LOW DIELECTRIC CONSTANT THIN FILMS, A METHOD OF PRODUCING THE SAME AND USES THEREOF

FIELD

[0001] The present invention relates to low dielectric constant films comprising organopolysiloxanes obtained by polymerization of organofunctionalized monomers. The invention also concerns a method of forming such films by preparing organopolysiloxane material by polymerization of the organofunctionalized monomers, by applying compositions comprising the organopolysiloxane material on a substrate in the form of a layer and by curing the layer to form a film. Further, the invention concerns uses of the low dielectric constant films of the invention in semiconductor devices and optical elements or optoelectronic devices. Another object of the present invention is to provide a method of manufacturing semiconductor devices or optical elements or optoelectrical devices comprising the low k dielectric films of the invention.

BACKGROUND

[0002] Built on semiconductor substrates, integrated circuits comprise millions of transistors and other devices, which communicate electrically with one another 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 integrated circuit input and output (I/O) connections. The patterning for a given layer is often performed by a multi-step process comprising layer deposition, photoresist coating, 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.

[0003] As an interconnect material, aluminum has been utilized for many years due to its high conductivity, good adhesion to SiO_2, 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 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 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 of 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. Potential metals for sub-20-nm processes include cobalt (Co), ruthenium (Ru), tungsten (W) and molybdenum (Mo). 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.

[0005] 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). In particular, aside from possessing a low dielectric constant, new dielectrics especially for sub-20-nm processes should also exhibit a low shrinkage and high electric breakdown voltage, along with sufficiently high modulus and hardness and good thermal stability.

[0006] Therefore, 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 a low dielectric constant, high electric breakdown voltage values and a low shrinkage, without compromising other properties of the dielectric polymer film, such as modulus and hardness. It is also one aim of the present invention to provide dielectric films, which, when corresponding film forming compositions are deposited as a layer in liquid form on a substrate and cured, fill dimensions or gap widths of 20 nm or less.

SUMMARY OF THE INVENTION

[0007] The invention is defined by the features of the independent claims. Some specific embodiments are defined in the dependent claims.

[0008] It is one object of the present invention to provide novel polymer films having a low dielectric constant for use as insulators in semiconductor devices and optical elements or optoelectronic devices. It is also one object of the present invention to provide a method of manufacturing said films. Another object of the present invention is to provide a method of manufacturing semiconductor devices comprising the low k dielectric films of the invention, in particular semiconductor devices which comprise substrates deposited with metals selected from cobalt (Co), ruthenium (Ru), tungsten (W) and molybdenum (Mo). A still further object of the invention is a method of manufacturing optical elements or optoelectronical devices, which comprise the low k dielectric films of the invention.

[0009] The present invention is based on the finding that polymers obtained by polymerization of certain organo functionalized monomers provide excellent polymer

films for low k dielectric applications, in particular low k polymer films with low shrinkage and high electric breakdown voltage.

[0010] According to a first aspect of the present invention, there is thus provided an organopolysiloxane composition for forming a low dielectric constant polymer film, the composition comprising polymerized organopolysiloxane material obtained by polymerization of compounds having formula I

$$X^1{}_mR^1{}_{3-m}Si\text{-}O\text{-}(R^3{}_2Si\text{-}O)_n\text{-}\ SiX^2{}_pR^2{}_{3-p} \qquad I$$

wherein each X^l and X^2 is independently selected from the group of hydrogen and organic or inorganic hydrolyzable groups;

each R^1 and R^2 is independently selected from the group of hydrocarbyl residues, which optionally are substituted;

each R^3 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 5;

m is an integer of 1 to 3; and

p is an integer of 1 to 3.

[0011] According to a second aspect of the present invention, there is provided a low dielectric constant polymer film comprising a cured organopolysiloxane composition of the invention.

[0012] According to a third aspect of the invention, there is a provided a method of forming a low dielectric constant polymer film, wherein the method comprises the steps of hydrolysing a compound having the formula I defined above, polymerizing the compound, optionally with other organo functionalized monomers, to produce a polymerized organopolysiloxane material, and shaping the polymerized organopolysiloxane material into a layer, which is cured into a film.

[0013] The invention also relates to a method of manufacturing a semiconductor device, which comprises the organopolysiloxane composition of the invention cured to a low-k dielectric polymer film.

[0014] In a further aspect the invention relates to a method of manufacturing an optical element or an optoelectrical device, which comprises the organopolysiloxane composition of the invention cured to a low-k dielectric polymer film.

[0015] Embodiments of the invention relate to the use of the low dielectric constant polymer films of the invention in semiconductor devices or optical or optoelectronic devices.

[0016] Finally, the invention relates also to semiconductor devices, optical elements or optoelectronic devices comprising the low dielectric constant polymer film of the invention.

[0017] More specifically, the present invention is characterized by what is stated in the independent claims.

[0018] Considerable advantages are obtained by the invention. First, the present materials provide thin polymeric films with a low dielectric constant and a low shrinkage. Shrinkage refers to the thickness loss of the film between soft bake and high temperature cure. Low shrinkage decreases the amount of stress formation in the polymer films during high temperature cure.

[0019] Second, the present polymer films provide a high electric breakdown voltage. A high electric breakdown voltage prevents the device or transistor becoming non-operational due to sudden voltage changes.

[0020] Third, the present polymer films provide sufficiently high modulus and hardness, which contribute to the binding together of the maze of metal interconnects and vias when manufacturing semiconductor devices or optoelectronic devices, particularly in the final chip packaging step. Further, as a result of their good adhesive properties, the films will contribute to forming of stable interface between the dielectric and contacting materials.

