

HIGH BREAKDOWN VOLTAGE DIELECTRIC POLYMER FILMS, A METHOD OF
PRODUCING THE SAME AND USES THEREOF

FIELD

5 **[0001]** The present invention relates to polymer compositions capable of forming
gap-fill material for use in the production of dielectric polymer films. The present
invention also concerns dielectric polymer films comprising said polymer compositions,
and uses of the dielectric polymer films in semiconductor devices, optical elements and
optically active devices. The present invention also relates to methods of producing gap-fill
10 material forming compositions and dielectric polymer films comprising said compositions.

BACKGROUND

[0002] 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
15 embedded in a dielectric material. Within the metallization structure, “vias” make up the
vertical wiring, whereas “interconnects” form the horizontal wiring. Fabricating the
metallization structure 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-
20 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
25 dielectric.

[0003] 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. Initially, aluminum alloys have also been developed over the years
to improve the melting point, diffusion, electromigration and other qualities as compared to
30 pure aluminum. Spanning successive layers of aluminum, tungsten has traditionally served
as the conductive via plug material. The drive to faster microprocessors and more powerful

electronic devices have resulted in increasingly high circuit densities and faster operating speeds which - in turn - have required that higher conductivity metals and improved dielectrics with lower dielectric constants compared to silicon dioxide (preferably below 3.0) are used. After aluminum metallization the industry moved 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.

[0004] The copper “dual damascene” process has been utilized by the industry two decades successfully. The critical dimensions of copper interconnects in future devices will reach 10–20 nm, or even below. Consequently, the dielectric material between the interconnects are exhibiting similar critical dimensions. For the copper “dual damascene” process, this is in part very problematic since copper ions are very mobile which means that these ions will migrate to the dielectric layers. Eventually, an increase in copper ion concentration will lead to dielectric breakdown leading the device or transistor non-operational. To prevent copper ion migration, various barrier layers have been deposited, which typically are nitrides of titanium or tantalum. In a sub 30 nm pitch design, the barrier layers would fill most of the space between the metal interconnects thus leading to an inadequate dielectric layer due to poor dielectric properties of said nitrides. Due to the above-mentioned challenges, there is an on-going search for new metals where interconnect critical dimension is 10–20 nm or below. Depending on the metal used, metal lines may be formed using a subtractive process similar to that of aluminum and tungsten, or by a single damascene process where an alternative metal is deposited followed by deposition of Cu. Thus, new dielectrics with suitable electrical and mechanical properties, which are also able to fill critical dimensions of 10–20 nm or lower are needed to realize future devices and device architectures. In addition, the new dielectrics must withstand conditions used in subsequent process steps, which include for example high temperatures (400 °C or more), various chemicals and mechanical forces (chemical mechanical polishing).

[0005] Moreover, new advanced spin-on dielectrics for logic chip back-end-of-line (BEOL) interlayers are needed, as commonly used CVD dielectric coatings cannot fulfill requirements of next generation processes and devices due to shrinking of interconnect dimensions. Benefits of spin-on dielectrics include for example excellent gap-fill
5 properties, cost effective processing and low dielectric constant, compared to CVD silicon oxide based materials.

[0006] US 7074690 B1 discloses a gap-fill process based on gas phase deposition, describing CVD and ALD (atomic layer deposition), including their plasma assisted processes. US 2019177488 A1 relates to a solvent-free particulate silicone composition
10 and to hydrosilylation in the presence of metal catalyst, typically a Pt-catalyst. JP 2015206019 A1 describes the use of surface-treated metal oxide particles to impart improvements in a silicone resin. JP 2007254595 A relates to film forming compositions comprising polymers produced by hydrolysing silane monomers and a hydrolysable polycarbosilane.

15 [0007] Although current siloxane-based spin-on dielectric coatings provide lower dielectric constant compared to silicon oxide, they cannot match the breakdown voltage (BDV) values. Therefore, CVD dielectrics are still commonly used due to the low breakdown voltage of spin-on dielectric siloxane coatings- Higher breakdown voltage is needed to guarantee reliability of the final device. On the other hand, low dielectric
20 constant reduces capacitance, making processing faster due to decreased RC delay.

[0008] . Other commonly faced issues with spin-on dielectrics include poorer mechanical properties and high coefficient of expansion (CTE).

[0009] In addition to microelectronics, several optoelectronic applications require coatings whose optical properties, such as refractive index, or properties affecting optical
25 properties need to be optimized, for example to minimize reflections at interfaces between stacked coatings or to maximize the output of light from optoelectronic devices for improving optical clarity and image resolution.

[0010] It is one of the aims of the present invention to eliminate at least a part of the problems relating to the art and to provide dielectric polymer films with increased
30 breakdown voltage values without compromising other properties of the dielectric polymer film, such as dielectric constant. It is also one aim of the present invention to provide gap-

fill material forming compositions, which are deposited in liquid form by spin-coating process to provide dielectric films with advantageous properties, such as increased breakdown voltage, low shrinkage, low dielectric constant and capability to fill gap widths of 20 nm or less.

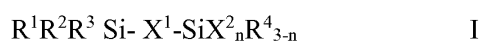
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SUMMARY OF THE INVENTION

[0011] The invention is defined by the features of the independent claims. Some specific embodiments are defined in the dependent claims.

[0012] The present invention is based on the concept of providing semiconductor devices, optical elements and/or optically active devices comprising dielectric polymer
 10 films containing a gap-fill material forming composition as herein disclosed. The novel gap-fill material forming composition and the dielectric polymer films comprising the same provide improved properties, in particular a higher breakdown voltage but also other advantageous properties, such as low shrinkage and low dielectric constant, compared to the solutions of the prior art. The gap-fill material composition comprises alkyl-
 15 triorganosilyl side groups in siloxane polymers as discussed below in more detail.

[0013] According to a first aspect of the present invention, there is provided a gap-fill material forming composition, comprising a polymer obtained by polymerization of monomers having formula I



20 wherein each X^1 is selected from the group of oxygen, optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms;

each X^2 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

each R^1 and R^2 and R^3 is independently selected from alkyl groups having 1 to 6 carbon
 25 atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

each R^4 is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted; and

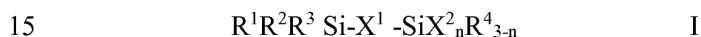
n is an integer of 1 to 3.

[0014] The invention also provides use of the gap-fill material forming composition for preparing a gap-fill dielectric film for semiconductor devices or optical elements. Typically, the gap-fill material forming composition is deposited, in the form of a thin layer, on a substrate, and the thin layer is cured to a gap-fill dielectric polymer film. In particular, the gap-fill material forming composition, which comprises siloxanes or silsesquioxane polymers in solution, is deposited in liquid form by a spin-coating process.

[0015] According to a further aspect of the present invention, there is thus provided a dielectric polymer film comprising a cured gap-fill material forming composition as defined above.

