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(54) **ORGANO FUNCTIONALIZED SILANE MONOMERS AND SILOXANE POLYMERS OF THE SAME**

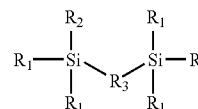
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(57) **ABSTRACT**

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A thin film comprising a composition obtained by polymerizing a monomer having the formula I:

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wherein:

R₁ is a hydrolysable group,

R₂ is an organic crosslinking group, a reactive cleaving group or a polarizability reducing organic group, and

R₃ is a bridging linear or branched bivalent hydrocarbyl group to form a siloxane material. The organo-functionalized molecule is capable of further reacting in the matrix so as to undergo cross-linking, cleaving or combination of both. The present invention provides excellent chemical resistance and very low chemical adsorption behavior due to high cross-linking bridging group density.

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**ORGANO FUNCTIONALIZED SILANE
MONOMERS AND SILOXANE POLYMERS OF
THE SAME**

[0001] This application claims priority of U.S. Provisional Application for Patent Ser. No. 60/689,541 filed Jun. 13, 2005, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a method making novel organo functionalized silane precursors and polymers of the same that are applicable for thin films used for example as dielectrics in integrated circuits, optoelectronic applications and for other similar applications. In particular, the invention concerns first making an intermediate monomer and then converting the monomer to an organo functionalized silane monomer and finally forming a polymer or polymer compositions of the functionalized monomers. The invention also concerns a method for producing such films by preparing siloxane compositions by polymerization of the organo functionalized monomers, by applying the polymerized compositions on a substrate in the form of a layer and by curing the layer to form a film. Further, the invention concerns integrated circuit and optoelectronic devices and methods of manufacturing them.

[0004] 2. Description of Related Art

[0005] Built on semiconductor substrates, integrated circuits comprise millions of transistors and other devices, which communicate electrically with one another and with outside packaging materials through multiple levels of vertical and horizontal wiring embedded in a dielectric material. Within the metallization structure, "vias" make up the vertical wiring, whereas "interconnects" form the horizontal wiring. Fabricating the metallization can involve the successive depositing and patterning of multiple layers of dielectric and metal to achieve electrical connection among transistors and to outside packaging material. The patterning for a given layer is often performed by a multi-step process comprising layer deposition, photoresist spin, photoresist exposure, photoresist develop, layer etch, and photoresist removal on a substrate. Alternatively, the metal may sometimes be patterned by first etching patterns into a layer of a dielectric material, filling the pattern with metal, then subsequently chemically/mechanically polishing the metal so that the metal remains embedded only in the openings of the dielectric. As an interconnect material, aluminum has been utilized for many years due to its high conductivity, good adhesion to SiO₂, known processing methods (sputtering and etching) and low cost. Aluminum alloys have also been developed over the years to improve the melting point, diffusion, electromigration and other qualities as compared to pure aluminum. Spanning successive layers of aluminum, tungsten has traditionally served as the conductive via plug material.

[0006] In IC's, silicon dioxide, having a dielectric constant of around 4.0, has been the dielectric of choice, used in conjunction with aluminum-based and tungsten-based interconnects and via for many years.

[0007] The drive to faster microprocessors and more powerful electronic devices in recent years has resulted in very high circuit densities and faster operating speeds which—in

turn—have required that higher conductivity metals and significantly lower-k dielectrics compared to silicon dioxide (preferably below 3.0) be used. In the past few years, VLSI (and ULSI) processes have been moving to copper damascene processes, where copper (or a copper alloy) is used for the higher conductance in the conductor lines and a spin-on or CVD process is used for producing low-k dielectrics which can be employed for the insulating material surrounding the conductor lines. To circumvent problems with etching, copper along with a barrier metal is blanket deposited over recessed dielectric structures consisting of interconnect and via openings and subsequently polished in a processing method known as the "dual damascene." The bottom of the via opening is usually the top of an interconnect from the previous metal layer or, in some instances, the contacting layer to the substrate.

[0008] Summarizing: aside from possessing a low dielectric constant, the ideal dielectric should have the following properties:

[0009] 1. High modulus and hardness in order to bind the maze of metal interconnects and vias together in particular in the final chip packaging step as well as abet chemical mechanical polishing processing steps.