[0021] Further, the substrate, which is used for deposition of the siloxane material, may contain a variety of topographies. These include narrow trenches which may have high aspect ratio, meaning that the trenches exhibit a depth-to-width ratio (or aspect ratio) exceeding 2:1, for example 3:1 or higher. The present materials have excellent capabilities to fill even trench widths below 20 nm or more preferably below 10 nm. In parallel, the

siloxane materials exhibit excellent planarization properties. The planarization property refers to the ability of the siloxane material to even out height differences on the substrate arising from the variety of topographies present on the substrate prior to coating. The ability to planarize the substrate has significant benefits as subsequent processes to flatten the substrate surface may be eliminated or reduced. In this way, considerable benefits can be achieved in manufacturing cost and time. In addition, the films are readily processible by chemical mechanical polishing or by an etch back process in cases where the film thickness needs to be reduced or a more flat topography is needed in subsequent manufacturing process steps.

[0022] The siloxane materials according to the present invention are thus also thermally stable. As apparent from above, good thermal stability is required in order for the coatings to withstand multiple thermal cycles in the semiconductor manufacturing process. Further, the present materials exhibit a low coefficient of thermal expansion (CTE), which is beneficial to prevent bowing of the substrate in the manufacturing process.

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

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIGURE 1 illustrates in a schematic fashion the various stages in the production of a semiconductor device comprising a low k dielectric.

[0025] FIGURE 2 illustrates illustrates in a schematic fashion the various stages in the production of a semiconductor device comprising a low k dielectric consisting of a film of organopolysiloxane material according to the present technology.

EMBODIMENTS

[0026] In the following, embodiments of the present technology are described in more detail.

[0027] The present invention is based on the finding that polymers obtained by polymerization of certain organofunctionalized monomers provide excellent polymer films for low k dielectric applications, in particular low k polymer films with low shrinkage and high electric breakdown voltage.

[0028] The embodiments disclose the production and use of low dielectric constant polymer films which comprise organopolysiloxane polymers which exhibit –(Si-O-Si)– segments, in which the silicon atoms typically bear hydrocarbyl substituents, such as lower alkyl groups. Such polymeric films are obtained by polymerizing, either by homopolymerization or by copolymerization, of monomers as herein disclosed.

[0029] 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 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 ethers.

[0030] 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, hydrocholoric 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.

[0031] Bases used in the synthesis may similarly be inorganic or organic. Typical inorganic bases and 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 P_1-t-Bu, P_2-t-Bu, P_4-t-Bu), and quarternary ammonium compounds (such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide).

[0032] 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.

[0033] Using appropriate conditions, embodiments of the present method yield polymerized organopolysiloxane material in a solution, preferably in an organic solvent system, said polymerized organopolysiloxane material having a molecular weight of about 500 to 50,000 g/mol, measured against polystyrene standards.

[0034] In some embodiments, the solvent in which hydrolysis and polymerization is carried out, is after polymerization changed for a solvent that provides the material better coating performance and product storage properties through some form of stabilization. Such stabilizing organic solvent system is formed by an organic ether optionally in mixture with other co-solvent or co-solvents. The organic ether is a linear, branched or cyclic ether comprising generally 4 to 26 carbon atoms and optionally other functional groups, such as hydroxyl groups. Particularly suitable examples are five and six membered cyclic ethers, which optionally bear substituents on the ring, and ethers, such as (C1-20) alkanediol (C1-6) alkyl ethers. Examples of said alkanediol alkyl ethers are propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, dipropyleneglycol n-butyl ether, tripropylene glycol monomethyl ether and mixtures thereof. Particularly preferred examples of the present ethers are methyl tetrahydrofurfuryl ether, tetrahydrofurfuryl alcohol, propylene glycol n-propyl ether, dipropylene glycol dimethyl ether, propylene glycol n-methyl ether, propylene glycol n-ethyl ether and mixtures thereof. The stabilizing solvent system consists of a solvent comprising of the ether of this kind alone, or of a mixture-of such ether with a typical reaction medium of the hydrolyzation or other solvents such as propylene glycol monomethyl ether acetate. The proportion of the ether is, in such

a case, about 10 to 90 wt-%, in particular about 20 to 80 wt-% of the total amount of the solvent.

[0035] The solid content of the organopolysiloxane composition, consisting of selected solvents and the hydrolysis and polymerization product, is typically in the range of 0.1 to 50 %, preferably 1 to 20 % and most preferably 5 to 10 % by weight. In some embodiments, the organopolysiloxane composition comprises the polymerized organopolysiloxane material in a solution in an amount of 5 to 10 %, such as about 6%.

[0036] In one embodiment, the polymerized organopolysiloxane material in a solution has a dynamic viscosity of 0.5-50 mPas, measured by a viscosimeter.

[0037] The polymerized organopolysiloxane material in a solution is deposited in the form of a thin layer on a substrate and cured into a polymer film.

[0038] Thus the present invention relates in its first embodiment to an organosiloxane composition for forming a low dielectric constant polymer film, the organosiloxane composition comprising polymerized organopolysiloxane material obtained by polymerization of compounds having formula I

$$X^1{}_mR^1{}_{3-m}Si\text{-}O\text{-}(R^3{}_2Si\text{-}O)_n\text{-}\ SiX^2{}_pR^2{}_{3-p} \qquad I$$

wherein

each X^1 and X^2 is independently selected from the group of hydrogen and organic or inorganic hydrolyzable groups;

each R^1 and R^2 is independently selected from the group of hydrocarbyl residues, which optionally are substituted;

each R^3 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 5;

m is an integer of 1 to 3; and

p is an integer of 1 to 3.

[0039] According to one embodiment, in formula I, each X^1 and X^2 is independently selected from hydrogen, halogen, acyloxy, alkoxy and OH groups.