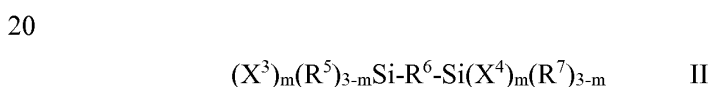
[0016] A further aspect of the present invention relates to a method of forming a gap-fill dielectric polymer film, wherein the method comprises the steps of:

- hydrolysing a first silicon compound having the formula I



wherein R^1 , R^2 , R^3 , X^1 , R^4 , X^2 and n have the same meanings as above; and

- polymerizing the first silicon compound, optionally with at least one second silicon compound obtained by hydrolysing a compound having the formula II



wherein each X^3 and X^4 is independently selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

each R^5 and R^7 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

each R^6 is selected from the group of optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms; and m is an integer of 1 to 3,

and/or a compound having the formula III



- 5 wherein each X^4 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;
each R^{14} is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted; and n is an integer of 1 to 3,
to provide a gap-fill coating composition; and
10 depositing the gap-fill coating composition on a substrate and curing the composition to form the gap-fill dielectric polymer film.

[0017] According to a further aspect of the present invention, there is provided a method of producing a semiconductor device, wherein the method comprises the steps of

- providing a semiconductor device substrate;
- 15 - applying a gap-fill material forming composition of the invention onto the semiconductor device substrate and curing the composition to provide a gap-fill dielectric film on the semiconductor device substrate.

[0018] According to a still further aspect of the present invention, there is provided a method of producing an optical element or an optically active device, wherein the method
20 comprises the steps of

- providing an optical element or optically active device substrate
- applying a gap-fill material forming composition of the invention onto the optical element or onto the optically active device substrate and baking the composition to form a gap-fill dielectric film.

25 [0019] The invention also provides a semiconductor device comprising the dielectric polymer film of the invention. Further, the invention provides an optical element or an optical device comprising the dielectric polymer film of the invention.

[0020] Considerable advantages are obtained by the invention. First, the present materials provide higher breakdown voltage (BDV) values than current siloxane-based
30 spin-on dielectric coatings. Higher breakdown voltage is important to guarantee the

reliability of the final device. Typically, the dielectric polymer films of the invention have an electric breakdown voltage of at least 3.8 MV/cm.

[0021] Second, the present materials provide a dielectric constant that is lower compared to silicon oxide and at the same level compared to current siloxane-based spin-on dielectric coatings. Typically, the dielectric polymers films of the invention have a dielectric constant at 1 MHz of 2.9 or less.

[0022] Therefore, the present materials provide increased breakdown voltage without compromising other properties of the materials, such as dielectric constant, coefficient of expansion, modulus and hardness. In addition, the present materials provide low shrinkage, decreasing the amount of stress formation in the polymer films during high temperature cure. For example, the dielectric polymer films of the invention have a shrinkage between soft bake and cure, which is less than 5%, more preferably less than 3% and most preferably less than 1%.

[0023] Further features and advantages of the present technology will appear from the following description of some embodiments.

EMBODIMENTS

[0024] DEFINITIONS

[0025] Unless otherwise stated herein or clear from the context, any percentages referred to herein are expressed as percent by weight based on a total weight of the respective composition.

[0026] Unless otherwise stated, properties that have been experimentally measured or determined herein have been measured or determined at room temperature. Unless otherwise indicated, room temperature is 25 °C.

[0027] Unless otherwise stated, properties that have been experimentally measured or determined herein have been measured or determined at atmospheric pressure.

[0028] As used herein, the term “about” refers to a value, which is $\pm 5\%$ of the stated value.

[0029] As used herein, the term “average molecular weight” refers to a weight average molecular weight (also abbreviated “ M_w ” or “ M_w ”).

[0030] As used herein, the molecular weight is measured by gel-permeation chromatography using polystyrene standards.

[0031] Measurement of the “dielectric constant”, κ or ϵ_r , is achieved using a metal-insulator-semiconductor (MIS) structure on highly doped low resistivity N+ doped silicon wafers. A mercury probe (Materials Development Corporation, model 802) and precision impedance analyzer (Agilent 4294A) are used to determine the capacitance across the dielectric film which together with the mercury dot contact area and film thickness can be used to calculate the dielectric constant using the following equation:

$$\kappa = \frac{Cd}{\epsilon_0 A}$$

10 where κ is dielectric constant, C is capacitance, d is film thickness, ϵ_0 is permittivity of vacuum and A is capacitor area.

[0032] Film thickness can be determined by means and equipment known to persons skilled in the art, for example by using J.A. Woollam M2000D-ESM-200AXY spectroscopic ellipsometer.

15 [0033] “Breakdown voltage” is measured using a similar MIS structure with mercury probe (Materials Development Corporation, model 802) and semiconductor parameter analyzer (Agilent 4155B).

[0034] “Refractive index” (RI) is determined using a refractometer at a wavelength of 633 nm. The RI can be calculated by, e.g. interferometry, the deviation method, or the Brewster Angle method from a polymeric film sample having a thickness of 400 nm.

[0035] “Shrinkage” is determined measuring the thickness loss of the film between low temperature soft bake and high temperature cure. Thickness measurement is done with spectroscopic ellipsometer.

[0036] “Hardness” and “elastic modulus” of films can be calculated from curve of nanoindentation by the Oliver-Pharr method.

[0037] In the present context, the term “gap-fill material” refers to material capable to fill gaps between different topographies on a semiconductor device substrate or on optical elements or optically active device substrates, typically when the gap-fill material is

deposited, in the form of a thin layer in liquid form, on said substrate and cured. A gap-fill material forming composition refers to material capable to form a polymer film on the surface of semiconductor devices or optical elements or optically active devices when cured. The gap-fill material forming compositions of the present invention are capable to
5 fill gaps with a width of 20 nm or less, in particular when coated by spin-coating.

[0038] “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
10 are phenyl, naphthyl, or pentafluorophenyl propyl. More specifically, the alkyl, alkenyl or alkynyl may be linear or branched. As used herein, “alkoxy” and “acyloxy” groups typically have 1 to 6 carbon atoms.

[0039] In the following, embodiments of the present technology are described in more detail.

15 [0040] The present invention is based on the finding that by polymerizing monomers of formula I, optionally together with silane monomers of formula II and/or of formula III, polymer compositions are obtained, which when cured form dielectric polymer films having a high electric breakdown voltage, in particular an electric breakdown voltage of at least 3.8 MV/cm.

20 [0041] The embodiments disclose the production and use of dielectric polymer films which comprise alkyl-triorganosilyl side groups in siloxane polymers. Such polymer films are obtained by polymerizing, either by homopolymerization or by copolymerization, of silane monomers of at least formula I. The polymers are siloxanes or silsesquioxanes, which are different from linear siloxanes, commonly known as silicones. Preferably, the
25 polymers are free of polycarbosilanes.

[0042] Typically, in the present technology, silane monomers containing hydrolyzable groups are first subjected to hydrolysis and then to polymerization typically in liquid phase and at a temperature between room temperature and the boiling point of the liquid. The liquid may consist of one or more solvents, in addition to the silicon monomers
30 and the water added for hydrolysis of the monomers. Specific, suitable solvents include acetone, ethyl methyl ketone, methanol, ethanol, isopropanol, butanol, methyl acetate,

ethyl acetate, propyl acetate, butyl acetate and tetrahydrofuran. Particularly suitable solvents are alcohols, ketones, and ether.