[0010] 2. Low thermal expansion, typically less than or equal to that of metal interconnects.

[0011] 3. Excellent thermal stability, generally in excess of 350° C., but more often even better than 500° C. after final curing.

[0012] 4. No cracking even as thick films structures, excellent fill and planarization properties.

[0013] 5. Excellent adhesion to dielectric, semiconductor, diffusion barrier and metal materials.

[0014] 6. Sufficient thermal conductivity to dissipate joule heating from interconnects and vias.

[0015] 7. Material density that precludes absorption of solvents, moisture, or reactive gasses.

[0016] 8. Allows desired etch profiles at very small dimensions.

[0017] 9. Low current leakage, high breakdown voltages, and low loss-tangents.

[0018] 10. Stable interfaces between the dielectric and contacting materials.

[0019] By necessity, low-k materials are usually engineered on the basis of compromises.

[0020] 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.

[0021] Therefore most of the current developments are focusing on SSQ (silsesquioxane or siloxane) or silica based dielectric 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.

[0022] The silica-based materials have the tetrahedral basic structure of SiO₂. 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/cm³. 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 CH₃ 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.

[0023] Quite recently there have been some efforts to develop enhanced MSQ polymers by co-polymerizing them with disilanes, i.e., bistrimethoxysilane, that contain bridging alkyl groups between silanes and thus crosslinking density has been increased. However, these materials still contain significant amount of methyl-based silanes, i.e. methyl-trimethoxysilane, as comonomers and due to methyl co-polymer nature only moderate Young's modulus and hardness properties has been obtained, with dielectric constant of around 2.93.

SUMMARY OF THE INVENTION

[0024] It is an object of the present invention to provide a silane intermediate monomer.

[0025] It is another object to provide a method of modifying the monomer so as to form a novel organo-functionalized molecule.

[0026] It is a third object of the invention to provide methods of producing poly(organo siloxane) compositions, which are suitable for the preparation of thin films having excellent dielectric properties.

[0027] It is a fourth object of the invention, to provide novel thin films, having low dielectric constant, excellent mechanical and thermal properties, said films being formed by the above-mentioned polymer.

[0028] It is a fifth object of the invention to provide dielectric layers on silicon wafers.

[0029] It is a still a sixth object of the invention is to provide light (preferably UV wavelength) enhanced curing for the poly(organo siloxane) film containing novel organic moieties.

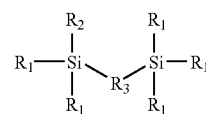
[0030] These and other objects, together with the advantages thereof over the known dielectric thin films and methods for the preparation thereof, which shall become apparent from specification which follows, are accomplished by the invention as hereinafter described and claimed.

[0031] 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.

[0032] 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.

[0033] 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 partially fluorinated.

[0034] The general formula I of the precursor used in the present invention is the following:



wherein:

[0035] R₁ is a hydrolysable group, such as hydrogen, a halide, an alkoxy or an acyloxy group,

or combination of all previous, such as an alkyl, alkenyl, alkynyl, aryl, polycyclic group or organic containing silicon group, and

[0056] R_3 is a bridging linear or branched bivalent hydrocarbyl group.

[0057] 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 alkylenylene groups, bivalent alicyclic groups (polycyclic groups) and bivalent aromatic groups which all are included in the definition of a bivalent hydrocarbyl group.

[0058] 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.

[0059] '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 alkynyl may be linear or branched.

[0060] 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.

[0061] 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 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 particularly preferred.

[0062] 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. Branched alkenyl is preferably branched at the alpha or beta position with one and more, preferably two, C_1 to C_6 alkyl, alkenyl or alkynyl groups, particularly preferred fluorinated or per-fluorinated alkyl, alkenyl or alkynyl groups.

[0063] Alkynyl contains preferably 3 to 18, more preferably 3 to 14 and particularly preferred 3 to 12 carbon atoms.

The ethylenic 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, C_1 to C_6 alkyl, alkenyl or alkynyl groups, particularly preferred per-fluorinated alkyl, alkenyl or alkynyl groups.

[0064] 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)

[0065] 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.

[0066] "Hydrolysable group" stands for halogen (chlorine, fluorine, bromine), alkoxy (in particular C_{1-10} 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.