[0040] In one embodiment, in formula I each X^1 and X^2 is independently selected from hydrogen, chlorine, bromine, fluorine, and R^4O-, wherein R^4 stands for an alkyl having 1 to 6 carbon atoms.

[0041] In one embodiment, in formula I each X^1 and X^2 is independently selected from R^4O-, wherein R^4 stands for an alkyl having 1 to 6 carbon atoms, preferably methyl or ethyl.

[0042] In one embodiment, in formula I each R^1 and R^2 is independently selected from the group of optionally functionalized linear, branched or cyclic, bivalent, saturated or unsaturated hydrocarbyl radicals.

[0043] In one embodiment, in formula I each R^1 and R^2 is independently selected from the group of linear, branched and cyclic alkyl groups having 1 to 10 carbon atoms, aryl groups containing 1 to 5 aromatic rings, optionally containing 1 to 3 heteroatoms, wherein each of the mentioned groups may optionally be substituted with 1 to 3 functional groups selected from halo, hydroxyl, alkoxy, vinyl and acetyl groups.

[0044] In one embodiment, in formula I each R^1 and R^2 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.

[0045] In one embodiment, hydrocarbyl groups such as R^1 and R^2, may decompose during the film curing procedure and leave behind a cross-linking group or polarizability reducing group or a combination of thereof. If group is a leaving group, still very small pore size is resulted in, i.e., typically 1.5 nm or less. However, the polymer formed according to the present technology is also compatible with traditional type porogens such as cyclodextrin, which can be used to form micro-porosity into the polymer and thus reduce the dielectric constant of the polymer.

[0046] Examples of organic crosslinking groups, reactive cleaving groups or polarizability reducing organic groups are an alkyl, alkenyl, alkynyl, aryl, polycyclic group or organic containing silicon group. The group may also be fully or partially halogenated.

[0047] In one embodiment, in formula I the symbol n stands for an integer of 1 to 3, preferably 2.

[0048] In one embodiment, the symbols m and p in the compound of formula I are independently of each other 2 or 3, preferably 3.

[0049] As used herein, “alkoxy” and “acyloxy” groups typically have 1 to 6 carbon atoms.

[0050] As used herein, “halogen” has the conventional meaning and stands in particular for chloro, fluoro or bromo. As used herein, “halide” has the conventional meaning and stands for a halogen compound.

[0051] In one embodiment the low dielectric constant polymer film comprises polymerized organopolysiloxane material obtained by homopolymerization of compounds of formula I.

[0052] In one embodiment, the polymerized organopolysiloxane material comprises 1,3-bis(triethoxysiloxy)tetramethyldisiloxane as a compound of formula I, preferably in an amount of at least 40 mol%, more preferably at least 70 mol%, of the total amount of polymerized compounds.

[0053] In one embodiment, the low dielectric constant polymer film comprises polymerized organopolysiloxane material obtained by homopolymerization of 1,3-bis(triethoxysiloxy)tetramethyldisiloxane. Thus in one embodiment 100 mol% of the total amount of polymerized compounds may consist of 1,3-bis(triethoxysiloxy)tetramethyldisiloxane.

[0054] Typically, the polymerized organopolysiloxane material, such as polymerized compounds of formula I, have a weight average molecular weight in the range of 500 - 50 000 g/mol, measured by gel-permeation chromatography using polystyrene standards.

[0055] In one embodiment the organopolysiloxane composition is obtained by copolymerization of compounds of general formula I with silane monomers. Typically, the compounds of formula I are present in an amount of at least 40 mol% of the total amount of polymerized compounds and monomers.

[0056] In one embodiment, the organopolysiloxane composition is obtained by copolymerization of compounds of formula I

- with compounds of formula II

$$(R^5)_2R^6Si\text{-}R^7\text{-}SiR^5{}_3 \qquad \text{II}$$

wherein

R^5 is a hydrolysable group, such as hydrogen, a halide, an alkoxy or an acyloxy group;

R^6 is hydrogen, an organic crosslinking group, a reactive cleaving group or a polarizability reducing organic group; and

R^7 is a bridging linear or branched bivalent hydrocarbyl group; and/or

- with compounds of formula III

$$(X^3)_{4-n}SiR^8{}_n \qquad \text{III}$$

wherein

X^3 is hydrogen or a hydrolysable group selected from halogen, acyloxy, alkoxy and OH groups;

R^8 is selected from halogen, acyloxy, alkoxy and OH groups, and alkyl groups having 1 to 6 carbon atoms, vinyl groups having from 2 to 6 carbon atoms, and aryl groups having 6 carbon atoms; and

n is an integer of 1 to 3, preferably 2.

[0057] In formula II, R^5 is preferably selected from the group of halides, alkoxy groups, acyloxy groups and hydrogen, R^6 is preferably selected from alkyl groups, alkenyl groups, alkynyl and aryl groups, polycyclic group or organic containing silicon group, and R^7 is preferably selected from linear and branched alkylene groups, alkenylene groups and alkynylene groups, bivalent alicyclic groups (polycyclic groups) and bivalent aromatic groups which all are included in the definition of a bivalent hydrocarbyl group.

[0058] “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.

[0059] 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.

