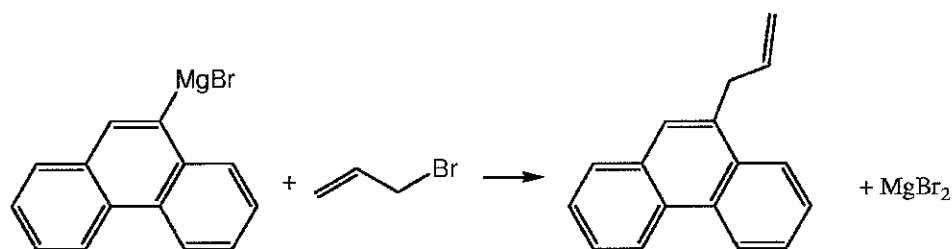
Example 16

3-(9-Phenanthrenyl)propyl trimethoxysilane

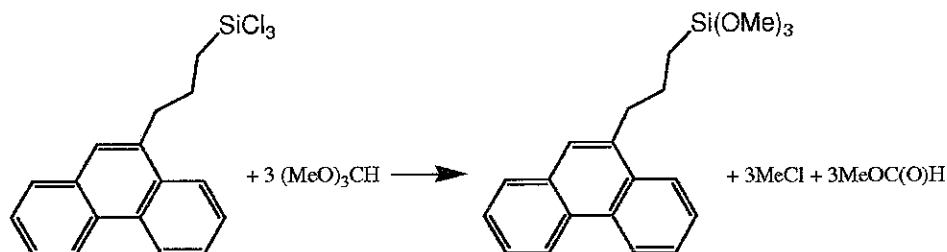
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6.90 g (0.284 mol) magnesium powder and a few crystals of iodine were added to a 1000ml vessel followed by 73.07 g (0.284 mol) 9-bromophenanthrene. 90 ml THF was added after which exothermic reaction occurred. While the solution had cooled down back to room temperature 30 ml THF was added and the solution was heated up to 65 °C and stirred for over night.

Solution was allowed to cool down to 50 °C and 34.42 g (0.285 mol) allylbromide was added dropwise during 30min at a rate that kept solution gently refluxing. After addition solution was stirred for 2 hours at 65 °C. Solution was cooled down to room temperature and most of THF was removed by vacuum. 700 ml DCM was added and solution moved to separation funnel. Solution was washed twice with 700 ml water. Organic layer was collected and dried with anhydrous magnesium sulfate. Solution was filtered followed by evaporation of solvents. Remained material was purified by distillation. B.p. 110-115 °C / <0.5 mbar. Yield 54.5 g (88%).

Allylphenanthrene (41.59 g, 0.191 mol) was added to a 250ml round bottomed flask and heated up to 90 °C. 50 µl 10% H₂PtCl₆ in IPA was added. Addition of HSiCl₃ was started and exothermic reaction was observed. 26.59 g (0.196 mol) HSiCl₃ was added slowly during 40 min. After addition solution was stirred for an hour at 100 °C. Excess HSiCl₃ was removed by vacuum and 100 ml (97 g, 0.914 mol) trimethyl orthoformate was added followed by 50 mg Bu₄PCl as a catalyst. Solution was stirred for 90 hours at 70 °C and product was purified by distillation. B.p. 172 °C / <0.5 mbar. Yield 50 g (74% based on amount of allylphenanthrene).

10 Example 17

High Index of Refraction Polymer 1

9-Phenanthrenyl triethoxysilane (15 g, 44 mmol), acetone (22.5 g) and 0.01M HCl (7.2 g, 400 mmol) were placed in a 100 mL rb flask and refluxed for 23 hours. The volatiles were evaporated under reduced pressure. White solid polymer (11.84 g) was obtained. The polymer was diluted in PGMEA (29.6 g, 250%) and then casted on a silicon wafer. Soft bake 150 °C / 5 min, followed by cure at 400 °C/ 15 min. The index of refraction was 1.6680 at 632.8nm wavelength range and dielectric constant 3.5 at 1MHz. However, polymer did not have excellent chemical resistance against standard organic solvent and alkaline wet etch chemicals.

