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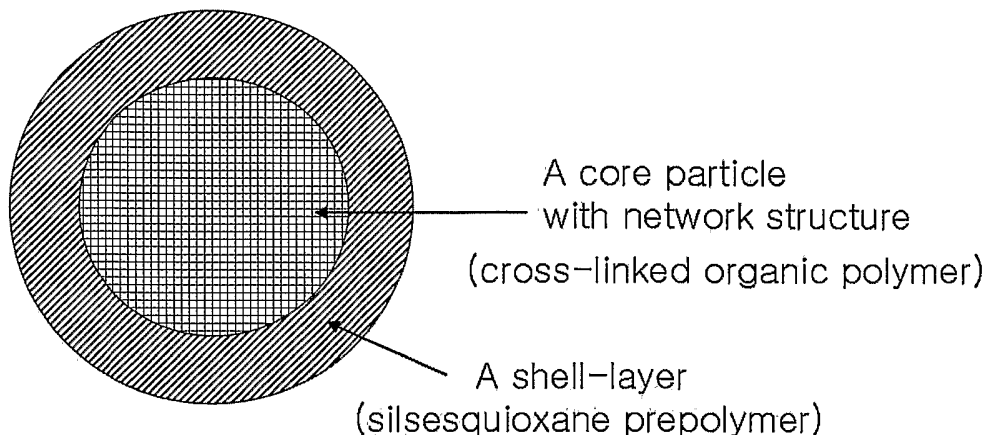
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(54) Title: A NANOPARTICLE OF CORE-SHELL TYPE, A METHOD FOR PREPARING THE SAME, A METHOD FOR PREPARING A LOW DIELECTRIC INSULATION FILM BY USING THE SAME, AND A LOW DIELECTRIC INSULATION FILM PREPARED THEREFROM



(57) Abstract: Disclosed is a nanoparticle of core-shell type and a method of preparing the same, a method of preparing a low dielectric insulation film using the same, and a low dielectric insulation film prepared therefrom. More specifically, the present invention discloses nanoparticles which include an organic polymer core particle with a network structure and a shell-layer of a silsesquioxane prepolymer surrounding the core particle. In addition, a method of preparing these nanoparticles is described.

A NANOPARTICLE OF CORE-SHELL TYPE, A METHOD FOR PREPARING THE SAME, A METHOD FOR PREPARING A LOW DIELECTRIC INSULATION FILM BY USING THE SAME, AND A LOW DIELECTRIC INSULATION FILM PREPARED THEREFROM

FIELD OF THE INVENTION

5 The present invention relates to a nanoparticle of core-shell type, a method for preparing the same, a method for preparing a low dielectric insulation film by using the same, and a low dielectric insulation film prepared from the method. Specifically, it relates to a nanoparticle of core-shell type, which can evenly form minute pores of a nanometer size inside silicate polymers used as a material of a low dielectric insulation film, a method for
10 preparing the nanoparticle, a method for preparing a low dielectric insulation film by using the nanoparticle, and a low dielectric insulation film prepared from the aforementioned method.

BACKGROUND OF THE INVENTION

15 Recent research in the electronic business has been actively performed on the density of an integrated circuit (I.C.) with multiple structures to improve the capacity of a circuit as well as to decrease the cost, for example, by increasing memory and improving logic chips. Accordingly, research on a chip having a smaller size and on a new low dielectric material with a lower dielectric constant has been promoted.

20 Currently, silicon dioxide, whose dielectric constant is in a range from about 3.5 to 4.0, is most comprehensively used as a dielectric material. This is due to the strong physical qualities of silicon dioxide and its thermal stability. Silicon dioxide can endure various chemical and thermal treatments which occur in the manufacturing process of a semiconductor.

25 However, more attention has recently been paid to copper as one of the promising materials used for highly efficient integrated circuits (herein referred to as I.C.) with multiple structures due to its excellent conductivity despite a low price. Accordingly, research on the development of a new dielectric material having a dielectric constant of less than about 2.5 using copper has been getting more attention. However, as the size of an integrated circuit is getting smaller, there appears to be some problematic phenomena (e.g., cross-talk and
30 delayed signal) impeding the improved quality of a device. Therefore, further research on the development of a low dielectric insulation material to solve these problems is expected.