[0060] Specific examples of compounds of formula III include, but are not limited to, tetramethoxysilane, tetrachlorosilane, tetraacetoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane, methyltrimethoxysilane, methyltriethoxysilane, methyltrichlorosilane, methyltriacetoxysilane, methyltripropoxysilane, methyltributoxysilane, methyltriphenoxysilane, methyltribenzyloxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriacetoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, phenyltrichlorosilane, phenyltriacetoxysilane, phenyltriethoxysilane, γ-chloropropyltrimethoxysilane, γ-chloropropyltriethoxysilane, γ-chloropropyltriacetoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, γ-methacryloxypropyltrimethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane, β-cyanoethyltriethoxysilane, chloromethyltrimethoxysilane, chloromethyltriethoxysilane, dimethyldimethoxysilane, phenylmethyldimethoxysilane, dimethyldiethoxysilane, phenylmethyldiethoxysilane, γ-chloropropylmethyldimethoxysilane, γ-chloropropylmethyldiethoxysilane, dimethyldiacetoxysilane, γ-methacryloxypropylmethyldimethoxysilane, γ-methacryloxypropylmethyldiethoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptomethyldiethoxysilane, methylvinyldimethoxysilane, methylvinyldiethoxysilane, 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-glycidoxypropylvinyldimethoxysilane, γ-glycidoxypropylvinyldiethoxysilane, and phenylsulfonylaminopropyltriethoxysilane

[0061] When compounds of formula II are present, *i.e.* when copolymers are produced, the organopolysiloxane composition is typically obtained by copolymerization of a compound of formula I with a compound of formula II in a molar ratio of 90:10 to 10:90, for example 80:20 to 20:80, in particular 60:40 to 40:60, preferably 90:10.

[0062] When compounds of formula III are present, the organopolysiloxane composition is typically obtained by copolymerization of a compound of formula I with a compound of formula III in a molar ratio of 90:10 to 10:90, for example 80:20 to 20:80, in particular 60:40 to 40:60, preferably 90:10.

[0063] The organopolysiloxane composition may also comprise compounds of formula I with compounds of formula II and formula III. In one embodiment, the organopolysiloxane composition comprises a copolymer obtained by polymerization of a compound of formula I with a compound of formula II and/or a compound of formula III, wherein the copolymer comprises at least 10 mol%, preferably at least 30 mol%, more

preferably at least 40 mol%, and still more preferably at least 50 mol% of a compound of formula I, based on the total amount of polymerized compounds and monomers.

[0064] As stated above, typically the polymerized organopolysiloxane material has a (weight average) molecular weight in the range of 500 - 50 000 g/mol, preferably 500 to 10,000 g/mol, and most preferably 600 to 3,000 g/mol, measured by gel-permeation chromatography using polystyrene standards.

[0065] The organopolysiloxane composition typically comprises the polymerized organopolysiloxane material in a solution, preferably in an organic solvent or solvents. In some embodiments the organopolysiloxane composition comprises the polymerized organopolysiloxane material in a solution in an amount of 1 to 10 wt%, preferably about 6 wt%, providing a composition with a low viscosity, such as 0.5-50 mPas, measured by viscosimeter.

[0066] As stated above, the invention also relates to a low dielectric constant polymer film comprising a cured organopolysiloxane composition of the invention. Preferably, the low dielectric constant polymer film has a dielectric constant at 1 MHz of 2.85 or less, more preferably 2.8 or less.

[0067] Surprisingly, it has been found that using monomers of formula I in polymeric films, optionally together with monomers of formula II and/or formula III, excellent electric properties are obtained. Further, it has also been found that by incorporating a short linear segment (n having a value of 1 to 5) a material can be obtained which exhibits a combination of low thermal expansion and modest elasticity/softness or significant hardness.

[0068] The polymer film according to the invention has an electric breakthrough voltage of 3.3 MV/cm or more. A high breakdown voltage is needed to guarantee reliability of the final device.

[0069] Moreover, the polymer film according to the invention has a low shrinkage. Shrinkage is determined by measuring the thickness loss of the film between soft bake and cure. “Soft bake” refers to baking at 150-300 °C, whereas high temperature cure typically takes place at 400 °C. The thickness of the film is measured with a spectroscopic ellipsometer. Typically, the polymeric film of the invention has a shrinkage between soft bake and cure, which is less than 5%, more preferably less than 3% and most preferably

less than 1%. Low shrinkage decreases the amount of stress formation in the polymer films during high temperature cure.

[0070] In embodiments, using monomers of formula I in amounts of at least 40 mol% of the total amount of silane monomers, significant improvement of shrinkage values can be observed compared to films made of other monomers, such as monomers of formula II and/or formula III. The improvement in shrinkage values is detected for both homopolymers and copolymers which include monomers of formula I.

[0071] Preferably, the low constant dielectric polymer film according to the invention has a thickness of less than 1 µm, in particular less than 500 nm, typically 50 to 350 nm.

[0072] The present polymer films have also good optical properties. Thus, a polymer film of the present kind may have a refractive index (RI) greater than 1.35, preferably greater than 1.37, determined at a wavelength of 633 nm.

[0073] The present polymer films exhibit also sufficient mechanical properties. Thus, a polymer film of the present kind may have an elastic modulus of > 5 GPa, preferably > 7 GPa, most preferably >10 GPa. Typically, the present polymer films have a hardness of > 1 GPa, preferably >1.3 GPa, most preferably >1.6 GPa. Hardness and elastic modulus of films can be calculated from curve of nanoindentation by the Oliver-Pharr method.

[0074] The present polymer films provide also excellent thermal properties. As discussed above, a good thermal stability is required for the coatings to withstand multiple thermal cycles in the semiconductor manufacturing process. Further, the polymer films herein disclosed exhibit low coefficients of thermal expansion (CTE), which is beneficial to prevent bowing of the substrate in the manufacturing process. In addition, the present polymer films also have suitable glass transition temperatures for the purposes of the invention.

[0075] The organopolysiloxane composition 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 organopolysiloxane amount, preferably 0.005 to 10 % by mass and most preferably 0.01 to 5 % or 0.05 to 2.5 % by mass.