20

Example 18

High Index of Refraction Polymer 2

9-Phenanthrenyltriethoxysilane (17.00 g, 0.05 mol, prepared by Grignard reaction between 9-bromophenanthrene, magnesium, and tetraethoxysilane in THF) and acetone (15.00 g) were stirred until solids dissolved. Dilute nitric acid (0.01M HNO₃, 6.77 g, 0.38 mol) was then added. Two phases (water and organic) separated. The system was refluxed until the solution became clear (~15 min). Glycidyoxypropyltrimethoxysilane (3.00 g, 0.01) was added and the flask was refluxed for six hours. Volatiles were evaporated in rotary evaporator until 25.00 g polymer solution remained. N-Propyl acetate (32.50 g) was added and evaporation continued again until 27 g remained. Next, propylene glycol monomethyl ether acetate (30 g) was added

30

and again evaporated until 24.84 g was left as viscous polymer. Amount of non-volatiles was measured to be 69.24%. More PGMEA (8.89 g) was added so that solid content was ~50%. The solution was heated in oil bath (165°C) and refluxed for 4 hours 20 minutes. The water that formed during the reaction was removed in rotary evaporator, along with PGMEA until 18 g remained. More PGMEA (42 g) was added to give solution with solid content 22.16%. Polymer had $M_n/M_w = 1,953/2,080$ g/mol, as measured by GPC against monodisperse polystyrene standards in THF.

Sample preparation: The solution above (9.67 g) was formulated with PGMEA (5.33 g), surfactant (BYK-307 from BYK-Chemie, 4mg) and cationic initiator (Rhodorsil 2074, 10 mg). It was spin-coated on a 4" wafer at 2,000 rpm. The film was soft baked at 130°C / 5 mins and cured at 200°C / 5 mins. Film thickness after cure was 310 nm and index of refraction of 1.66 at 632.8nm and dielectric constant 3.4 at 1MHz. The film did not dissolve with acetone, indicating that cross-linking had been successful. Similarly, a more concentrated PGMEA solution (solids 25%) was prepared, spun and cured. The film was 830 nm thick and had modulus 7.01 GPa and hardness 0.41 GPa as measured by nanoindentation.

Example 19

High Index of Refraction Polymer 3

1-(9-Phenanthrenyl)-1,1,4,4,4-pentamethoxy-1,4-disilabutane (9.55 g, 22.9 mmol), 9-Phenanthrenyl triethoxysilane (9.02 g, 26.5 mmol) and SLSI-grade acetone (14.0 g) were placed in a 250 ml rb flask with a teflon coated magnetic stir bar. Distilled water (6.0 g, 333 mmol) was added and system was refluxed for 15 mins. Then, 2 drops of dil.HCl (3.7 w-%) was dripped in. In two minutes the solution became homogenous, indicating the progress of hydrolysis. A solution of 1-(9-Phenanthrenyl)-1,1,4,4,4-pentamethoxy-1,4-disilabutane (11.45 g, 27.5 mmol) in acetone (16.0 g) was poured in, followed by 0.01M HCl solution (8.4 g, 466 mmol). The reaction was allowed to reflux for 14 hours. After the reflux, all volatiles were removed under vacuum, yielding 28.1 g dry polymer as clear colorless solids. It was thermally stable up to 500 °C in argon atmosphere, measured by TGA (Figure 2.).

The solids were diluted in n-butyl acetate (NBA, 73.06 g, 260 %) and surfactant (56 mg, BYK®-307 of Byk-Chemie). Alternatively, solutions in propylene glycol mono methyl ether acetate (PGMEA, 240 %) and methyl ethyl ketone (MEK, 400 %) were also prepared. The solution in NBA was filtered through a 0.2 μ teflon filter, and spin casted on a 4" silicon wafer at 3000 rpm. Soft bake at 150 °C/ 5 mins and 200 °C/ 5 mins, followed by the cure at 400 °C / 15 mins in N₂ ambient gave film with index of refraction 1.6511 at 632.8nm and thickness of 683 nm. The dielectric constant of the film was 3.4 at 1MHz. Films with final thicknesses up to 1850 nm were prepared, and they showed no sign of cracking. The film could be rubbed with organic solvents such as acetone without damaging it.