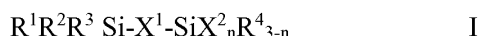
[0043] Controlled hydrolysis of the monomers is obtained by addition of an acid or base solution with molarity ranging from 0.0001 M to 1 M. Organic or inorganic acid can be used in the synthesis. Inorganic acids such as nitric acid, sulfuric acid, hydrochloric acid, hydriodic acid, hydrobromic acid, hydrofluoric acid, boric acid, perchloric acid, carbonic acid and phosphoric acid can be used. Preferably, nitric acid or hydrochloric acid is used due to their low boiling point, which make purification of product simple. In other options, various organic acids are used instead of inorganic acid. Organic acids are carboxylic acid, sulfonic acid, alcohol, thiol, enol, and phenol groups. Examples are methanesulfonic acid, acetic acid, ethanesulfonic acid, toluenesulfonic acid, formic acid, and oxalic acid.

[0044] Bases used in the synthesis may similarly be inorganic or organic. Typical inorganic bases are metal hydroxides, carbonates, bicarbonates and other salts that yield an alkaline water solution. Examples of such materials are sodium hydroxide, potassium hydroxide, cesium hydroxide, calcium hydroxide, sodium carbonate, and sodium bicarbonate. Organic bases on the other hand comprise a larger group consisting of metal salts of organic acids (such as sodium acetate, potassium acetate, sodium acrylate, sodium methacrylate, sodium benzoate), linear, branched or cyclic alkylamines (such as diaminoethane, putrescine, cadaverine, triethylamine, butylamine, dibutylamine, tributylamine, piperidine) amidines and guanidines (such as 8-diazabicyclo(5.4.0)undec-7-ene, 1,1,3,3-tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]-dec-5-ene), phosphazanes (such as P₁-t-Bu, P₂-t-Bu, P₄-t-Bu), and quaternary ammonium compounds (such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide).

[0045] The temperature of the reaction mixture during the hydrolysis and condensation process can be varied in the range from -30 to 170 °C. Lower reaction temperatures provide improved control of the reaction at the cost of long reaction times, while excessively high temperatures may make the process too fast for adequate control. A reaction time of 1–48 h at a temperature of 0–100 °C is preferred. A reaction time of 2–24 h is even more preferred.

[0046] Using appropriate conditions, embodiments of the present method yield a polymer in an organic solvent system, said polymer having a molecular weight of about 500 to 100,000 g/mol, preferably 800 to 50,000 g/mol, and most preferably 1000 to 10,000 g/mol measured against polystyrene standards.

- 5 [0047] In one particular embodiment, a gap-fill material forming composition is obtained, which comprises a polymer obtained by polymerization of monomers having formula I



- 10 wherein each X^1 is selected from the group of oxygen, optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms;

each X^2 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

- 15 each R^1 and R^2 and R^3 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

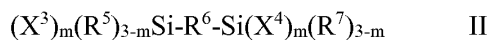
each R^4 is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted; and

n is an integer of 1 to 3.

- 20 [0048] Typically, the gap fill material forming composition comprises at least 5 mol-%, preferably at least 10 mol-%, such as 10-20 mol-%, more preferably about 15 mol-%, of a polymer according to formula I.

- 25 [0049] In some embodiments, the gap-fill material composition is obtained by copolymerization of compounds of formula I with silane monomers. Preferably, the compounds of formula I amount to at least 5 mol% of the total amount of monomers of the polymer composition obtained by copolymerization of compounds of formula I with silane monomers.

[0050] In some embodiments, the gap-fill material composition is obtained by copolymerization of a compound of formula I with a compound or several compounds of formula II



5 wherein

each X^3 and X^4 is independently selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

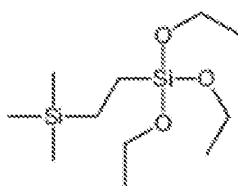
each R^5 and R^7 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups
10 optionally being substituted;

each R^6 is selected from the group of optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms; and

m is an integer of 1 to 3.

15 [0051] Preferably, in the above formulas I and II, each X^1 and R^6 is independently selected from alkylene having 1 to 4, in particular 2 carbon atoms.

[0052] Further preferably, the monomers according to formula I are selected from monomers having formula Ia



Ia

20 [0053] The synthesis of the monomer according to formula Ia or 1-trimethylsilyl-2-triethoxysilyl-ethane has been described by Khudobin et al (1976).

[0054] In some preferred embodiments, the compounds of formula I amount to at least 10 mol-% and the compounds of formula II amount to at least 40 mol-% of the total amount of monomers of the gap-fill material forming composition.

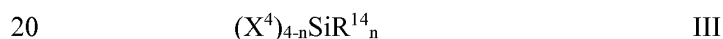
[0055] In some embodiments, the monomers of the gap-fill material forming composition consist of compounds of formula I and compounds of formula II, the compounds of formula I amounting to at least 10 mol-%, preferably to at least 15 mol-%, of the total amount of monomers of the gap-fill material forming composition.

- 5 [0056] Specific examples of compounds of formula II include but are not limited to 1,2-bis(trimethoxysilyl)ethane, 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane and 1,2-bis(dimethoxymethylsilyl)ethane.

[0057] In some embodiments, the monomers of the gap-fill material forming composition consist of compounds of formula I, in particular 1-trimethylsilyl-2-triethoxysilyl-ethane, and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane as compounds of formula II.

[0058] In some embodiments, the monomers of the gap-fill material forming composition consist of 1-trimethylsilyl-2-triethoxysilyl-ethane, preferably in an amount of at least 10 mol-%, preferably at least 15 mol-% or about 20 mol-% of the total amount of monomers of the gap-fill material forming composition, and compounds of formula II, preferably 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane.

[0059] In some embodiments, the gap-fill material forming composition is obtained by polymerization of a compound of formula I with a compound or several compounds of formula III



wherein each X^4 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

each R^{14} is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted; and

n is an integer of 1 to 3.

[0060] Preferably, in the above formulas (I, II and III), each X^2 , X^3 and X^4 is independently selected from the group of hydrogen and organic or inorganic hydrolysable groups selected from halogen, acyloxy, alkoxy and OH groups. Typically, the halogen is

selected from fluoro, chloro and bromo. More preferably, each X^2 , X^3 and X^4 is independently selected from the group of hydrogen and R^9O- , wherein R^9 stands for an alkyl having 1 to 6 carbon atoms.

[0061] In some embodiments, each R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^8 and R^{14} in the above
 5 formulas is independently selected from alkyl groups having 1 to 4 carbon atoms and phenyl groups.