[0076] Further, the organopolysiloxane composition can be optimized with various types of photo or thermally labile catalysts or compounds added to formulation mixture to enhance crosslinking of the organosiloxane films. If present, the amount of thermo- or photo-labile compounds in the formulation is in the range of 0.05 to 20 % by mass compared to the amount of the organopolysiloxane, preferably 0.1 to 10 % and most preferably 0.5 to 5 % or 0.5 to 3 % by mass, corresponding to the solid content of the polymer.

[0077] The invention also relates to a method of forming a low dielectric constant polymer film, wherein the method comprises

- hydrolysing a first compound having the formula I

$$X^1{}_mR^1{}_{3-m}Si\text{-}O\text{-}(R^3{}_2Si\text{-}O)_n\text{-}\ SiX^2{}_pR^2{}_{3-p} \qquad I$$

wherein X^1, X^2, R^1, R^2, R^3, m, n and p have the same meanings as above in formula I; and

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

$$(R^5)_2R^6Si\text{-}R^7\text{-}SiR^5{}_3 \qquad II$$

wherein R^5, R^6 and R^7 have the same meanings as above in formula II; and/or with a compound having the formula III

$$(X^3)_{4-n}SiR^8{}_n \qquad III$$

wherein X^3, R^8 and n have the same meanings as above in formula III;

to produce a polymerized organopolysiloxane material and

- depositing the polymerized organopolysiloxane material in a solution on a substrate in the form of a thin layer; and
- curing the thin layer to form a film.

[0078] The present organopolysiloxane material is curable at a high temperature but not at room temperature. Therefore, curing is performed at a high temperature, typically at about 400 °C or more. Prior to the final curing at a high temperature, baking or “soft bake” typically takes place at lower temperatures, such as at 150-300 °C, for example at at 150°C and 250°C.

[0079] The polymerized organopolysiloxane material is typically deposited on a semiconductor substrate. Alternatively or additionally, the polymerized organopolysiloxane material may be deposited on an optical element or an optoelectronic device substrate.

[0080] The invention also relates to a method of manufacturing a semiconductor device, which comprises the organopolysiloxane composition or the low dielectric constant polymer film of the invention. Typically, the method comprises the following steps:

- providing a substrate;
- depositing a metal layer;
- depositing photoresist and auxiliary underlayers on top of the metal;
- exposing the said photoresist stack to light or an electron beam through a mask to form a desired pattern;
- developing the soluble parts of the photoresist and transferring the formed pattern to the metal layer by selective etch processes;
- removing residual parts of the photoresist stack;
- depositing and curing the organopolysiloxane composition to obtain the low-k dielectric polymer film; and

removing excess of deposited low-k dielectric polymer film by an etch back or chemical mechanical polishing process.

[0081] In one preferred embodiment, the step of depositing a metal layer on the substrate comprises depositing metals selected from cobalt (Co), molybdenum (Mo), ruthenium (Ru) and tungsten (W) on the substrate. Typically, the semiconductor device has metal interconnect dimensions of less than 50 nm, preferably less than 30 nm, such as 10-20 nm or below.

[0082] The semiconductor devices or optical elements or optoelectronical devices may also comprise another dielectric layer, such as a dielectric layer formed by CVD or

ALD, in addition to the dielectric polymer film of the present invention. The other dielectric layer may bring additional benefits, for example a decreased dielectric damage during etch process. Therefore, for example the above method of manufacturing a semiconductor device may also comprise a step of depositing another dielectric layer, typically before or after the step of depositing and curing the organopolysiloxane composition of the present invention.

[0083] Figure 1 illustrates the various stages in the production of a semiconductor device according to the present technology, comprising a low k dielectric consisting of a film of a polysiloxane material as disclosed herein.

[0084] As will appear, first a substrate 1 is provided. Such a substrate may for example comprise a silicon wafer. The substrate is subjected to metal deposition 2 in a second stage. The metal layer consists of an electrically conductive metal 3. Conventionally copper has been used for such purposes, but for patterned devices with spaces having diameters of 1 to 50 nm, such as 1 to 20 nm or even 5 to 15 nm, the metals are selected from cobalt, molybdenum, tungsten, ruthenium or some other suitable metal, preferably from cobalt (Co), molybdenum (Mo) and ruthenium (Ru).

[0085] The substrate 1 with the metal layer 3 is subjected to patterning by known steps in lithography including photoresist coating 4 (and required photoresist underlayers) using a suitable photoresist coating material 5, such as a material suitable for patterning with electromagnetic radiation in the UV range or even the Extreme UV range (EUV). After an exposure and development step 6, pattern transfer by etching 7 of the metal layer 3 is carried out. Thereafter, the remaining photoresist and photoresist underlayers are stripped off 8 to leave the substrate with a patterned metal layer 3.

[0086] In the two following steps, a dielectric coating 10 is applied 9 onto the patterned metal layer 3 and on the substrate 1 to fill the spaces between the metal patterns. Finally, the metal 10, separated by the dielectric, are opened 11 by etch-back for example using gas or chemical mechanical polishing (CMP). As a result, a semiconductor device is provided comprising a dielectric formed by a polymer film according to the present technology.

[0087] Figure 2 illustrates the various stages of an alternative production of a semiconductor device comprising a low k dielectric consisting of a film of a polysiloxane materials as disclosed herein according to the present technology.

[0088] As will appear, first a substrate 11 is provided. Such a substrate may for example comprise a silicon wafer. The substrate is subjected to dielectric coating in a second stage 12 to provide a layer of a low k dielectric 13 on top of (at least one surface of) the substrate 11. The thus coated substrate is then subjected, in a second step, to etching to remove predetermined parts of the dielectric and, thus, to pattern the surface. In a third stage a barrier material 16 and an overlapping layer of a metal 17 are deposited upon the surface. The metal layer may for example comprise a conductive layer, such as copper.