35 In general, a low dielectric material is required to establish thermal stability, mechanical quality, suitability for chemical-mechanical polishing, electric properties, interfacial suitability, etching, etc. In addition, a low dielectric material should have a dielectric constant of less than about 2.5. To develop a low dielectric material with a lower dielectric constant, research efforts have been expended on silicates, nanoporous silicates, aromatic polymers, fluoridated aromatic polymers, organic-inorganic composite materials, and so on.

 An insulation material with an ultra low dielectric constant is required to have minute

pores of a nanometer size inside it or in the film made of it. In general, the minute pores are induced by thermal decomposition of a polymer compound. However, the current conventional art has many limits in the establishment of the ideal pore size and even the distribution of pores, since phase separation occurs between an insulation material and an organic polymer such as a pore generator, resulting in large and irregular sizes of the pores, and non-uniform distribution of the pores.

SUMMARY OF THE INVENTION

An aspect of the present invention provides a nanoparticle of core-shell type which includes a silsesquioxane prepolymer shell and an organic polymer core particle with a network structure.

The present invention also provides a method of preparing a nanoparticle of core-shell type by using micro-emulsion.

In addition, the present invention provides a method of preparing a low dielectric insulation film by using the nanoparticle of core-shell type.

In addition, the present invention provides a low dielectric insulation film prepared by the method.

In order to accomplish these aspects, the present invention provides a nanoparticle of core-shell type comprising an organic polymer core particle with a network structure, and a shell-layer which comprises a silsesquioxane prepolymer and covers the core particle.

The present invention provides a method for preparing a nanoparticle of core-shell type as follows: a) preparing micro-emulsion by mixing i) a multifunctional unsaturated monomer with more than two vinyl groups or ii) a multifunctional unsaturated monomer with more than two vinyl groups and an unsaturated monomer with one vinyl group, with a surfactant solution including a surfactant and a co-surfactant; b) preparing an organic polymer core particle with a network structure by reacting the unsaturated monomers after adding an initiator into the micro-emulsion; and c) preparing a silsesquioxane prepolymer shell-layer covering the organic polymer core particle by adding a silsesquioxane monomer and a catalyst into the solution comprising the organic polymer core particle with a network structure, and then reacting them.

The present invention provides a method for preparing a low dielectric insulation film as follows: a) mixing a nanoparticle of core-shell type and a silicate polymer to form a mixture; b) reacting the mixture of the nanoparticle of core-shell type and the silicate polymer by sol-gel reaction; and c) heat-treating the reacted mixture such that nanopores are formed.

The present invention provides a low dielectric insulation film with nanopores which is prepared by said method and comprises a complex of a silsesquioxane prepolymer and a silicate polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the present invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by

reference to the following detailed description when considered in conjunction with the accompanying drawings.

Fig. 1 is a schematic diagram showing a cross-sectional view of a nanoparticle of core-shell type of the present invention.

Fig. 2 shows the FT-IR spectrum of the organic polymer core particle with a network structure according to Example 1.

Fig. 3 shows the FT-IR spectrum of the nanoparticle of core-shell type according to Example 1.

Fig. 4 is a Guinier plot of small angle X-ray scattering showing the radius of gyration of the nanoparticle of core-shell type according to Example 1 in both water and a methyl isobutyl ketone (MIBK) solution.

Fig. 5 is an atomic force microscopic (AFM) photograph of the nanoparticle of core-shell type according to Example 1.

Fig. 6 is a distribution graph of the nanopores in the low dielectric insulation film according to Examples 1 to 4.

DETAILED DESCRIPTIONS OF THE INVENTION

A nanoparticle in the present invention indicates a particle with an average diameter of less than hundreds of nanometers. According to an embodiment of the present invention, the nanoparticle comprises an organic polymer core particle with a network structure, and a silsesquioxane prepolymer shell-layer covering the core particle. Accordingly, the nanoparticle of core-shell type has excellent compatibility with a low dielectric insulation film.