[0067] 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.

[0068] 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.

[0069] 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.

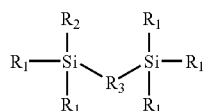
[0070] In the monomer of formula I, the silicon atoms are linked to each other via a linker group. Typically, the linker comprises 1 to 20, preferably about 1 to 10, carbon atoms. Examples of suitable linker groups R_3 include alkylene, alkenylene and alkylenylene groups. "Alkylene" groups generally 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. "Alkylenylene" groups, by contrast, contain at least one triple bond in the hydrocarbon backbone corresponding to the alkylene residues.

[0071] 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, pref-

erably a lower alkyl group or 1 to 4 carbon atoms. As a result of the substitution, a branched linker chain is obtained. The 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.

[0072] 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.

[0073] As mentioned above, in a first step of the method according to the present invention, a monomer is produced having the formula:



wherein:

[0074] R_1 is a hydrolysable group

[0075] R_2 is hydrogen, and

[0076] R_3 is a bridging linear or branched bivalent hydrocarbyl group.

[0077] 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.

[0078] 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 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.

[0079] This reaction is illustrated below in Example 1, wherein vinyltrichlorosilane is reacted with dichlorosilane to form 1,1,1,4,4-pentachloro-1,4-disilabutane.

[0080] 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 R_2 position.

[0081] The present invention provides a low dielectric constant siloxane polymer applicable for forming thermally and mechanically stable, 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 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 integration to a semiconductor device.

[0082] 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 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.

[0083] 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 having a higher molecular weight.

[0084] 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 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.

[0085] According to one preferred embodiment, in order to modify the properties, the siloxane 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.

[0086] According to a particular embodiment, the film is baked after spin coating at a temperature 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.

[0087] The polymer of the present invention is capable of forming low dielectric films having a dielectric constant of 3.0 or less, in particular 2.9 or less, preferably about 2.5 to 1.9, a Young's modulus of 10.0 GPa or more, a porosity of 5% or less and cracking threshold of 2 μm 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 500° C. or more after subjecting the film for thermal treatment at 450° C. or less for 1 hour or less.

[0088] As mentioned above, the present invention also provides methods of producing integrated circuit devices. Such methods typically comprise the steps of:

[0089] forming a plurality of transistors on a semiconductor substrate;

[0090] forming multilayer interconnects by:

[0091] depositing a layer of metal;

[0092] patterning the metal layer;

[0093] depositing a first dielectric material having a first modulus and a first k value;

[0094] 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

[0095] patterning the first and second dielectric materials and depositing a via filling metal material into the patterned areas.

[0096] 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:

[0097] a k value of 2.9 or less or even more preferably 2.5 or less,

[0098] a CTE 30 ppm or less, and

[0099] Young's modulus 4 GPa or more.

[0100] 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.

[0101] 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 .

[0102] Whereas one of the dielectric materials comprises a material in accordance with the present 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.

[0103] Generally, the organosiloxane material is a spin coated material.

[0104] The organosiloxane material is an organic-inorganic and has a coefficient of thermal expansion of 12 to 20 ppm. It can have a dielectric constant of 2.7 or less.

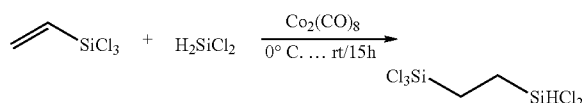
[0105] Further details of the invention will be discussed in connection with the following working examples:

EXAMPLES

Example 1

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

[0106]