[0089] As can be seen the barrier material 16 and metal 17 typically cover both the etched parts and the non-etched parts of the surface. In a final, fourth stage 18 the multilayered structure is thence subjected to metal via opening, e.g. by chemical mechanical polishing. As a result, a semiconductor device is obtained, comprising a low k dielectric with embedded metal vias.

[0090] The invention further relates to a method of manufacturing an optical element or an optoelectrical device, which comprises the organopolysiloxane composition or the low dielectric constant polymer film of the invention, wherein the method comprises the steps of

- providing an optical element or optoelectrical device substrate;
- applying the polyorganosiloxane composition onto the optical element or onto the optoelectrical device substrate; and
- curing the organopolysiloxane composition to form the low-k dielectric polymer film.

[0091] Typically, the organopolysiloxane composition is deposited in the form of a thin layer on the substrate and cured at a temperature of 350 ℃ or more, such as at 400 ℃, to form the film.

[0092] 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 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.

[0093] Reference throughout this specification to one embodiment or an embodiment means that a particular feature, structure, or characteristic described in 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.

[0094] 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 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 present invention.

[0095] 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 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.

EXPERIMENTAL

[0096] 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.

[0097] 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.

[0098] Unless otherwise stated, properties that have been experimentally measured or determined herein have been measured or determined at atmospheric pressure.

[0099] As used herein, the term “about” refers to a value, which is ± 5 % of the stated value.

[00100] As used herein, the term “average molecular weight” typically refers to a weight average molecular weight (also abbreviated “M_W” or “M_w”). However, a number average molecular weight may also be given. As used herein, the molecular weight is measured by gel-permeation chromatography using polystyrene standards.

[00101] Measurement of the “dielectric constant”, κ or εr, 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 a 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:

$$\kappa = \frac{Cd}{\varepsilon_0 A}$$

where κ is dielectric constant, C is capacitance, d is film thickness, ε0 is permittivity of vacuum and A is capacitor area.

[00102] “Breakdown voltage” or ”electric breakdown voltage” (EBD) is measured using a similar MIS structure with a mercury probe (Materials Development Corporation, model 802) and a semiconductor parameter analyzer (Agilent 4155B).

[00103] Film thickness and refractive index (RI) 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.

[00104] “Shrinkage” is determined measuring the thickness loss of the film between soft bake and high temperature cure. Soft bake takes place at a temperature of 150-300° C, for example at 150°C and 250°C. Temperature during the high temperature cure is 400 °C. Thickness measurement is done with a spectroscopic ellipsometer.

[00105] “Hardness” and “elastic modulus” of films can be calculated from curve of

nanoindentation by the Oliver-Pharr method.

Monomers

Monomer A: 1,3-bis(triethoxysiloxy)tetramethyldisiloxane

Polymer preparation examples

Polymer 1:

A polymer of monomer A was prepared in a 250ml round bottom flask. The monomer A (29 g), acetone (29 g) and 0.01M HCl (7.1 g) were added to flask. The reaction mixture was refluxed 1h and cooled down to room temperature after that. PGMEA (50 g) was added to the reaction mixture. Acetone and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 41 %. 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 1105/608, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

Polymer 2:

A co-polymer of monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane was prepared in a 250ml round bottom flask. The monomer A (29 g), 1-trimethoxysilyl-2-dimethoxymethyl-ethane (15 g), acetone (45 g) and 0.01M HCl (12 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. Acetone 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 1641/662, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

Polymer 3:

A co-polymer of monomer A and 1-trimethoxysilyl-2-dimethoxymethylsilyl-ethane was prepared in a 250ml round bottom flask. The monomer A (29 g), 1-trimethoxysilyl-2-

dimethoxymethyl-ethane (7 g), acetone (36 g) and 0.01M HCl (8.8 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. Acetone and hydrolysis products were removed under reduced pressure yielding a formulation having a solid content of 28 %. 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 1218/415, respectively. The 6% formulation of polymer was prepared with PGMEA and spin-coated on silicon wafer for film characterization.

Table 1. Polymer data

Polymer #	Monomer A %	Mw (g/mol)	n @633nm	Shrinkage %	EBD (MV/cm)	k
1	100	1105	1.370	-2.4	3.95	2.79
2	50	1641	1.396	0.4	3.40	2.83
3	70	1218	1.387	-1.0	3.35	2.82

Table 2. 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 %	Modulus (GPa)	Hardness (GPa)
C1	0	12.8	2.4
C2	0	12.5	2.4
1	100	6.4	1.5
2	50	7.3	1.6
3	70	7.3	1.5

As will appear from the above, by means of the present materials a combination of low shrinkage and low dielectric constant can be achieved, while achieving also good mechanical properties. In addition, a sufficiently high breakdown voltage can be seen by the present materials.

Comparative examples

Comparative example 1 (C1): A polymer consisting of TEOS, MTEOS 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 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 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.

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.

[00106] 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.

[00107] 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.

INDUSTRIAL APPLICABILITY

[00108] At least some embodiments of the present invention find industrial application in semiconductor devices, optical elements and optoelectric devices. In particular, the present low dielectric constant films are suitable as barrier layers for filling spaces between metal interconnects having largest dimensions of less than 50 nm, typically less than 30 nm, such as 10-20 nm or below. The present low constant dielectric films provide a low shrinkage and a high electric breakdown voltage which make them ideal dielectrics for semiconductor and optical applications.