[0062] Specific examples of compounds of formula III include but are not limited to tetramethoxysilane, tetraacetoxysilane, tetrachlorosilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane, methyltrimethoxysilane,
 10 methyltriethoxysilane, methyltrichlorosilane, methyltriacetoxysilane, methyltripropoxysilane, methyltributoxysilane, methyltriphenoxysilane, methyltribenzyloxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriacetoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, phenyltrichlorosilane, phenyltriacetoxysilane,
 15 phenyltriethoxysilane, γ -chloropropyltrimethoxysilane, γ -chloropropyltriethoxysilane, γ -chloropropyltriacetoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, β -cyanoethyltriethoxysilane, chloromethyltrimethoxysilane, chloromethyltriethoxysilane, dimethyldimethoxysilane,
 20 phenylmethyldimethoxysilane, dimethyldiethoxysilane, phenylmethyldiethoxysilane, γ -chloropropylmethyldimethoxysilane, γ -chloropropylmethyldiethoxysilane, dimethyldiacetoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptomethyldiethoxysilane, methylvinylmethyldimethoxysilane, methylvinylmethyldiethoxysilane,
 25 glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane, α -glycidoxyethyltrimethoxysilane, α -glycidoxyethyltriethoxysilane, β -glycidoxyethyltrimethoxysilane, β -glycidoxyethyltriethoxysilane, α -glycidoxypropyltrimethoxysilane, α -glycidoxypropyltriethoxysilane, β -glycidoxypropyltrimethoxysilane, β -glycidoxypropyltriethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropyltripropoxysilane, γ -glycidoxypropyltributoxysilane, γ -glycidoxypropyltriphenoxysilane, α -glycidoxybutyltrimethoxysilane, α -glycidoxybutyltriethoxysilane, β -glycidoxybutyltriethoxysilane, γ -

glycidoxybutyltrimethoxysilane, γ -glycidoxybutyltriethoxysilane, δ -glycidoxybutyltrimethoxysilane, δ -glycidoxybutyltriethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane, (3,4-epoxycyclohexyl)methyltriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltripropoxysilane, β -(3,4-epoxycyclohexyl)ethyltributoxysilane, β -(3,4-epoxycyclohexyl)ethyltriphenoxysilane, γ -(3,4-epoxycyclohexyl)propyltrimethoxysilane, γ -(3,4-epoxycyclohexyl)propyltriethoxysilane, δ -(3,4-epoxycyclohexyl)butyltrimethoxysilane, δ -(3,4-epoxycyclohexyl)butyltriethoxysilane, glycidoxymethylmethyldimethoxysilane, glycidoxymethylmethyldiethoxysilane, α -glycidoxyethylmethyldimethoxysilane, α -glycidoxyethylmethyldiethoxysilane, β -glycidoxyethylmethyldimethoxysilane, β -glycidoxyethylethyldimethoxysilane, α -glycidoxypropylmethyldimethoxysilane, α -glycidoxypropylmethyldiethoxysilane, β -glycidoxypropylmethyldimethoxysilane, β -glycidoxypropylethyldimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, γ -glycidoxypropylmethyldipropoxysilane, γ -glycidoxypropylmethyldibutoxysilane, γ -glycidoxypropylmethyldiphenoxysilane, γ -glycidoxypropylethyldimethoxysilane, γ -glycidoxypropylethyldiethoxysilane, γ -glycidoxypropylvinylmethyldimethoxysilane, γ -glycidoxypropylvinylmethyldiethoxysilane, and phenylsulfonaminopropyltriethoxysilane.

[0063] The polymer material of the gap-fill material forming composition may typically comprise polymer material having a (weight average) molecular weight of from 500 to 100 000 g/mol, preferably 800 to 50,000 g/mol, and most preferably 1000 to 10,000 g/mol, measured against polystyrene standards.

[0064] The polymer material of the gap-fill material forming composition is typically formulated in organic solvent or organic solvents. In some embodiments, the polymer is formulated in organic solvent or solvents containing a curing catalyst. These curing catalysts are for the condensation of silanols to enhance crosslinking of the organosiloxane films. Typically, such metal-free silanol condensation catalysts are acids or bases, particularly latent acids or bases, which may be activated for example by light. By way of an example, it is also possible to employ an acid that decomposes during the heating step in film formation, thus releasing the latent organic base.

[0065] In some embodiments, the polymer is formulated in an organic solvent or organic solvents having a thermally labile curing catalyst to enhance crosslinking of the organosiloxane films.

5 [0066] In some embodiments, the polymer is formulated in an organic solvent or organic solvents having a photobase-containing curing catalyst.

[0067] In some embodiments, the polymer is formulated in an organic solvent or organic solvents having a photoacid-containing curing catalyst.

[0068] The amount of curing catalyst in the gap-fill forming material composition may be in the range of 0.05 to 10 % by weight, based on the solid content of the polymer, preferably 0.1 to 5 %, for example 0.5 to 3 % by weight, based on the solid content of the polymer.

15 [0069] The formulation can be optimized with various type of surfactants, such as silicone or fluoro surfactants, as they lower surface tension of the silanol-containing polysiloxane formulation coating. The use of such surfactants may improve coating quality if needed. The amount of surfactant is in a range of 0.001 % to 20 % by mass compared to silanol-containing organosiloxane amount, preferably 0.005 to 10 % by mass and most preferably 0.01 to 5 % or 0.05 to 2.5 % by mass.

[0070] The gap-fill material forming compositions of the present invention find use in the manufacture of gap-fill dielectric polymer films for semiconductor devices, optical elements and optical devices.

25 [0071] The dielectric polymer film of the present invention comprises a cured gap-fill material forming composition as discussed above. The gap-fill material forming compositions of the invention and the dielectric films comprising the cured gap-fill material forming composition are capable to fill gaps having a gap width of 20 nm or less, the gaps being located between different topographies, such as metal interconnects, on a semiconductor device substrate or on optical elements or optically active device substrates. Typically, the dielectric films as such are free of metals, which would cause a dielectric failure.

30 [0072] Surprisingly, it has been found that using monomers of formula I in polymeric films, optionally together with compounds of formula II and/or compounds of

formula III, excellent electric and mechanical properties are obtained. The dielectric polymer film comprising a cured gap-fill forming composition of the present kind has an electric breakdown voltage of at least 3.8 MV/cm, preferably at least 3.9 MV/cm, more preferably at least 4.0 MV/cm. In some embodiments, the dielectric polymer film may
5 have an electric breakdown voltage of at least 4.2 MV/cm or more, when measured using a MIS structure with mercury probe (Materials Development Corporation, model 802) and semiconductor parameter analyzer (Agilent 4155B).

[0073] The dielectric polymer film comprising a cured gap-fill forming composition of the present kind may have a dielectric constant at 1 MHz of 2.9 or less.

10 [0074] The present dielectric polymer films provide good optical properties. In some embodiments, the dielectric polymer film has a refractive index of at least 1.37 measured at a wavelength of 633 nm.

[0075] Typically, the dielectric polymer film has a shrinkage between soft bake and cure, which is less than 5%, more preferably less than 3% and most preferably less than
15 1%. Further, the dielectric polymer film exhibits a combination of low thermal expansion and modest elasticity/softness or significant hardness.

[0076] In some embodiments, the dielectric polymer film exhibits an elastic modulus of 8.5 GPa or more, such as 9.0 GPa or more.

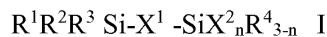
[0077] In some embodiments, the dielectric polymer film exhibits a hardness of 2.0
20 GPa or more, such as 2.2 GPa or more.

[0078] In some embodiments, by using monomers of formula I, in particular monomers of formula Ia, in amounts of at least 10 mol-%, of the total amount of monomers of the polymer composition, an increase in the breakdown voltage can be observed compared to dielectric films made of only monomers of formula II or III. At the
25 same time low dielectric constant is achieved.

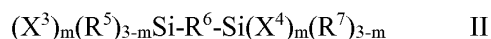
[0079] The dielectric polymer film has typically a thickness of less than 1 μm , in particularly less than 500 nm, more typically 50 to 350 nm.