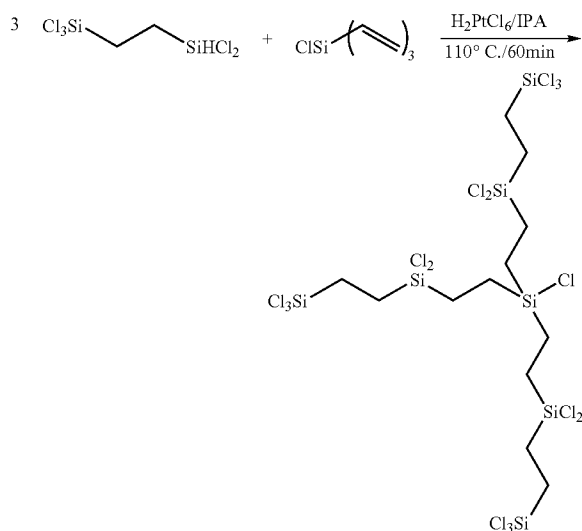


[0107] Vinyltrichlorosilane (68.8 g, 426 mmol) and cobalt octacarbonyl (700 mg) were placed in a 100 mL rb flask and cooled in an ice bath to 0° C. Dichlorosilane (bp. 8° C., 44.3 g, 439 mmol) was then condensed into the flask. The system was allowed to warm up to room temperature during night. Distillation at 60 . . . 62° C./8 mbar gave 1,1,1,4,4-Pentachloro-1,4-disilabutane (120.8 g, 460 mmol) in 93% yield.

Example 2

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

[0108]



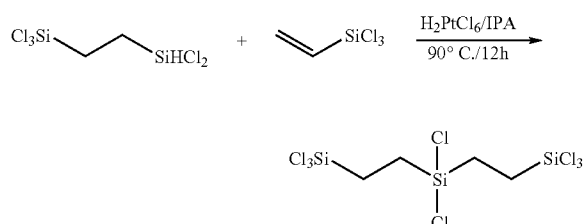
[0109] 11.00 g (0.076 mol) trivinylchlorosilane was added to a 100 ml vessel followed by 2 ml 1,1,1,4,4-pentachloro-1,4-disilabutane. The solution was heated to 80° C. and 15 μL of a 10% $\text{H}_2\text{PtCl}_6/\text{IPA}$ -solution was added. Strong exothermic reaction was observed and heat was switched off. Rest of 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min 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-disilohexyl)chlorosilane. B.p. 264° C./<0.5 mbar.

Example 3

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

[0110]

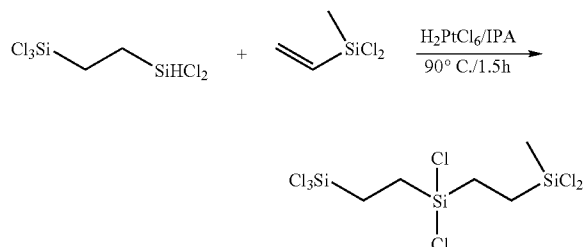


[0111] Vinyltrichlorosilane (16.8 g, 104 mmol) was heated to 60° C. and 100 μ L 10% H_2PtCl_6 /IPA-solution was added. 1,1,1,4,4-pentachloro-1,4-disilabutane (20.4 g, 77.7 mmol) was added slowly during 20 min so that the temperature did not exceed 100° C. The reaction was allowed to proceed for 12 hours 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

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

[0112]



[0113] 1,1,1,4,4-Pentachloro-1,4-disilabutane (51.6 g, 196 mmol) was heated to 80° C. and 20 μ L 10% H_2PtCl_6 /IPA-solution was added. Vinylmethylchlorosilane (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%).

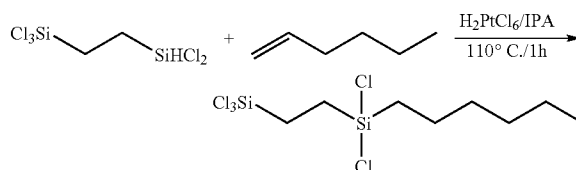
Examples 5 to 7

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-disilatetradecaidecane

[0114]

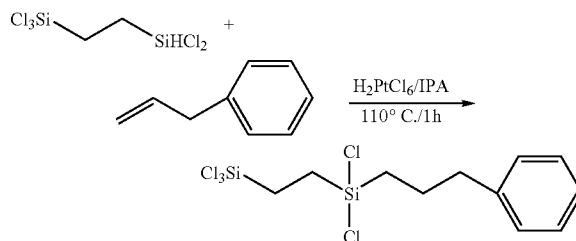


[0115] 32 ml (21.53 g, 0.256 mol) 1-hexene and 20 μ L H_2PtCl_6 /IPA solution were added to a 100 ml vessel. Solution was heated up to 80° C. and 46.90 g (0.179 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min. Heat was switched off when exothermic reaction was observed. Temperature 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./0.8 mbar. 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-disilatetradecaidecane (b.p. 138° C./0.8 mbar, 82% yield), respectively.