Fig. 1 is a cross-sectional view illustrating the nanoparticle of core-shell type of the present invention. Referring to the Fig. 1, the nanoparticle of core-shell type may include a core particle having a pore-forming material and a shell-layer including a silsesquioxane prepolymer which covers the core particle.

The core particle of the nanoparticle of core-shell type may include organic polymers with a network structure prepared by reacting a multifunctional unsaturated monomer with more than two vinyl groups (herein, referred to as a first unsaturated monomer), or a first unsaturated monomer and an unsaturated monomer with one vinyl group (herein, referred to as a second unsaturated monomer) together.

The shell layer of the nanoparticle of core-shell type may include a silsesquioxane prepolymer prepared from a silsesquioxane monomer.

The average diameter of the nanoparticle of core-shell type preferably ranges from about 2 nm to 120 nm. When the average diameter is more than about 120 nm, the formation of nanopores may be inhibited, and if the average diameter is less than about 2 nm, there may be difficulties in the preparation thereof.

The average diameter of the organic polymer core particle that functions as a pore-forming part preferably ranges from about 1 nm to 100 nm. When the average diameter of the core particle is more than about 100 nm, the formation of nanopores may be inhibited,

and if the average diameter of the core particle is less than about 1 nm, there may be difficulties in the preparation thereof.

The organic polymer in the core particle may be prepared by polymerizing the first unsaturated monomer system, or by polymerizing the first unsaturated monomer system and the second unsaturated monomer system together. The resulting organic polymer core particle has a polymerized-network structure and may decompose when heated to a temperature in a range from about 200°C to 500 °C .

The first unsaturated monomer system used for the preparation of the aforementioned organic polymer core particle includes di-, tri-, tetra-, or more multifunctional groups. One or more monomers may be selected from the group consisting of divinyl benzene, trivinyl benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane, allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, trimethylol propane trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, bisphenol-A diacrylate ethylester, bisphenol-A dimethacrylate ethylester, polyethylene glycol 600 dimethacrylate, polybutanediol diacrylate, pentaerythritol triacrylate, trimethylolpropane triethoxy triacrylate, glycerylpropyloxytriacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxy pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxide siloxane, and polyphenyl vinyl siloxane. In some embodiments, it may be advantageous to select a multifunctional unsaturated monomer from the group consisting of divinyl benzene, trivinyl benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, and trivinyl phenyl silane. However, the first unsaturated monomer is not limited to these compounds.

The second unsaturated monomer system may include one or more compounds selected from the group consisting of ethylene and acetylene derivatives, alkylmethacrylates, aromatic vinyl compounds, and nitrogen compounds. In some embodiments, it may be advantageous to select the unsaturated monomer group from the group consisting of methacrylic acid, methacryl amide, methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene,

vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, vinyl piperidine, etc. However, the second unsaturated monomer used is not limited to these compounds.

The shell-layer of the nanoparticle comprises a silsesquioxane prepolymer prepared by polymerization of a silsesquioxane monomer. Examples of the silsesquioxane monomer in an embodiment may be one or more compounds selected from the group consisting of trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethylbenzene, bis(trimethoxy silyl)ethylbenzene, etc. However, the silsesquioxane monomer used to prepare the silsesquioxane prepolymer is not limited to the aforementioned items. In addition, the silsesquioxane prepolymer only has to form a coating layer and is not restricted to a particular molecular weight.

In conclusion, the aforementioned nanoparticle of core-shell type may include an organic polymer core particle with a network structure, which may decompose when heated to a temperature in a range from about 200°C to 500°C. In addition, the nanoparticle may include a silsesquioxane prepolymer with an end group of ethoxy or methoxy surrounding the organic polymer. The unit size of the nanoparticle of core-shell type is a nanometer. This particle may be used as a derivative to induce pores inside the silicate polymer insulation film like a silsesquioxane polymer.