Example 20

High Index of Refraction Polymer 4

3-(9-Phenanthrenyl)propyl trimethoxysilane (11.0 g, mmol) acetone (16.5 g) and 0.01M HCl were placed in a 100 ml rb flask and refluxed for 16 hours. At the beginning, the solution was milky white, but became clear soon after the hydrolysis started. When the polymerization further progressed, the solution turned again slightly cloudy. The volatiles were removed by evaporation under reduced pressure, giving white colorless powder 9.60 g. The polymer was stable up to 450 °C under argon, measured by TGA (Figure 3.).

The casting solution was prepared by dissolving 2.06 g polymer in 8.24 g methyl ethyl ketone (400%) and a surfactant (5 mg, BYK®-307 of Byk-Chemie), and filtered through 0.2 μ Teflon filter. The polymer was spin casted on a 4" silicon wafer at 3000 rpm. Soft bake at 150 °C/ 5 mins, followed by the cure at 400 °C / 15 mins in N₂ ambient gave a film with index of refraction 1.671 at 632.8nm and thickness of 840 nm. The dielectric constant of the film was 3.4 at 1MHz. The film showed no sign of cracking. The film could be rubbed with organic solvents such as acetone without damaging it.

Example 21

High Index of Refraction Polymer 5

9-Phenanthrenyltriethoxysilane (17.00 g, 0.05 mol, prepared by Grignard reaction between 9-bromophenanthrene, magnesium, and tetraethoxysilane in THF) and acetone (15.00 g) were stirred until solids dissolved. Dilute nitric acid (0.01M HNO₃, 6.77 g, 0.38 mol) was then added. Two phases (water and organic) separated. The system was refluxed until the solution became clear (~15 min). Glycidyloxypropyltrimethoxysilane (3.00 g, 0.01) was added and the flask was refluxed for six hours. Volatiles were evaporated in rotary evaporator until 25.00 g polymer solution remained. N-propyl acetate (32.50 g) was added and evaporation continued again until 27 g remained. Next, propylene glycol monomethyl ether acetate (30 g) was added and again evaporated until 24.84 g was left as viscous polymer. Amount of non-volatiles was measured to be 69.24 %. More PGMEA (8.89 g) was added so that solid content was ~50%. The solution was heated in oil bath (165 °C) and refluxed for 4 hours 20 minutes. The water that formed during the reaction was removed in rotary evaporator, along with PGMEA until 18 g remained. More PGMEA (42 g) was added to give solution with solid content 22.16 %. Polymer had $M_n/M_w = 1,953/2,080$ g/mol, as measured by GPC against monodisperse polystyrene standards in THF.

A 14 % solution in PGMEA was prepared and a curing catalyst (0.3 % Rhodorsil 2074 from Rhodia) and surfactant (0.2 %, BYK307 from BYK-Chemie) were added. The material was spin coated on a silicon wafer and cured at 200 °C/5min. Film could be rinsed with acetone without damage to the film, indicating successful cure. As can be seen from FTIR, the silanol amount of the film was very low (wide peak at 3200...3800 cm⁻¹):

25

If no curing catalyst was used, the film did not cure but was washed away by acetone. Also, silanol peak in FTIR was high.

Example 22

Preparation of blend of Polymer 5 and rutile TiO₂ nanoparticles

Polymer 5 concentrate was formulated with rutile TiO₂ nanoparticles (trade name 'nSol-101-5K' from NanoGram, 5 % in MEK) so that the polymer/particles mass ratio varied from 3/1 to 1/3. Surfactant (BYK-307 from BYK-Chemie, 0.2%) and cationic initiator (Rhodorsil 2074, 0.3 %) was added to each sample. They were spin-coated on a 4" wafer at 2,000 rpm. The films were soft baked at 130 °C / 5 min and cured at 200 °C / 5 min. Film thicknesses and refractive indices are summarized in table 1, along with a reference sample, diluted with PGMEA to ~400 nm film thickness..