Example 8

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

[0116]

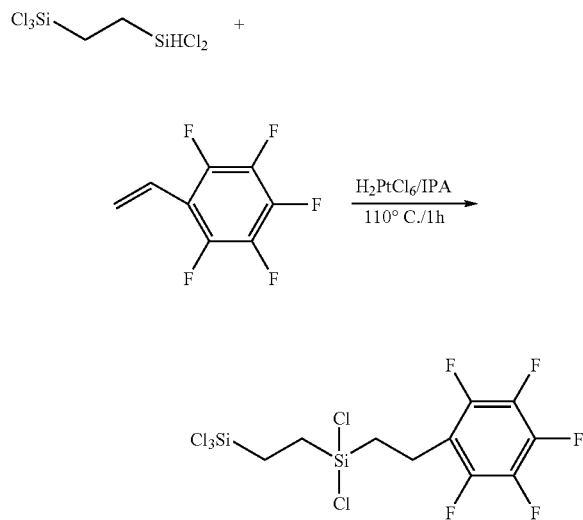


[0117] 18.77 g (0.159 mol) allylbenzene and 50 μ L H_2PtCl_6 /IPA solution were added to a 100 ml vessel. Solution was heated up to 80° C. and 41.85 g (0.159 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added slowly during 30 min. Heat was switched off when exothermic reaction was observed. Temperature 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./0.8 mbar. Yield 35.10 g (58%).

Example 9

1,1,1,4,4-Pentachloro-6-pentafluorophenyl-1,4-disilahexane

[0118]

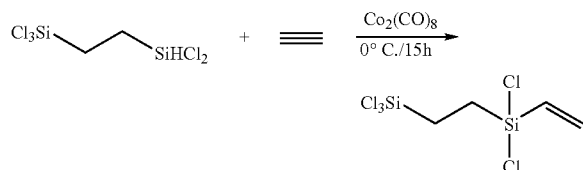


[0119] 116.15 g (0.442 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 250 ml vessel followed by 100 μl $\text{H}_2\text{PtCl}_6/\text{IPA}$ solution. Solution was heated up to 85°C . and 85.80 g (0.442 mol) pentafluorostyrene was added slowly during 30 min. After addition solution was stirred for an hour at 100°C . and then distilled. Bp. $122^\circ\text{C}/<1\text{ mbar}$, yield 158.50 g (78%).

Example 10

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

[0120]

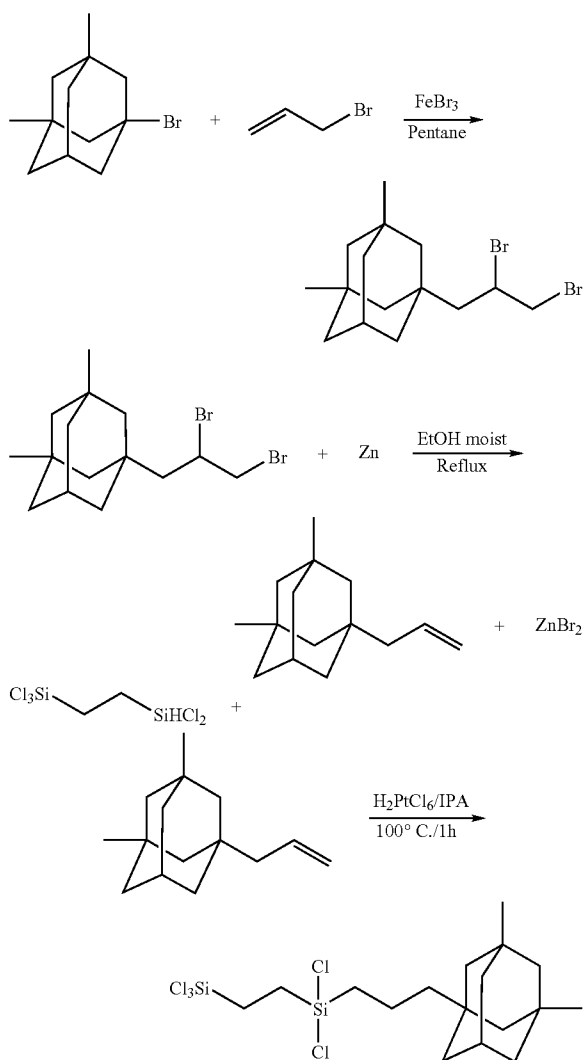


[0121] 40.00 g (0.152 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was dissolved in 1000 ml 1,4-dioxane in a 2000 ml vessel. The solution was cooled down to 0°C . and acetylene was bubbled to solution until it was saturated. The solution thus obtained was slowly warmed up to room temperature. 1,4-dioxane was evaporated and obtained crude 1,1,1,4,4-pentachloro-1,4-disila-5-hexene was purified by distillation.