[0080] The invention also relates to a method of forming a gap-fill dielectric polymer film, wherein the method comprises

- hydrolysing a first silicon compound having the formula I



- 5 wherein R^1 , R^2 , R^3 , X^1 , R^4 , X^2 and n have the same meanings as above; and
- polymerizing the first silicon compound, optionally with at least one second silicon compound obtained by hydrolysing a compound having the formula II



10

wherein R^5 , R^6 , R^7 , X^3 , X^4 and m have the same meanings as above,
and/or a compound having the formula III



15

wherein R^{14} , X^3 and n have the same meanings as above,
to provide a gap-fill coating composition; and
depositing the gap-fill coating composition on a substrate and curing the composition to form the gap-fill dielectric polymer film.

20 **[0081]** In some embodiments, the substrate is a semiconductor substrate. In some embodiments, the substrate is an optical element or an optically active device.

[0082] A semiconductor device may be produced by a method comprising the steps of providing a semiconductor device substrate, applying gap-fill material forming composition as disclosed herein onto the semiconductor device substrate and curing the composition to provide a gap-fill dielectric film on the semiconductor device substrate.

25

[0083] In some embodiments, the gap-fill material forming compositions may be applied for example by spin coating on the semiconductor substrate. In some embodiments, the curing step may comprise combining thermal and UV curing.

[0084] An optical element or an optically active device may be produced by a method comprising the steps of providing an optical element or an optically active device substrate, applying a gap-fill material forming composition as disclosed herein onto the

30

optical element or onto the optically active device substrate and curing the composition to provide a gap-fill dielectric film.

[0085] It is to be understood that the embodiments of the invention disclosed are not limited to the particular structures, process steps, or materials disclosed herein, but are
5 extended to equivalents thereof as would be recognized by those ordinarily skilled in the relevant arts. It should also be understood that terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting.

[0086] Reference throughout this specification to one embodiment or an embodiment means that a particular feature, structure, or characteristic described in
10 connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment. Where reference is made to a numerical value using a term such as, for example, about or substantially, the exact numerical value is also disclosed.

15 [0087] As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on
20 their presentation in a common group without indications to the contrary. In addition, various embodiments and example of the present invention may be referred to herein along with alternatives for the various components thereof. It is understood that such embodiments, examples, and alternatives are not to be construed as de facto equivalents of one another, but are to be considered as separate and autonomous representations of the
25 present invention.

[0088] Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of lengths, widths, shapes, etc., to provide a thorough understanding of embodiments of the invention. One
30 skilled in the relevant art will recognize, however, that the invention can be practiced without one or more of the specific details, or with other methods, components, materials, etc. In other instances, well-known structures, materials, or operations are not shown or

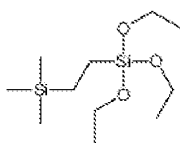
described in detail to avoid obscuring aspects of the invention.

[0089] The following non-limiting examples illustrate further embodiments.

EXPERIMENTAL

5 [0090] Monomers

[0091] **Monomer A:** 1-(trimethylsilyl)-2-(triethoxysilyl)-ethane



[0092] Synthesis of Monomer A:

Monomer A was prepared by adding vinyltrimethylsilane (VinTMS, 30 g), platinum catalyst (0.06 g), and acetic acid (0.02 g) to 250 ml flask. Solution was mixed thoroughly at 35 °C and triethoxysilane (HTEOS, 41 g) was added to solution. After the addition of HTEOS, the reaction mixture was kept at 35 °C overnight. After completion of reaction, distillation was carried out under reduced pressure. The amount of product obtained was 58 g (yield 88%, GC-MS purity 100%).

15 [0093] Polymer preparation

[0094] Polymer 1:

A co-polymer of the obtained monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane was prepared in a 250ml round bottom flask. The monomer A (2.4 g), 1-trimethoxysilyl-2-dimethoxymethyl-ethane (20.4 g), methanol (45 g) and 0.01M HCl (8.5 g) were added to flask. The reaction mixture was refluxed for 30 minutes and cooled down to room temperature after that. PGMEA (60 g) was added to the reaction mixture. Methanol and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 44 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number average molecular weights were determined to be 1086/773, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated

on silicon wafer for film characterization.

[0095] Polymer 2:

A co-polymer of the obtained monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane was prepared in a 250ml round bottom flask. The monomer A (3.7 g), 1-trimethoxysilyl-2-dimethoxymethyl-ethane (20.4 g), methanol (48 g) and 0.01M HCl (8.8 g) were added to flask. The reaction mixture was refluxed for 1 hour and cooled down to room temperature after that. PGMEA (90 g) was added to the reaction mixture. Methanol and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 31 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number average molecular weights were determined to be 996/729, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

[0096] Polymer 3:

A co-polymer of the obtained monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane was prepared in a 250ml round bottom flask. The monomer A (5.3 g), 1-trimethoxysilyl-2-dimethoxymethyl-ethane (20.4 g), methanol (51 g) and 0.01M HCl (9.1 g) were added to flask. The reaction mixture was refluxed for 1 hour and cooled down to room temperature after that. PGMEA (90 g) was added to the reaction mixture. Methanol and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 38 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number average molecular weights were determined to be 979/725, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

[0097] Polymer 4:

A polymer of the obtained monomer A and TEOS, MTEOS and HTEOS was prepared in a 250ml round bottom flask. The monomer A (5.7 g), TEOS (7.4 g), MTEOS (8.9 g), HTEOS (5.9 g), isopropanol (42 g) and 0.01M HCl (12.5 g) were added to flask. The reaction mixture was refluxed for 1 hour and cooled down to room temperature after that. PGMEA (90 g) was added to the reaction mixture. Methanol and hydrolysis products were

removed under reduced pressure yielding a formulation having a solid content of 50 %.
Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel
permeation chromatography (GPC). Weight average and number average molecular
weights were determined to be 1517/1057, respectively. The 6% formulation of polymer
5 was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

[0098] Polymer 5:

A polymer of the obtained monomer A and TEOS, MTEOS and HTEOS was prepared in a
250ml round bottom flask. The monomer A (6.2 g), TEOS (6.1 g), MTEOS (6.2 g),
HTEOS (4.8 g), isopropanol (35 g) and 0.01M HCl (10.2 g) were added to flask. The
10 reaction mixture was refluxed for 1 hour and cooled down to room temperature after that.
PGMEA (90 g) was added to the reaction mixture. Methanol and hydrolysis products were
removed under reduced pressure yielding a formulation having a solid content of 38 %.
Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel
permeation chromatography (GPC). Weight average and number average molecular
15 weights were determined to be 1369/996, respectively. The 6% formulation of polymer
was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

[0099] Polymer 6:

A co-polymer of the obtained monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-
ethane was prepared in a 250ml round bottom flask. The monomer A (3.5 g), 1-
20 trimethoxysilyl-2-dimethoxymethyl-ethane (5.1 g), methanol 13 g) and 0.01M HCl (2.8 g)
were added to flask. The reaction mixture was refluxed overnight and cooled down to room
temperature after that. PGMEA (60 g) was added to the reaction mixture. Methanol and
hydrolysis products were removed under reduced pressure yielding a formulation having a
solid content of 39 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and
25 characterized by gel permeation chromatography (GPC). Weight average and number
average molecular weights were determined to be 2061/1225, respectively. The 6%
formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for
film characterization.