Table 1:

Material	blend ratio w/w	Tx after 130C/5min	RI after 130C/5min	Tx after 200C/5min	RI after 200C/5min	S%
Polymer 5 (ref.)	-	424	1.67	409	1.66	3.5
Polymer 5 - TiO ₂	3 - 1	744	1.71	732	1.71	1.6
Polymer 5 - TiO ₂	1 - 1	322	1.76	313	1.77	2.8
Polymer 5 - TiO ₂	1 - 3	177	1.85	170	1.86	4.0

As can be seen in Table 1, RI of the material increased with increasing TiO₂ loading. It can also be seen that shrinkage did not change significantly.

Example 23

Preparation of blend of Polymer 3 and rutile TiO₂ nanoparticles

Polymer 3 solution (17% in MEK) was blended with the same 5 % TiO₂ solution as in Example 22 at a mass ratio of 1 – 2. The solution was evaporated back to a solids content of ~17 %. The solution was spin coated at 2000 rpm, soft baked at 150+200 °C/5+5 min and cured at 300 °C/15min. The results are given in Table 2.

Table 2:

Material	blend ratio w/w	Tx after 150+200C / 5+5min	RI after 150+200C / 5+5min	Tx after 300C/15min	RI after 300C/15min	S%
Polymer 3 (ref.)	-	846	1.66	822	1.65	2.8
Polymer 3 - TiO ₂	1 - 2	549	-	511	1.85	7.0

As will appear, index of refraction of the film increased 0.2 units with 1 – 2 ratio of polymer -
5 rutile TiO₂ nanoparticles.

Example 24

Preparation of blend of Polymer 5 and anatase TiO₂ nanoparticles

- 10 Polymer 5 was blended with anatase TiO₂ nanoparticles (trade name 'ZRM-001', from Sumitomo, 12 % in MEK) with solid ratios 1 – 1 and 1 – 3. The films were baked at 200 °C/5min. The results are indicated in Table 3.

Table 3:

Material	blend ratio w/w	Tx after 130C/5min	RI after 130C/5min	Tx after 200C/5min	RI after 200C/5min	S%
Polymer 5 (ref.)	-	424	1.67	409	1.66	3.5
Polymer 5 - TiO ₂	1 - 1	NM	NM	910	1.73	-
Polymer 5 - TiO ₂	1 - 3	NM	NM	591	1.80	-

15

As can be seen in Table 3, refractive index of the film increased with increasing anatase TiO₂ loading.

- 20 All high index of refraction polymers were also tested for trench gap-fill with trenches 1µm (width) x 4µm (height). All polymers showed excellent gap-fill performance and showed no cracking after 400 °C / 15 min in N₂ ambient.

It was also found out that all high index of refraction polymers 1 – 5 that are compatible with
25 CMP (chemical mechanical polishing). It was found advantageous that cure films first at 150 to 300 °C prior performing CMP with traditional oxide CMP slurry and then applying

additional higher temperature cure at 180 to 450 °C. When first cured at lower temperature the film gets only partially cured, i.e., some residual silanols remains in the film. Due to silanols the polymer films is still slightly hydrophilic, which preferable when performing oxide CMP process. All polymers were also compatible with etch back process by using oxygen plasma.

- 5 The polymer film etched very uniformly about 100 nm per minute when applying oxygen plasma and the plasma process did not cause any index of reaction shift, surface roughness increase or defect formation. It is worth notifying that conventional high index of refraction organic polymers cannot be CMP and etch back processed without damaging the film surface quality or changing the film optical properties.

10

There are also three important technical issues for new generations of CMOS image sensors (Figure 1) that can be reached with above-mentioned chemistries: size of the device; speed and power consumption; quantum efficiency.