The nanoparticle of core-shell type may prevent phase separation of organic polymers during formation of pores. Consequently, a uniform distribution of pores inside the silicate insulation film or silicate polymer may be established, because the silsesquioxane prepolymer forming the shell layer of the nanoparticle is compatible with a silicate polymer used to prepare a low dielectric insulation film. In addition, the unit size of a particle can be regulated to a nanometer (nm) regardless of the density of the organic polymer used.

A method of preparing the aforementioned nanoparticle of core-shell type may include preparing a surfactant solution by mixing a surfactant, a co-surfactant, and water. In some embodiments, the surfactant solution includes a concentration of the surfactant in a range from 0.1 M to 10 M, and a concentration of the co-surfactant in a range from 0.01 M to 10 M. When the concentration of the surfactant is less than 0.1 M, the mixture of the surfactant solution and monomers may not reach sufficient micro-emulsion, and a concentration of the surfactant greater than 10 M may not increase micro-emulsion.

As for the surfactant, any cationic, anionic, or nonionic surfactant can be used. In some embodiments, a cationic surfactant such as octyl trimethyl ammonium bromide, decyl

trimethyl ammonium bromide, dodecyl trimethyl ammonium bromide, etc.; an anionic surfactant such as sodium dodecyl sulfate (SDS), sodium bis(2-ethyl hexyl)sulfosuccinate (AOT), dodecyl benzene sulfonic acid, sodium dioctyl sulfosuccinate, sodium alkyl phenol ether sulfonate, sodium alkyl sulfonate, etc.; or a nonionic surfactant such as a polyethylene-polypropylene-polyethylene block copolymer, a sorbitan fatty acid ester, a polyoxyethylene fatty-acid ester, etc., can be used. In addition, a mixture of one or more of these compounds can be used for the surfactant. In some embodiments, the surfactant may include anion surfactants such as sodium dodecyl sulfate (SDS), sodium bis(2-ethyl hexyl)sulfosuccinate (AOT), dodecyl benzene sulfonic acid, sodium dioctyl sulfosuccinate, sodium alkyl phenol ether sulfonate, sodium alkyl sulfonate, etc.

Co-surfactants may be added with the surfactant. Any alcohol including an alkyl group with more than 4 carbons can be used. In an embodiment, the co-surfactants may include one or more alcohols selected from the group consisting of butanol, pentanol, hexanol, heptanol, octanol, etc.

A micro-emulsion may be prepared by adding the first unsaturated monomer, or the mixture including the first unsaturated monomer and the second unsaturated monomer, drop by drop into the prepared surfactant solution and stirring them.

Embodiments of the micro-emulsion solution may include unsaturated monomers from 0.1 % by weight to 40 % by weight (e.g., the first unsaturated monomer, or the mixture of the first unsaturated monomer mixture and the second unsaturated monomer). The amount of the first unsaturated monomer included in the monomer system may be regulated to control the degree of the crosslink of the prepared organic polymer core particle with a network structure. Accordingly, the amount of the first unsaturated monomer may be in a range between 0.1 % by weight and 100 % by weight of the total monomer. In other embodiments, the first unsaturated monomer may constitute between 10 % by weight and 100 % by weight of the total monomer. When the amount of the first unsaturated monomer is less than 0.1 % by weight, the degree of the crosslink of the organic polymer core particle may decrease, and the core particles may be dissolved into the organic solvent and fail to establish a sphere shape.

In addition, a weight ratio of the monomer and the surfactant may be regulated to control a particle size of the organic polymer core particle to be prepared from the emulsion. In some embodiments, the weight ratio of the monomer and the surfactant is in a range from about 0.1:100 to 100:0.1, and more preferably in a range from about 1:10 to 10:1. When the weight ratio is under 0.1:100, the size of particles does not grow over a nanometer, and the ratio is over 100:0.1, the number of nanoparticles decreases.