[00100] Polymer 7:

30 A co-polymer of the obtained monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-
ethane was prepared in a 250ml round bottom flask. The monomer A (11.9 g), 1-

trimethoxysilyl-2-dimethoxymethyl-ethane (7.6 g), methanol (30 g) and 0.01M HCl (5.6 g) were added to flask. The reaction mixture was refluxed overnight and cooled down to room temperature after that. PGMEA (60 g) was added to the reaction mixture. Methanol and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 30 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number average molecular weights were determined to be 1407/1001, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

10 [00101] Polymer data

Polymers 1 to 7 described above and comparative examples 1 to 2 described below were analysed for their properties.

The measurements of the dielectric constant were done at 100 kHz frequency on films with target thickness of 340 nm ± 20 nm. The wafers were prebaked prior to measurement at 150 °C/5 min to remove any accumulated moisture and the measurement was carried out at room temperature.

Mechanical properties were measured by nanoindentation with Nanovea mechanical tester PB1000 with target load of 0.05 mN, loading and unloading rate of 0.02 V/min, approach speed 0.5 µm/min and contact load of 0.006 mN, and using Berkovich indenter and diamond as material. Hardness and elastic modulus were directly calculated from the curve of indentation by the Oliver-Pharr method.

Table 1. Polymer data

Polymer #	Monomer A mol-%	Mw (g/mol)	n @633nm	Shrinkage %	EBD (MV/cm)	k
1	10	1086	1.418	0.8	4.1	2.90
2	15	996	1.424	0.4	4.4	2.84
3	20	979	1.424	0.2	4.2	2.90
4	15	1517	1.384	0.6	3.5	2.80
5	20	1369	1.386	0.3	3.4	2.79
6	40	2061	1.417	-1.8	3.9	2.69
7	60	1407	1.424	-0.4	5.3	2.55

Table 2. Polymer data from comparative examples

Polymer #	Mw (g/mol)	n @633nm	Shrinkage %	EBD (MV/cm)	k
C1	1877	1.376	2.8	3.6	2.9
C2	1313	1.420	1.8	3.6	2.9

Table 3. Mechanical properties

Polymer #	Monomer A mol-%	Modulus (GPa)	Hardness (GPa)
C1	0	12.8	2.4
C2	0	12.4	2.4
1	10	10.1	2.3
2	15	11.4	2.4
3	20	9.1	2.4

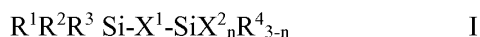
- 5
- As will appear from the above, by means of the present materials a combination of high electric breakdown voltage and low dielectric constant can be achieved, while maintaining mechanical properties at sufficient level. In addition, significant improvement in shrinkage performance can be seen by the present materials.
- 10
- [00102] Comparative examples**
- [00103] Comparative example 1 (C1):**
- A polymer consisting of TEOS, MTEOS (methyltriethoxysilane) and triethoxysilane (HTEOS) was prepared in a 4L flask. TEOS (57 g, 0.27 mol), MTEOS (98 g, 0.55 mol), HTEOS (45 g, 0.27 mol), isopropyl alcohol (301 g) and 0.01M HCl (97 g) were added to
- 15
- flask. The reaction mixture was refluxed for 30 minutes and cooled down to room temperature after that. PGMEA (900 g) was added to the reaction mixture. Acetone and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 40 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number
- 20
- average molecular weights were determined to be 1624/900, respectively. The 5% formulation of polymer was prepared with PGMEA and PGEE, and spin-coated on silicon wafer for film characterization.
- [00104] Comparative example 2 (C2):**

A homopolymer of 1-trimethoxysilyl-2-methyldimethoxysilyl-ethane was prepared in a 4L flask. 1-trimethoxysilyl-2-methyldimethoxysilyl-ethane (200 g, 0.78 mol), methanol (402 g) and 0.01M HCl (71 g) were added to flask. The reaction mixture was refluxed for 30 minutes and cooled down to room temperature after that. PGME (870g) was added to the reaction mixture. Acetone and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 25 %. Obtained polymer solution was filtered with 0.2 um PTFE filter and characterized by gel permeation chromatography (GPC). Weight average and number average molecular weights were determined to be 1313/629, respectively. The 5% formulation of polymer was prepared with PGMEA and PGME, and spin-coated on silicon wafer for film characterization.

[00105] Embodiments

[00106] As will be understood from the preceding description of the present invention and the illustrative examples, the present invention can be described by reference to the following embodiments:

1. A gap-fill material forming composition, comprising a polymer obtained by polymerization of monomers having formula I



wherein

- each X^1 is selected from the group of oxygen, optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms;

each X^2 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

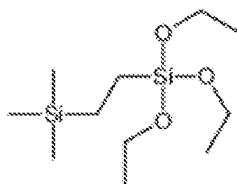
- each R^1 and R^2 and R^3 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

each R^4 is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

n is an integer of 1 to 3.

2. The gap-fill material forming composition according to embodiment 1, comprising at least 5 mol-%, preferably at least 10 mol-%, such as 10-20 mol-%, more preferably about 15 mol-%, of a polymer according to formula I.

3. The gap-fill material forming composition according to embodiment 1 or 2, obtained by copolymerization of compounds of formula I with silane monomers.
4. The gap-fill material forming composition according to embodiment 1, 2 or 3, obtained by copolymerization of compounds of formula I with silane monomers, wherein the
- 5 compounds of formula I amount to at least 5 mol% of the total amount of monomers of the polymer composition.
5. The gap-fill material forming composition according to any of the preceding embodiments, obtained by copolymerization of a compound of formula I with a compound of formula II
- 10 $(X^3)_m(R^5)_{3-m}Si-R^6-Si(X^4)_m(R^7)_{3-m}$ II
- wherein
- each X^3 and X^4 is independently selected from the group of hydrogen, organic or inorganic hydrolyzable groups;
- each R^5 and R^7 is independently selected from alkyl groups having 1 to 6 carbon atoms
- 15 and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;
- each R^6 is selected from the group of optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms; and
- 20 m is an integer of 1 to 3.
6. The gap-fill material forming composition according to any one of the preceding embodiments, wherein each X^1 and R^6 is independently selected from alkylene having 1 to 4, in particular 2 carbon atoms.
7. The gap-fill material forming composition according to any one of the preceding
- 25 embodiment, wherein the monomers according to formula I are selected from monomers having formula Ia



Ia.

8. The gap-fill material forming composition according to any one of embodiments 4-6, wherein the compounds of formula I amount to at least 10 mol-% and the compounds of formula II amount to at least 40 mol-% of the total amount of monomers.

9. The gap-fill material forming composition according to any of the preceding
5 embodiments, obtained by copolymerization of a compound of formula I with a compound of formula III



wherein

each X^4 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

10 each R^{14} is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted; and

n is an integer of 1 to 3.

10. The gap-fill material forming composition according to any one of the preceding
15 embodiments, wherein each X^2 , X^3 and X^4 is independently selected from the group of hydrogen and organic or inorganic hydrolysable groups selected from halogen, acyloxy, alkoxy and OH groups.

11. The gap-fill material forming composition according to any one of the preceding
20 embodiments, wherein each X^2 , X^3 and X^4 is independently selected from the group of hydrogen and R^9O- , wherein R^9 stands for an alkyl having 1 to 6 carbon atoms.

12. The gap-fill material forming composition according to any one of the preceding
embodiments, wherein each R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^8 and R^{14} is independently selected from alkyl groups having 1 to 4 carbon atoms and phenyl groups.