Example 11

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

[0122]



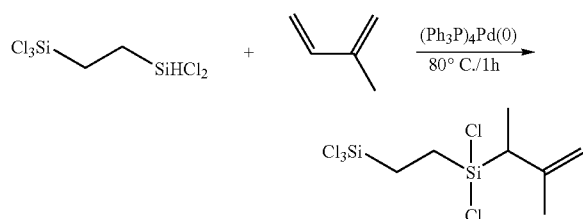
[0123] 81.71 g (0.336 mol) 3,5-dimethyladamantylbromide was dissolved in 500 ml pentane. The solution was cooled to below -10°C . by ice/acetone bath. 51.40 g (0.425 mol) allylbromide was added followed by 410 mg FeBr_3 . The solution was then stirred for three hours at $-20 \dots 10^\circ\text{C}$. after which analysis by GC-MS was carried out, indicating that some unreacted starting materials remained. 420 mg FeBr_3 was added and solution was stirred for an additional two hours after which GC-MS showed that all the dimethyladamantyl bromide had 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. After cooling down to room temperature the solution was filtered. 300 ml water was added and the product was extracted by washing twice with 500 ml 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-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.

Example 12

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

[0124]



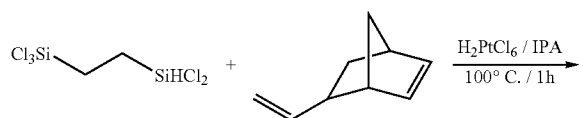
[0125] 49.85 g (0.190 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 100 ml vessel followed by ~20-30 mg tetrakis(triphenylphosphine)palladium(0). The solution was heated to 80° C. and 13.10 g (0.192 mol) iso-prene was added slowly during 30 min. After addition, the solution was stirred for an hour at 100° C. and then distilled. Bp. 96° C./<1 mbar, yield 58.50 g (93%).

[0126] If the same reaction is carried out with a $H_2PtCl_6/$ IPA catalyst at 80° C. or with a $Co_2(CO)_8$ catalyst at room temperature a 1:1 mixture of α and β substituted isomers is obtained.

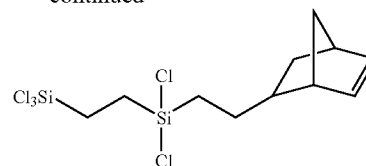
Example 13

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

[0127]



-continued

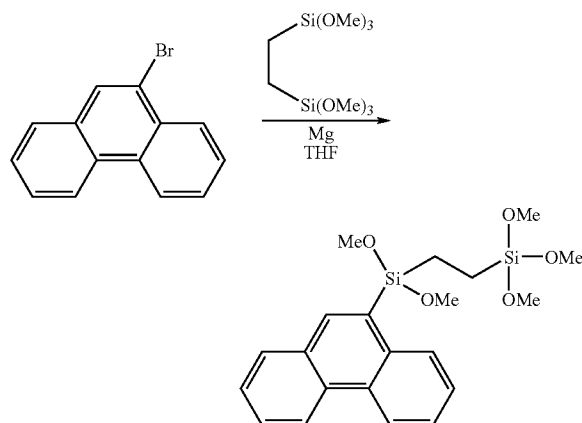


[0128] 22.63 g (0.086 mol) 1,1,1,4,4-pentachloro-1,4-disilabutane was added to a 100 ml vessel followed by 70 μ l of a $H_2PtCl_6/$ IPA solution. The solution obtained was heated to 85° C. and 10.81 g (0.090 mol) 5-vinyl-2-norbornene was then slowly added during 30 min. After addition, the solution was stirred for an hour at 100° C. and then distilled. Bp. 140° C./<1 mbar, yield 20.05 g (61%).