The first unsaturated monomer used to prepare the micro-emulsion can include di-, tri-, tetra-, or more multifunctional groups. Preferably, one or more multifunctional unsaturated monomers may be selected from the group consisting of divinyl benzene, trivinyl benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol

diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane, aryl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, trimethylolpropane trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, bisphenol-A diacrylate ethyl ester, bisphenol-A dimethacrylate ethyl ester, polyethylene glycol 600 dimethacrylate, polybutanediol diacrylate, pentaerythritol triacrylate, trimethylol propane triethoxy triacrylate, glycerylpropyloxytriacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxide pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxy siloxane, polyphenyl vinyl siloxane, etc. In a preferred embodiment, a multifunctional unsaturated monomer may be selected from the group consisting of divinyl benzene, trivinyl benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, trivinyl silane, dimethyl vinyl silane, divinylmethylsilane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, and trivinyl phenyl silane. However, it is understood that the first unsaturated monomer is not limited to these compounds.

Alternately, the second unsaturated monomer may be more than one compound selected from the group consisting of ethylene and acetylene derivatives, alkylmethacrylates, aromatic vinyl compounds, and nitrogen compounds. In some embodiments, the second unsaturated monomer may be selected from the group consisting of, methacrylic acid, methacryl amide, methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene, vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, vinyl piperidine, etc. However, the unsaturated monomer in the present invention is not limited to these compounds.

The organic polymer core particle with a network structure may be prepared by adding the initiator into the prepared micro-emulsion and reacting the unsaturated monomers.

A commonplace initiator may be used, and the amount of the initiator may be in a range from 0.01 mmol to 100 mmol per 1 mol of the monomers in the micro-emulsion

polymerization, and preferably the initiator may be added in a range from 0.01 mmol to 10 mmol per 1 mol of the monomers. When the amount of the initiator is less than 0.01 mmol, the speed of the initiative reaction may not be rapid enough. Furthermore, if the amount of the initiator is over 100 mmol, it could be hard to obtain an organic polymer core particle with a sufficient molecular weight as well as a network structure.

The initiator can be either an oxidization-reduction initiator or a common radical reaction initiator producing a radical with heat. In some embodiments, a mixture of one or more is preferred. Initiators may be selected from a group consisting of azobisisobutyronitrile (AIBN), benzoylperoxide (BPO), hydrogen peroxide/iron salt, persulfate/bissulfate, persulfate ammonium/tetramethyl ethylene diamine, and cerium sulfate(IV)/nitrilotriacetic acid. However, the initiator in the present invention is not limited to these compounds.

In some embodiments, the organic polymer core particle may be prepared at a temperature of less than about 50°C. In an embodiment, it may be advantageous to prepare the organic polymer core particle at a temperature in a range from 20°C to 50 °C. In addition, the organic polymer core particle may be prepared in a nitrogen atmosphere.

The organic polymer core particle prepared through the aforementioned process is in a state of micro-emulsion in the reaction solution.

A silsesquioxane monomer may be slowly added drop by drop into the above described solution including the organic polymer core particle with a network structure, and stirring them into the micro-emulsion solution.

In some embodiments, an advantageous ratio of the silsesquioxane monomer to the unsaturated monomer is in a range from 100:1 to 1:100, and preferably in a range from 10:1 to 1:10. When the ratio is over 100:1, pores are not efficiently formed compared with the input amount of the pore derivative, and if the ratio is less than 1:100, the shell-layer of the silsesquioxane prepolymer may not be sufficiently formed.

In an embodiment, silsesquioxane monomers may include, but are not limited to, trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethylbenzene, or bis(trimethoxy silyl)ethylbenzene, etc. A mixture of one or more silsesquioxane monomers selected from the above-described group also can be used. The above group does not list all the possible compounds used to prepare the silsesquioxane prepolymer in the present invention.

The shell-layer of the silsesquioxane prepolymer may be formed on the surface of the organic polymer core particle with a network structure.

Any base catalyst or acid catalyst known in the art may be used to prepare the silsesquioxane prepolymer. In some embodiments, the catalyst may be selected from a group consisting of, but not limited to, base catalysts such sodium hydroxide, potassium

hydroxide, potassium carbonate, sodium carbonate, etc., and acid catalysts such as hydrochloric acid, sulfuric acid, acetic acid, citric acid, lactic acid, etc. Furthermore, one or more of these catalysts can be used alone, as a mixture, or one by one.