- 15 Explanation of Figure 1: 10 semiconductor substrate; 20 photo-diode; 30 metal lines, interlayer dielectrics and intermetal dielectrics; 40 colour filter array layer; 50 micro-lens array; 100 high aspect ratio photo-diode gap filled with high index of refraction siloxane polymer; 200 high index of refraction siloxane polymer for color filter planarization and passivation and; 300 micro-lens passivation siloxane polymer.

20

Size of the device: the smaller the pixel the greater the number of pixels on same area, i.e., improved field factor. This is can be achieved by reducing lens size, diode size, thinner metallization and applying multiple levels of metal.

- 25 Speed: shortening the metal lines, improving the conductor Cu versus Al and lowering the k value of the dielectric will improve speed and reduce power consumption.

Quantum efficiency: this is an opportunity to improve the device efficiency by using new materials that bring light into the lens and transmit light down to the diodes.

30

Materials deposited before the color filter array and be cured at relatively high temperatures to lock in their mechanical properties and being compatible with other materials used in chip construction. Materials deposited after the color filters are deposited must be fully cured at lower temperatures ca 250 °C or below. Materials of this invention are highly suitable for applications above and below the color filter array.

Maximizing quantum efficiency: Light incident on the lens is focused and passes through the color filter and is transmitted down to the diode in the device layer. The objective is to maximize the amount of light reaching the diode. For example the material immediately above the diode needs to be transparent and transmit the maximum amount of light. The interface of the sidewalls of material 100 at Figure 1 is a source of light loss due to refraction and reduces the light reflected down into the diode. A simple solution is to line the sidewall with a reflective coating but that would add expense and would be very difficult. Also CVD metal deposition will make the channel narrower (reducing light transmission) and eventually pinch off at the top for narrow features. However if material 100 has a higher index of refraction than the material used to make the wall next to it then refraction will be minimized and more light will be guided down to the diode. Thus the metallization is surrounded by CVD SiO₂ which forms the sidewall for the light channel. CVD oxide has an index of refraction approx of 1.46 at 632.8nm wavelength range and so the light channel needs to have refractive index > 1.46 to reduce refraction at the interface. Thus basically this is a vertical waveguide transmitting light to the diode. Thus a polymer from Example 19 based material with high index of refraction would function well for this application. This is a transparent film and thus would be mechanically compatible with the neighboring CVD SiO₂. The index of refraction of polymer from Example 19 is 1.65 and thus would increase the reflectivity of the light from the oxide sidewalls with refractive index of 1.46. While this material can be cured at low temperatures of 250 °C, it can also be cured at higher temperatures above 400 °C to be compatible with processes required with Al, Cu and SiO₂. Furthermore as devices are made smaller and metallization shortened to improve speed, the aspect ratio for the channel increases.

- Passivation of the Color Filters and the Lenses:* The material (200 in figure 1) above the color filter array is another opportunity for an inexpensive enhancement for device performance. A polymer from Example 18 is transparent to visible light yet effectively blocks UV thus light protecting both the color filter and the diode as well as signal noise. Also the polymer from
- 5 Example 18 is an excellent planarizing material and an effective passivation layer. The polymer also matches the index of refractions between color filter layer and micro-lens layer, thus reduces reflection from the film interfaces. Also this material can be cured at low temperatures ~ 200 °C and therefore does not cause thermal degradation to organic color filter materials.