Example 14

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

[0129]



[0130] 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 200 ml 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.

[0131] 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 15

Dielectric Polymer

[0132] The above described monomers can be polymerized via various hydrolysis and condensation polymerization

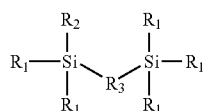
methods known in the art and are thus not limiting factors in course of this invention. Typical hydrolysis and condensation routes contain organic solvent or solvent "cocktails" and water as a hydrolysis compound. Also acids and bases are often used as a catalysts during the synthesis. The polymer can be polymerized up to various molecular weights ranging from oligomeric polymers to polymers having molecular weight of several million g/mol.

[0133] One typical dielectric polymer can be obtained as follows:

[0134] A solution of 1-(trichlorosilyl)-2-(methylchlorosilyl)-ethane (20.7 g, 75 mmol), 1-(trichlorosilyl)-2-([3'-{3",5"-dimethyladamantyl]-propyl]-dichlorosilyl)-ethane (11.0 g, 24 mmol) and 130 mL MTBE was dripped into a well-stirred solution of 130 mL distilled water and 130 mL MTBE at -2° C. during 40 minutes. After the addition was complete, the solution was allowed to warm to $+13^{\circ}$ C. in one hour. The water layer was discarded and the organic layer was washed with distilled water until neutral (5x30 mL). After filtration through a $0.45\ \mu$ glass fibre filter, all volatiles were removed under reduced pressure, and 21 g polymer was obtained. This was then dissolved in 85 g MTBE and 260 mg TEA, and was then refluxed for two hours. After cooling, the solution was washed once with 30 mL 2 w-% HCl, followed by three rinses with 30 mL of distilled water. Evaporation under reduced pressure gave 20.5 g of a white powder, that had Mw/Mn=6,300/4,100. It was dissolved in 61.35 g PGMEA and then spin coated on a silicon wafer.

[0135] Soft bake at 150° C./5 minutes, followed by cure at 450° C. for five hours in N_2 gave a film with dielectric constant $k=2.3$. Alternatively, the film was baked after spin coating at 150° C./5 minutes and then exposed to UV cure at 350° C. for five minutes and resulted in dielectric constant $k=2.2$. In both cases a reactivity of dimethyl adamantyl was confirmed by FTIR. The FTIR analysis also showed that the films made via both curing methods were free of silanols.

1. A thin film comprising a composition obtained by polymerizing a monomer having the formula I:



wherein:

R_1 is a hydrolysable group,

R_2 is 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.

to form a siloxane material.

2. The thin film according to claim 1, wherein independently

R_1 is selected from the group of hydrogen, halides, alkoxy and acyloxy groups,

R_2 is selected from alkyl groups, alkenyl groups and aryl groups, and

R_3 is selected from linear and branched alkylene groups, alkenylene groups, alkynylene groups, bivalent alicyclic groups, bivalent polycyclic groups, and bivalent aromatic groups.

3. The thin film according to claim 1, wherein the composition comprises a cross-linked poly(organosiloxane).

4. The thin film according to any of claims 1 to 3, wherein the composition is obtained essentially by homopolymerization of monomers having formula I.

5. The thin film according to any of claims 1 to 3, wherein the composition is obtained by copolymerizing first monomers 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.

6. The thin film according to any of the preceding claims, comprising a cured thin layer of the poly(organosiloxane) having a thickness of 0.01 to 50 μ m, in particular 0.5 to 5 μ m, preferably from 1 to 3 μ m.

7. The thin film according to any of the preceding claims, having a density of at least $1.2\ \text{g/cm}^3$, preferably $1.45\ \text{g/cm}^3$ or more, more preferably $1.60\ \text{g/cm}^3$ or more, in particular up to about $2.5\ \text{g/cm}^3$.

8. The thin film according to any of the preceding claims, having either or both of the following properties:

a glass transition temperature, which is higher than 200° C., in particular 400° C. or more, in particular 500° C. or more, and

a dielectric constant of 3.0 or less, in particular 2.9 or less, preferably about 2.5 to 1.9.