13. The gap-fill material forming composition according to any one of the preceding
25 embodiments, comprising polymer material having a (weight average) molecular weight of from 500 to 100 000 g/mol.

14. The gap-fill material forming composition according to any one of the preceding
embodiments, comprising polymer formulated in organic solvent or solvents.

15. The gap-fill material forming composition according to any one of the preceding
30 embodiments, comprising polymer formulated in organic solvent or solvents having a curing catalyst.

16. The gap-fill material forming composition according to any one of the preceding
embodiments, comprising polymer formulated in organic solvent or solvents having a thermally labile curing catalyst.

17. The gap-fill material forming composition according to any one of the preceding embodiments, comprising polymer formulated in organic solvent or solvents having photobase-containing curing catalyst.
18. The gap-fill material forming composition according to any one of the preceding
5 embodiments, comprising polymer formulated in organic solvent or solvents having photoacid-containing curing catalyst.
19. Use of the gap-fill material forming composition according to any one of the preceding embodiments for preparing a gap-fill dielectric film for semiconductor devices or optical elements.
- 10 20. A dielectric polymer film comprising a cured gap-fill material forming composition according to any one of embodiments 1 to 18.
21. The dielectric polymer film according to embodiment 20, having an electric breakdown voltage of at least 3.8 MV/cm, preferably at least 3.9 MV/cm, more preferably at least 4.0 MV/cm.
- 15 22. The dielectric polymer film according to embodiment 20 or 21, having an electric breakdown voltage of 4.2 MV/cm or more.
23. The dielectric polymer film according to any one of embodiments 20 to 22, having a dielectric constant at 1 MHz of 2.9 or less.
24. The dielectric polymer film according to any one of embodiments 20 to 23, having a
20 refractive index of at least 1.37 measured at a wavelength of 633 nm.
25. The dielectric polymer film according to any one of embodiments 20 to 24 having an elastic modulus of 8.5 GPa or more.
26. The dielectric polymer film according to any one of embodiments 20 to 25 having a shrinkage between soft bake and cure less than 5%, more preferably less than 3% and most
25 preferably less than 1%.
27. The dielectric polymer film according to any one of embodiments 20 to 26 having a thickness of less than 1 μm , in particularly less than 500 nm, typically 50 to 350 nm.
28. A method of forming a gap-fill dielectric polymer film, comprising:
- hydrolysing a first silicon compound having the formula I
30
$$\text{R}^1\text{R}^2\text{R}^3\text{Si-X}^1\text{-SiX}^2_n\text{R}^4_{3-n} \quad \text{I}$$

wherein R^1 , R^2 , R^3 , X^1 , R^4 , X^2 and n have the same meanings as above; and
 - polymerizing the first silicon compound, optionally with at least one second silicon compound obtained by hydrolysing a compound having the formula II

$$(\text{X}^3)_m(\text{R}^5)_{3-m}\text{Si-R}^6\text{-Si}(\text{X}^4)_m(\text{R}^7)_{3-m} \quad \text{II}$$

wherein R^5 , R^6 , R^7 , X^3 , X^4 and m have the same meanings as above,
and/or a compound having the formula III



wherein R^{14} , X^4 and n have the same meanings as above,

5 to provide a gap-fill coating composition; and

- depositing the gap-fill coating composition on a substrate and curing the composition to form the gap-fill dielectric polymer film.

29. The method according to embodiment 28, wherein the substrate is a semiconductor substrate.

10 30. The method according to embodiment 28, wherein the substrate is an optical element or an optically active device.

31. A method for producing a semiconductor device, the method comprising:

- providing a semiconductor device substrate;
 - applying gap-fill material forming composition according to any one of
- 15 embodiments 1 to 18 onto the semiconductor device substrate and curing the composition to provide a gap-fill dielectric film on the semiconductor device substrate.

32. The method according to embodiment 31, wherein the gap-fill material forming composition is cured by combining thermal and UV curing to provide the gap-fill

20 dielectric film.

33. A method for producing an optical element or an optically active device, comprising the steps of

- providing an optical element or optically active device substrate
 - applying a gap-fill material forming composition according to any one of
- 25 embodiments 1 to 18 onto the optical element or onto the optically active device substrate and baking the composition to form a gap-fill dielectric film.

34. A semiconductor device comprising a dielectric polymer film according to any one of embodiments 20 to 27.

35. An optical element or an optical device substrate comprising a dielectric polymer film

30 according to any one of embodiments 20 to 27.

[00107] While the forgoing examples are illustrative of the principles of the present invention in one or more particular applications, it will be apparent to those of ordinary

skill in the art that numerous modifications in form, usage and details of implementation can be made without the exercise of inventive faculty, and without departing from the principles and concepts of the invention. Accordingly, it is not intended that the invention be limited, except as by the claims set forth below.

- 5 **[00108]** The verbs “to comprise” and “to include” are used in this document as open limitations that neither exclude nor require the existence of also un-recited features. The features recited in depending claims are mutually freely combinable unless otherwise explicitly stated. Furthermore, it is to be understood that the use of "a" or "an", that is, a singular form, throughout this document does not exclude a plurality.

10

INDUSTRIAL APPLICABILITY

- [00109]** At least some embodiments of the present invention find industrial application in semiconductor devices, optical elements and optically active devices. The present dielectric polymer film may be used for coating of semiconductor device
- 15 substrates, optical elements and optically active devices, where they provide high breakdown voltage and low dielectric constant.

ACRONYMS LIST

- | | | |
|----|--------|--|
| | CVD | chemical vapor deposition |
| | GC-MS | gas chromatography – mass spectrometry |
| 20 | GPC | gel permeation chromatography |
| | HTEOS | triethoxysilane |
| | MIS | metal-insulator-semiconductor |
| | MTEOS | methyltriethoxysilane |
| | PGEE | propylene glycol ethyl ether |
| 25 | PGME | propylene glycol methyl ether |
| | PGMEA | propylene glycol methyl ether acetate |
| | PTFE | polytetrafluoroethylene |
| | TEOS | tetraethyl orthosilicate |
| | VinTMS | vinyltrimethylsilane |

CITATION LIST

Patent Literature

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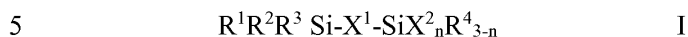
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Non Patent Literature

- 10 Khudobin, Y.I., Makarskaya, V.M., Makarskii, V.V. et al. 1-(Triorganylsilyl)-2-(triethoxysilyl)ethanes. Russ Chem Bull 25, 1538–1540 (1976).
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CLAIMS:

1. A gap-fill material forming composition, comprising a polymer obtained by polymerization of monomers having formula I



wherein

each X^1 is selected from the group of oxygen, optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms;

10 each X^2 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups; each R^1 and R^2 and R^3 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

each R^4 is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6
15 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being substituted;

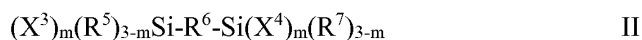
n is an integer of 1 to 3.

2. The gap-fill material forming composition according to claim 1, comprising at least 5
20 mol-%, preferably at least 10 mol-%, such as 10-20 mol-%, more preferably about 15 mol-%, of a polymer according to formula I.

3. The gap-fill material forming composition according to claim 1 or 2, obtained by
25 copolymerization of compounds of formula I with silane monomers.