5 Finally, miscible organic solvents such as methanol etc. may be added into the silsesquioxane prepolymer prepared in the previous step, obtaining the results with a sediment phase. Then, a nanoparticle of core-shell type can be prepared by applying separation methods, for example, a centrifuge method.

10 A nanoparticle of core-shell type prepared by the above method can be added as a pore formation material to prepare a low dielectric insulation film. This is due to the following features: the organic polymer core particle having a network structure is decomposed upon application of heat at a temperature between 200°C and 500°C; and the silsesquioxane prepolymer of the shell-layer of the nanoparticle forms a nanoparticle-silicate polymer composite, which reacts with the hydroxyl, methoxy, or ethoxy group at the end of the silicate polymer used as a matrix of a low dielectric insulation film, because both include the same
15 reactive hydroxyl, methoxy, or ethoxy group.

A method of preparing a low dielectric insulation film by using a nanoparticle of core-shell type is now described. A low dielectric insulation film may be prepared by: mixing a core-shell nanoparticle used as a pore formation material with a silicate polymer as the matrix of an insulation film; coating the equipment with the mixture; reacting the coated
20 equipment in a sol-gel method; and treating it with heat. In the process, the reactive ending group of the silsesquioxane prepolymer on the shell-layer of the nanoparticle is reacted with that of the silicate polymer, forming a nanoparticle-silicate polymer composite. In the final step of the heat treatment, the organic polymer core particle with a network structure, i.e., the organic polymer core particle of the nanoparticle, is decomposed with the heat and forms
25 minute pores inside the insulation film.

The mixture ratio of nanoparticles of core-shell type and silicate polymer added into the organic solvent for the coating is in a range of 1:99 to 50:50 by weight. This weight ratio can be regulated depending on the intended number of pores. When the amount of nanoparticles used corresponds to the weight ratio of less than 1:99, it is harder to establish
30 a lower dielectric rate, and the weight ratio is over than 50:50, the mechanical properties could be reduced.

The aforementioned silicate polymer used to prepare a low dielectric insulation film may include a hydrogen, methyl, or ethyl group as a core silicon element, and hydroxyl, methoxy, or ethoxy as a reactive end. In addition, the silicate polymer may have an average
35 molecular weight in a range from 3000 to 20,000 g/mol.

As for the aforementioned silicate polymer, methyl silsesquioxane, ethyl silsesquioxane, or hydrogen silsesquioxane etc. can advantageously be used. The silicate polymer may be one or more polymers prepared by sol-gel reaction with one or more silsesquioxane monomers selected from the group consisting of, but not limited to,

trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl alkyl diethoxysilane, methyl alkyl dimethoxysilane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl alkyl diethoxy silane, ethyl alkyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethylbenzene, and bis(trimethoxy silyl)ethylbenzene.

In addition, as for the aforementioned organic solvents used to prepare the composition for coating, any material known in the art and used for the coating of silicate polymer can be adopted. In an embodiment, a mixture of more than one organic solvent selected from a group including, but not limited to, methyl isobutyl ketone, acetone, methyl ethyl ketone, toluene, etc., can be more advantageous.

As for the aforementioned coating method, any coating method known in the art can be applied to coat the equipment with the prepared composition. In some embodiments, a spinning method is advantageous. The thickness of the coating can be regulated by controlling the density of the silicate polymer and the nanoparticle of core-shell type added into the solution, and also by controlling the spinning speed.

As for the aforementioned sol-gel reaction, any sol-gel method known in the art can be employed when the coating is complete, and the reaction can advantageously be performed at normal temperatures of less than about 400°C.

Finally, the heat treatment after the sol-gel reaction is performed at temperatures in a range from 200°C to 500°C. Minute pores are formed inside the insulation film through this heat-treatment, by hardening a low dielectric insulation film and completely decomposing the organic polymer core of the nanoparticle of core-shell type. When the temperature is under 200°C, the silicate polymer is not easily hardened with the heat, and if the temperature is over 500°C, the nanoparticle-silicate polymer composite is decomposed with the heat, such that the formation of pores is inhibited.