9. The thin film according to any of the preceding claims, having a coefficient of thermal expansion of 12-22 ppm, preferably about 15-20 ppm.

10. The thin film according to any of the preceding claims, comprising an organosiloxane material having a (weight average) molecular weight of from 500 to 100,000 g/mol.

11. The thin film according to any of the preceding claims, comprising 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, and the film exhibiting one or several of the following properties:

a k value of 2.9 or less or even more preferably 2.5 or less,

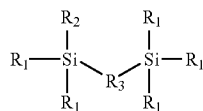
a CTE 30 ppm or less, and

Young's modulus 4 GPa or more.

12. An object comprising a low k dielectric film, the film comprising a material according to any of claims 1 to 10.

13. A method of forming a thin film having a dielectric constant of 2.9 or less, comprising

polymerizing a monomer having the formula I:



wherein R₁, R₂ and R₃ have the same meaning as above, 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.

14. The method according to claim 13, comprising

homopolymerizing a monomer having the formula I or copolymerizing isomers thereof 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.

15. The method according to claim 13 or 14, comprising homopolymerizing a monomer having the formula I or copolymerizing isomers thereof in a liquid medium formed by a first solvent to form a hydrolyzed product comprising a siloxane material;

recovering the hydrolyzed product;

mixing the hydrolyzed product with a second solvent to form a solution;

applying the solution on a substrate;

removing the second solvent to deposit 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.

16. The method according to claim 14 or 15, comprising carrying out the step of homopolymerizing to form a polymerized product and the step of curing the hydrolyzed product at a temperature of 50 to 425° C.

17. The method according to any of claims 13 to 16, comprising

depositing the siloxane material on a substrate of a semiconductor device; and

patterning the siloxane material to form a dielectric in a semiconductor device.

18. The method according to claim 17, comprising

patterning the siloxane material by removing siloxane material in selected areas and

depositing an electrically conductive material in the selected areas.

19. The method according to claim 18, wherein a barrier layer is deposited in the selected areas prior to depositing the electrically conductive material.

20. The method according to claim 18, wherein the electrically conductive material is deposited in the selected

areas without a barrier layer, and wherein the electrically conductive material comprises aluminum or copper.

21. The method according to claim 13, comprising

carrying our polymerization at conditions conducive to cross-linking between the monomer units so as to form a siloxane material;

depositing the siloxane material on a substrate;

heating the siloxane material to cause further cross-linking;

patterning the siloxane material to remove siloxane material in selected areas;

adding an electrically conductive material in the selected areas; and

performing chemical mechanical polishing on the electrically conductive material down to the siloxane material.

22. The method according to claim 21, wherein the siloxane material is patterned by selectively exposing the siloxane material to electromagnetic energy and removing non-exposed areas of siloxane material with a developer.

23. The method according to claim 22, wherein the siloxane material is patterned by RIE.

24. The method according to any of claims 21 to 23, wherein the patterning is performed without a capping layer.

25. The method according to any of claims 13 to 24, wherein the siloxane material is deposited on a substrate of a semiconductor device, and the siloxane material 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.

26. The method according to any of claims 13 to 25, wherein the compound of formula I is obtained from a compound of formula I wherein R₂ stands for hydrogen and R₁ and R₃ have the same meanings as above.

27. The method according to claim 26, wherein the compound of formula I, wherein R₂ stands for hydrogen, is selectively produced by hydrosilylation of halosubstituted silanes in the presence of a cobalt octoate catalyst.

28. The method according to any of claims 13 to 27, wherein the film is baked after spin coating at a temperature 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.

29. The method according to claim 28, wherein the curing is carried out for a sufficient period of time for reacting the organic substituent at position R₂ of the unit derived from a monomer having the formula I above.

30. A method of producing silane-based materials by hydrosilylation, wherein the reaction is carried out in the presence of cobalt octacarbonyl as a catalyst.

31. The method according to claim 30, wherein a trihalosilane is reacted with a dihalosilane in the presence of cobalt octacarbonyl.

32. The method according to claim 30 or 31, wherein a trihalosilane is used having a reactive organic group comprising an unsaturated bond.

33. The method according to claim 31 or 32, wherein vinyltrichlorosilane is reacted with dichlorosilane to form 1,1,1,4,4-pentachloro-1,4-disilabutane.