4. The gap-fill material forming composition according to claim 1, 2 or 3, obtained by
copolymerization of compounds of formula I with silane monomers, wherein the
compounds of formula I amount to at least 5 mol% of the total amount of monomers of the
polymer composition.

30 5. The gap-fill material forming composition according to any of the preceding claims, obtained by copolymerization of a compound of formula I with a compound of formula II



wherein

each X^3 and X^4 is independently selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

each R^5 and R^7 is independently selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups

5 optionally being substituted;

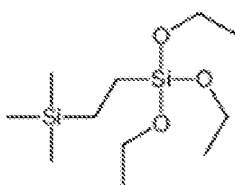
each R^6 is selected from the group of optionally substituted bridging linear or branched bivalent hydrocarbyl groups, such as alkylene having 1 to 6 carbon atoms and arylene having 6 to 10 carbon atoms; and

m is an integer of 1 to 3.

10

6. The gap-fill material forming composition according to any one of the preceding claims, wherein each X^1 and R^6 is independently selected from alkylene having 1 to 4, in particular 2 carbon atoms.

15 7. The gap-fill material forming composition according to any one of the preceding claims, wherein the monomers according to formula I are selected from monomers having formula Ia

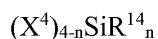


Ia.

20

8. The gap-fill material forming composition according to any one of the preceding claims, wherein the compounds of formula I or Ia amount to at least 10 mol-% and the compounds of formula II amount to at least 40 mol-% of the total amount of monomers.

25 9. The gap-fill material forming composition according to any of the preceding claims, obtained by copolymerization of a compound of formula I with a compound of formula III



III

wherein

each X^4 is selected from the group of hydrogen, organic or inorganic hydrolyzable groups;

each R^{14} is selected from alkyl groups having 1 to 6 carbon atoms and aryl groups having 6 to 18 carbon atoms, such as phenyl or benzyl groups, said groups optionally being

5 substituted; and

n is an integer of 1 to 3.

10. The gap-fill material forming composition according to any one of the preceding claims, wherein each X^2 , X^3 and X^4 is independently selected from the group of hydrogen
10 and organic or inorganic hydrolysable groups selected from halogen, acyloxy, alkoxy and OH groups.

11. The gap-fill material forming composition according to any one of the preceding claims, wherein each X^2 , X^3 and X^4 is independently selected from the group of hydrogen
15 and R^9O- , wherein R^9 stands for an alkyl having 1 to 6 carbon atoms.

12. The gap-fill material forming composition according to any one of the preceding claims, wherein each R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^8 and R^{14} is independently selected from
20 alkyl groups having 1 to 4 carbon atoms and phenyl groups.

13. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer material having a (weight average) molecular weight of from 500 to 100 000 g/mol, preferably 800 to 50 000 g/mol, more preferably less than 10 000 g/mol, typically 1000 to 10 000 g/mol.

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14. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer formulated in organic solvent or solvents.

15. The gap-fill material forming composition according to any one of the preceding
30 claims, capable of filling gaps having a width of 20 nm or less, particularly when deposited by spin-coating.

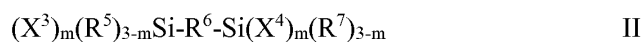
16. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer formulated in organic solvent or solvents having a curing catalyst.
- 5 17. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer formulated in organic solvent or solvents having a thermally labile curing catalyst.
- 10 18. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer formulated in organic solvent or solvents having photobase-containing curing catalyst.
- 15 19. The gap-fill material forming composition according to any one of the preceding claims, comprising polymer formulated in organic solvent or solvents having photoacid-containing curing catalyst.
- 20 20. Use of the gap-fill material forming composition according to any one of the preceding claims for preparing a gap-fill dielectric film for semiconductor devices or optical elements.
21. The use according to claim 20, wherein the gap-fill dielectric film has
- an electric breakdown voltage of at least 3.8 MV/cm, preferably at least 3.9 MV/cm, more preferably at least 4.0 MV/cm;
 - a dielectric constant at 1 MHz of 2.9 or less;
 - 25 - a refractive index of at least 1.37 measured at a wavelength of 633 nm;
 - an elastic modulus of 8.5 GPa or more;
 - a shrinkage between soft bake and cure less than 5%, more preferably less than 3% and most preferably less than 1%.
- 30 22. A dielectric polymer film comprising a cured gap-fill material forming composition according to any one of claims 1 to 19.

23. The dielectric polymer film according to claim 22, having an electric breakdown voltage of at least 3.8 MV/cm, preferably at least 3.9 MV/cm, more preferably at least 4.0 MV/cm.
- 5 24. The dielectric polymer film according to claim 22 or 23, having an electric breakdown voltage of 4.2 MV/cm or more.
25. The dielectric polymer film according to any one of claims 22 to 24, having a dielectric constant at 1 MHz of 2.9 or less.
- 10 26. The dielectric polymer film according to any one of claims 22 to 25, having a refractive index of at least 1.37 measured at a wavelength of 633 nm.
27. The dielectric polymer film according to any one of claims 22 to 26 having an elastic modulus of 8.5 GPa or more.
- 15 28. The dielectric polymer film according to any one of claims 22 to 27 having a shrinkage between soft bake and cure less than 5%, more preferably less than 3% and most preferably less than 1%.
- 20 29. The dielectric polymer film according to any one of claims 22 to 28 having a thickness of less than 1 μm , in particular less than 500 nm, typically 50 to 350 nm.
30. A method of forming a gap-fill dielectric polymer film, comprising:
- 25 – hydrolysing a first silicon compound having the formula I



wherein R^1 , R^2 , R^3 , X^1 , R^4 , X^2 and n have the same meanings as above; and

- 30 – polymerizing the first silicon compound, optionally with at least one second silicon compound obtained by hydrolysing a compound having the formula II



wherein R^5 , R^6 , R^7 , X^3 , X^4 and m have the same meanings as above,
and/or a compound having the formula III



5

wherein R^{14} , X^4 and n have the same meanings as above,
to provide a gap-fill coating composition; and

- depositing the gap-fill coating composition on a substrate and curing the composition to form the gap-fill dielectric polymer film.

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31. The method according to claim 30, wherein the substrate is a semiconductor substrate.

32. The method according to claim 30, wherein the substrate is an optical element or an optically active device.

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33. The method according to any one of claims 30 to 32, wherein the gap-fill coating composition is deposited on the substrate in liquid form by a spin-coating process.

34. A method for producing a semiconductor device, the method comprising:

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- providing a semiconductor device substrate;
- applying gap-fill material forming composition according to any one of claims 1 to 18 onto the semiconductor device substrate and curing the composition to provide a gap-fill dielectric film on the semiconductor device substrate.

25

35. The method according to claim 34, wherein the gap-fill material forming composition is cured by combining thermal and UV curing to provide the gap-fill dielectric film.

36. A method for producing an optical element or an optically active device, comprising the steps of

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- providing an optical element or optically active device substrate
- applying a gap-fill material forming composition according to any one of claims 1 to 18 onto the optical element or onto the optically active device substrate and baking the composition to form a gap-fill dielectric film.

37. A semiconductor device comprising a dielectric polymer film according to any one of claims 22 to 29.

38. An optical element or an optical device substrate comprising a dielectric polymer film
5 according to any one of claims 22 to 29.