In an embodiment, the heat-treatment may be performed in a vacuum or in a nitrogen atmosphere, because the oxidization and subsequent decomposition of a nanoparticle-silicate polymer composite can be promoted in an atmosphere that includes oxygen.

Consequently, according to an embodiment of the present invention, a low dielectric insulation film including a composite of the silsesquioxane layer of a core-shell nanoparticle and silicate polymer includes minute pores formed through the decomposition of an organic polymer core particle with a network structure, i.e. a core of the nanoparticle.

An embodiment may include pores inside the insulation film having a size of less than 100 nm. In some embodiments, it may be advantageous for the size of the pores inside the insulation film to be in a range between 1 nm and 10 nm. When the size is over 100 nm, mechanical properties of the insulation film may be reduced.

The low dielectric insulation film has the refractive index of 1.15 to 1.40 at a wavelength of 633 nm, and a dielectric constant of 1.15 to 1.40.

The following examples illustrate the present invention in further detail. However, it is understood that the present invention is not limited to these examples.

Example 1

Preparation of nanoparticles of core-shell type

5 First, 4.5g of sodium dodecyl sulfate (SDS) and 0.2 g of pentanol were added to 54g of water in a 250ml flask, and the solution was heated to a temperature of 40°C. Then, 1.2g of methyl methacrylate and 0.3g of divinyl benzene were added into the heated solution. The mixture was stirred in a nitrogen atmosphere until it changed into a clear solution without any phase separation, and the solution was then set aside for about an hour.

10 Second, an ammonium persulfate solution and an aqueous tetramethyl ethylene diamine solution were each added slowly drop by drop until the density of the solution reached 10-2mmol. Then, the mixture solution was allowed to react for two hours, while the solution was stirred in a nitrogen atmosphere and at a temperature of 40°C. Finally methyl methacrylate polymer core particles with a network structure were obtained.

15 Fig. 2 shows the measurements of an FT-IR spectrum taken to check the methyl methacrylate polymer core particles prepared in the above process.

20 Third, when the reaction in the second step was complete, a silsesquioxane prepolymer was prepared by slowly adding 5.6g of methyl silsesquioxane into the above solution, and stirring the resulting solution until it changed into a clear solution. Then 1.5 g of sodium hydroxide aqueous solution (0.75mmol) were added to the clear solution, and the resulting solution was stirred for 12 hours.

Finally, nanoparticles of core-shell type in the sediment phase were obtained after adding an excess of methanol into the solution prepared above and centrifugally separating it.

25 Likewise, Fig.3 shows the measurements of an FT-IR spectrum taken to check the nanoparticles of core-shell type prepared in the above process.

In addition, the diameter of the nanoparticles in both water and methyl isobutyl ketone (MIBK) solution was measured by small angle X-ray scattering. Fig. 4 shows the measurements of the size and the radius of gyration of the nanoparticles, employing Guinier plotting.

30 As shown in Fig. 4, the nanoparticles were not only dispersed in both the organic solvent such as methyl isobutyl ketone (MIBK) and a polar solvent like water due to crosslinking, but they also turned out to have an even size of radius of gyration, of 6.5 nm.

Fig. 5 shows the measurements of the size of the nanoparticles taken by an atomic force microscope (AFM).

Preparation of a low dielectric insulation film

35 First, a composition for coating was prepared by uniformly dispersing 0.1 g of nanoparticles as prepared above into 0.9 g of a methyl silsesquioxane polymer having an average molecular weight (Mw) of 10,000 g/mol dissolved in 0.9 g of the solvent methyl

isobutyl ketone.

Second, an insulation film with the thickness of 100 nm was prepared by spin-coating onto substrates such as silicon wafers and aluminum-deposited slide glasses at a speed of 3000 rpm. Next, the film was treated with heat in a nitrogen atmosphere. The temperature was raised by 2°C/min up to 400°C and then kept at 400°C for an hour. Then, it was cooled at the same rate as was used for heating, and a low dielectric methyl silsesquioxane insulation film with minute pores inside was obtained.