ACRONYMS LIST

CVD	chemical vapor deposition
GPC	gel permeation chromatography
HTEOS	triethoxysilane
MIS	metal-insulator-semiconductor
MTEOS	methyltriethoxysilane
PGEE	propylene glycol ethyl ether
PGME	propylene glycol methyl ether
PGMEA	propylene glycol methyl ether acetate
PTFE	polytetrafluoroethylene
TEOS	tetraethyl orthosilicate

REFERENCE SIGNS LIST

1 = substrate
2 = Metal deposition
3 = metal layer, e.g. Co or Ru
4 = Photoresist coating
5 = photoresist – EUV-material
6 = Exposure and development
7 = Etching
8 = Photoresist stripping
9 = Dielectric coating
10 = low k dielectric

11 = substrate

12 = Dielectric coating

13 = low k dielectric

14 = Etching

15 = Barrier material and metal coating

16 = barrier material

17 = metal, e.g. Cu

CLAIMS:

1. An organopolysiloxane composition for forming a low dielectric constant polymer film, comprising polymerized organopolysiloxane material obtained by polymerization of compounds having formula I

$$X^1{}_mR^1{}_{3-m}Si\text{-}O\text{-}(R^3{}_2Si\text{-}O)_n\text{-}\ SiX^2{}_pR^2{}_{3-p} \qquad I$$

wherein
each X^1 and X^2 is independently selected from the group of hydrogen and organic or inorganic hydrolyzable groups;
each R^1 and R^2 is independently selected from the group of hydrocarbyl residues, which optionally are substituted;
each R^3 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 5;
m is an integer of 1 to 3; and
p is an integer of 1 to 3.

2. The composition according to claim 1, wherein each X^1 and X^2 is independently selected from hydrogen, halogen, acyloxy, alkoxy and OH groups.

3. The composition according to claim 1 or 2, wherein each X^1 and X^2 is independently selected from hydrogen, chlorine, bromine, fluorine, and R^4O-, wherein R^4 stands for an alkyl having 1 to 6 carbon atoms.

4. The composition according to any one of the preceding claims, wherein each X^1 and X^2 is independently selected from R^4O-, wherein R^4 stands for an alkyl having 1 to 6 carbon atoms, preferably methyl or ethyl.

5. The composition according to any one of the preceding claims, wherein each R^1 and R^2 is independently selected from the group of optionally functionalized linear, branched or cyclic, bivalent, saturated or unsaturated hydrocarbyl radicals.

6. The composition according to any one of the preceding claims, wherein each R^1 and R^2 is independently selected from the group of linear, branched and cyclic alkyl groups having 1 to 10 carbon atoms, aryl groups containing 1 to 5 aromatic rings, optionally containing 1 to 3 heteroatoms, wherein each of the mentioned groups may optionally be substituted with 1 to 3 functional groups selected from halo, hydroxyl, alkoxy, vinyl and acetyl groups.

7. The composition according to any one of the preceding claims, wherein each R^1 and R^2 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.

8. The composition according to any one of the preceding claims, wherein n in the compound of formula I is 1 to 3, preferably 2.

9. The composition according to any one of the preceding claims, wherein m and p in the compound of formula I are independently of each other 2 or 3, preferably 3.

10. The composition according to any one of the preceding claims, wherein the compounds of formula I comprise 1,3-bis(triethoxysiloxy)tetramethyldisiloxane, preferably in an amount of at least 40 mol% of the total amount of polymerized compounds.

11. The composition according to any one of the preceding claims, obtained by homopolymerization of compounds of formula I.

12. The composition according to any one of the preceding claims, obtained by homopolymerization of 1,3-bis(triethoxysiloxy)tetramethyldisiloxane.

13. The composition according to any one of the preceding claims obtained by copolymerization of compounds of general formula I with silane monomers, wherein the

compounds of formula I are present in an amount of at least 40 mol% of the total amount of polymerized compounds and monomers.

14. The composition according to any one of claims 1 to 10 and 13, obtained by copolymerization of a compound of formula I

- with a compound of formula II

$$(R^5)_2R^6Si\text{-}R^7\text{-}SiR^5_3 \qquad \text{II}$$

wherein

R^5 is a hydrolysable group, such as hydrogen, a halide, an alkoxy or an acyloxy group;

R^6 is hydrogen, an organic crosslinking group, a reactive cleaving group or a polarizability reducing organic group; and

R^7 is a bridging linear or branched bivalent hydrocarbyl group; and/or

- with a compound of formula III

$$(X^3)_{4-n}SiR^8_n \qquad \text{III}$$

wherein

X^3 is hydrogen or a hydrolysable group selected from halogen, acyloxy, alkoxy and OH groups;

R^8 is selected from halogen, acyloxy, alkoxy and OH groups, and alkyl groups having 1 to 6 carbon atoms, vinyl groups having from 2 to 6 carbon atoms, and aryl groups having 6 carbon atoms; and

n is an integer of 1 to 3, preferably 2.

15. The composition according to claim 14, obtained by copolymerization of a compound of formula I with a compound of formula II in a molar ratio of compounds of formula I to compounds of formula II in a range of 90:10 to 10:90, for example 80:20 to 20:80, in particular 60:40 to 40:60, preferably 90:10.

16. The composition according to claim 14, obtained by copolymerization of a compound of formula I with a compound of formula III in a molar ratio of compounds of formula I to compounds of formula III in a range of 90:10 to 10:90, for example 80:20 to 20:80, in particular 60:40 to 40:60, preferably 90:10.

17. The composition according to claim 14, comprising a polymer obtained by polymerization of a compound of formula I with a compound of formula II and/or a compound of formula III, wherein the polymer comprises at least 10 mol%, preferably at least 30 mol%, more preferably at least 40 mol%, and still more preferably at least 50 mol% of a compound of formula I.