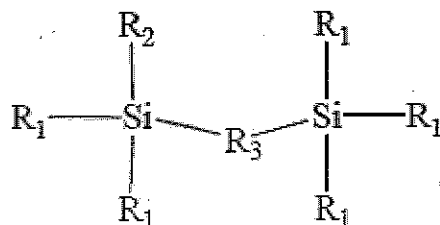
Claims:

1. A semiconductor device comprising:

- a semiconductor substrate;
- a plurality of photo-diodes arranged on the semiconductor substrate;
- metal lines and dielectric materials as interconnect layers on the substrate, said interconnect layers defining apertures at the photo-diodes;
- a first polymer which fills the gaps such as to cover the photo-diode;
- layers of color filters arranged on top the gap filling polymer layer opposite to the photo-diodes;
- a second polymer arranged on the interconnect layers for covering and for planarizing and passivating the color filter layers;
- a plurality of micro-lenses arranged on top of the planarizing polymer opposite to the color filters; and
- a third polymer layer arranged on top of the micro-lenses for passivating the micro-lenses;

wherein at least one of the polymer materials is comprised of a siloxane polymer and

wherein at least one of the polymers comprises the general chemical structure:



wherein:

R₁ is a hydrolysable group

R₂ is an organic crosslinking group, reactive cleaving group, polarizability reducing organic group or combination of all previous, such as an alkyl, alkenyl, alkynyl, aryl, polycyclic group or organic containing silicon group, and

R_3 is a bridging linear or branched bivalent hydrocarbyl group, aromatic group, polyaromatic group or polycyclic group,

wherein the first polymer has an at least 1% higher, or more preferably at least 5 % higher, index of refraction than the material defining the aperture.

2. The semiconductor device according to claim 1, wherein each of the three polymer materials are organo-siloxane polymers.

3. The semiconductor device according to claim 1 or 2, wherein at least one of the polymers, preferably all three of the polymers, comprise siloxane polymers which exhibit -Si-O-Si- and -Si-(CH_x)_y-Si- groups, wherein x is an integer 1 or 2 and y is an integer 1 to 20.

4. The semiconductor device according to any of the preceding claims, wherein the polymers have an index of refraction of more than 1.58 at 632.8 nm or higher.

5. The semiconductor device according to any of claims 1 to 3, wherein the polymers have an index of refraction of more than 1.65 at 632.8 nm or higher.

6. The semiconductor device according to any of claims 1 to 3, wherein the polymers have an index of refraction of more than 1.60 at 632.8 nm or higher and a dielectric constant (1MHz) of 4.0 or lower.

7. The semiconductor device according to any of claims 1 to 3, wherein the polymers have an index of refraction of more than 1.60 at 632.8 nm or higher and a dielectric constant (1MHz) of 3.5 or lower.

8. The semiconductor device according to any of claims 1 to 3, wherein the polymers have an index of refraction of more than 1.60 at 632.8 nm or higher and a Young's modulus higher than 4.0 GPa.

9. The semiconductor device according to any of the preceding claims, wherein the polymers are thermally cured at a temperature between 180 and 450 °C.

10. The semiconductor device according to claim 9, wherein the polymers are cured with a combination of thermal heat and UV radiation.
11. The semiconductor device according to claim 9 or 10, wherein the polymers are first cured with thermal heat and then further processed with chemical mechanical polishing.
12. The semiconductor device according to claims 9 to 11, wherein the polymers are first cured with thermal heat and then further etched with a dry etch plasma process.
13. The semiconductor device according to any of claims 9 to 12, wherein the polymers are treated in a UV radiation step.
14. The semiconductor device according to any of claims 1 to 13, wherein the polymers are first cured with thermal heat and then further processed with chemical mechanical polishing and are then subjected to a final thermal or UV curing.
15. The semiconductor device of any of claims 1 to 14, wherein at least one of the polymers has an index of refraction difference of less than 0.1, or more preferably less than 0.05, with color filter layers or with micro-lens layer at visible wavelength range.
16. The semiconductor device according to any of the preceding claims, wherein the polymeric material has been modified by incorporation of nanoparticles.
17. The semiconductor device according to claim 16, wherein 100 parts by weight of the polymer is combined with 1 to 500 parts by weight, preferably about 5 to 100 parts by weight, in particular about 10 to 50 parts by weight of nanoparticles to form a nanoparticle containing composition.

18. The semiconductor device according to claim 16 or 17, wherein the nanoparticles are selected from the group of metals, metal alloys, metal oxides, carbides and nitrides and mixtures thereof.