18. The composition according to any one of the preceding claims, wherein the polymerized organopolysiloxane material has a (weight average) molecular weight in the range of 500 - 50 000 g/mol, measured by gel-permeation chromatography using polystyrene standards.

19. The composition according to any one of the preceding claims, comprising the polymerized organopolysiloxane material in a solution, preferably in an organic solvent or solvents.

20. The composition according to any one of the preceding claims, comprising the polymerized organopolysiloxane material in a solution in an amount of 0.1-50 wt%, preferably 1-20 wt%, most preferably 5 to 10 wt%, such as about 6 %.

21. The composition according to any one of the preceding claims, wherein the polymerized organopolysiloxane material in a solution has a viscosity of 0.5-50 mPas, measured by viscosimeter.

22. A low dielectric constant polymer film comprising a cured organopolysiloxane composition according to any one of claims 1 to 21.

23. The polymer film according to claim 22, having a dielectric constant at 1 MHz of 2.85 or less, preferably 2.8 or less.

24. The polymer film according to claim 22 or 23, having an electric breakthrough voltage of 3.3 MV/cm or more.

25. The polymer film according to any one of claims 22 to 24, having a shrinkage between soft bake and cure, which is less than 5%, more preferably less than 3% and most preferably less than 1%, determined by measuring the thickness loss of the film between soft bake at 150-300 °C and high temperature cure at 400 °C with a spectroscopic ellipsometer.

26. The polymer film according to any one of claims 22 to 25, having a thickness of less than 1 µm, in particular less than 500 nm, typically 50 to 350 nm.

27. The polymer film according to any one of claims 22 to 26, having an RI greater than 1.35, preferably greater than 1.37, determined at a wavelength of 633 nm.

28. The polymer film according to any one of claims 22 to 27, having an elastic modulus of > 5 GPa, preferably > 7 GPa, most preferably >10 GPa.

29. The polymer film according to any one of claims 22 to 28, having a hardness of > 1 GPa, preferably >1.3 GPa, most preferably >1.6 GPa

30. A method of forming a low dielectric constant polymer film, comprising the steps of:

- hydrolysing a first silicon compound having the formula I

$$X^1_mR^1_{3-m}Si\text{-}O\text{-}(R^3_2Si\text{-}O)_n\text{-}\ SiX^2_pR^2_{3-p} \qquad I$$

wherein X^1, X^2, R^1, R^2, R^3, m, n and p have the same meanings as above in formula I; and

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

$$(R^5)_2R^6Si\text{-}R^7\text{-}SiR^5_3 \qquad II$$

wherein R^5, R^6 and R^7 have the same meanings as above in formula II; and/or with a compound having the formula III

$$(X^3)_{4-n}SiR^8_n \qquad III$$

wherein X^3, R^8 and n have the same meanings as above in formula III;

to produce a polymerized organopolysiloxane material and

- depositing the polymerized organopolysiloxane material in a solution on a substrate in the form of a thin layer; and
- curing the thin layer to form a film.

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 optoelectronic device.

33. A method of manufacturing a semiconductor device, comprising the organopolysiloxane composition according to any one of claims 1 to 21 or the low dielectric constant polymer film according to any one of claims 22 to 29, the method comprising the following steps:

- providing a substrate;
- depositing a metal layer;
- depositing photoresist and auxiliary underlayers on top of the metal;
- exposing the said photoresist stack to light or an electron beam through a mask to form a desired pattern;
- developing the soluble parts of the photoresist and transferring the formed pattern to the metal layer by selective etch processes;
- removing residual parts of the photoresist stack;
- depositing and curing the organopolysiloxane composition to obtain the low-k dielectric polymer film; and

removing excess of deposited low-k dielectric polymer film by an etch back or chemical mechanical polishing process.

34. The method according to claim 33, wherein the step of depositing a metal layer on the substrate comprises depositing metals selected from cobalt (Co), molybdenum (Mo), ruthenium (Ru) and tungsten (W) on the substrate.

35. The method according to 33 or 34, wherein the semiconductor device has metal interconnect dimensions of less than 50 nm, preferably less than 30 nm, such as 10-20 nm or below.

36. The method according to any one of claims 33 to 35, further comprising a step of depositing another dielectric layer before or after the step of depositing and curing the organopolysiloxane composition.

37. A method of manufacturing an optical element or an optoelectrical device comprising the organopolysiloxane composition according to any one of claims 1 to 21 or the low dielectric constant polymer film according to any one of claims 22 to 29, wherein the method comprises the steps of
- providing an optical element or optoelectrical device substrate;
- applying a polyorganosiloxane composition according to any one of claims 1 to 21 onto the optical element or onto the optoelectrical device substrate; and
- curing the organopolysiloxane composition to form the low-k dielectric polymer film.

38. The method according to any one of claims 33 to 37, comprising depositing the organopolysiloxane composition in the form of a thin layer on the substrate; and curing the thin layer at a temperature of 350 °C or more to form the film.

39. Use of the low dielectric constant polymer film according to any one of claims 22 to 29 in semiconductor devices or optical devices.

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

41. An optical element or an optoelectronic device comprising a low dielectric constant polymer film according to any one of claims 22 to 29.

LOW DIELECTRIC CONSTANT THIN FILMS, A METHOD OF PRODUCING THE SAME AND USES THEREOF

ABSTRACT

The present invention relates to low dielectric constant films comprising polymerized organopolysiloxane material obtained by polymerization of organo functionalized monomers. The invention also concerns a method of forming such films by applying organopolysiloxane material containing compositions on a substrate in the form of a layer and by curing the layer to form a film. Further, the invention concerns uses of the low dielectric constant films of the invention in semiconductor devices, optical elements and optoelectronic devices.

Figure 1