Example 2

Preparation of nanoparticles of core-shell type

Nanoparticles of core-shell type were prepared using the same method as in Example 1.

Preparation of a low dielectric insulation film

A low dielectric methyl silsesquioxane insulation film was prepared by the same method as in Example 1, except for changing the amount of the nanoparticles used to 0.2 g and the amount of the methyl silsesquioxane polymer (Mw=10,000g/mol) used to 0.8 g to prepare a composition for coating.

Example 3

Preparation of nanoparticles of core-shell type

Nanoparticles of core-shell type were prepared by the same method as in Example 1.

Preparation of a low dielectric insulation film

A low dielectric methyl silsesquioxane insulation film was prepared by the same method as in Example 1 except for changing the amount of the nanoparticles used to 0.3 g and the amount of the methyl silsesquioxane polymer (Mw=10,000g/mol) used to 0.7g to prepare a composition for coating.

Example 4

Preparation of nanoparticles of core-shell type

Nanoparticles of core-shell type were prepared by the same method as in Example 1.

Preparation of a low dielectric insulation film

A low dielectric methyl silsesquioxane insulation film was prepared by the same method as in Example 1 except for changing the amount of the nanoparticles to 0.4 g and the amount of the methyl silsesquioxane polymer(M_w=10,000g/mol) to 0.6g to prepare a composition for coating.

Comparative Example 1

Preparation of an organic polymer with a network structure

Only a methyl methacrylate polymer with a network structure was prepared by the same method as in Example 1.

Preparation of a low dielectric insulation film

A low dielectric methyl silsesquioxane insulation film was prepared by the same method as in Example 1 except for using the methyl methacrylate polymer with a network structure prepared above instead of nanoparticles of core-shell type.

5

Comparative Examples 2 to 4

Preparation of an organic polymer with a network structure

Only a methyl methacrylate polymer with a network structure was prepared by the same method as in Example 1.

Preparation of a low dielectric insulation film

10

A low dielectric methyl silsesquioxane insulation film was prepared by the same method as in the Examples 2 to 4 except for using the methyl methacrylate polymer with a network structure prepared above instead of nanoparticles of core-shell type.

Experiment Example 1

Measurement of the radius and distribution of pores

15

The size and distribution of the pores inside the low dielectric insulation films prepared in Examples 1 to 4 were measured by using small angle X-ray scattering and the Peterson formula.

However, the size and the distribution of the pores inside the low dielectric insulation films prepared in Comparative Examples 1 to 4 were not measured due to the phase separation.

20

The measurements of the other low dielectric insulation films in Examples 1 to 4 are represented in the following Table 1 and Fig. 6.

Experiment Example 2

Measurement of a dielectric constant

25

Two different kinds of devices were fabricated to measure the dielectric constant of the low dielectric insulation films prepared in Examples 1 to 4 and Comparative Examples 1 to 4.

2-1. A metal/insulator/metal (MIM) device

30

A metal/insulator/metal (MIM) device was fabricated by plating an aluminum bottom electrode with a diameter of 5mm on a slide glass of the size of $1.2 \times 3.8 \text{ cm}^2$, then forming a low dielectric insulation film on the bottom electrode according to Examples 1 to 4 and Comparative Examples 1 to 4, and vacuum-plating an aluminum upper electrode on the film.

2-2. A metal/insulator/semi-conductor (MIS) device

35

A metal/insulator/semi-conductor (MIS) device was fabricated by plating a silicon (Si)-wafer bottom electrode, forming a low dielectric insulation film on the bottom electrode according to Examples 1 to 4 and Comparative Examples 1 to 4, and vacuum-plating an aluminum upper electrode with a diameter of 1 mm on the film.

As for these MIM and MIS devices prepared above, dielectric constants were

measured at the normal temperature by using a dielectric constant log (HP 4194A, Frequency: 1MHz). The measurements of the MIM device are charted in the following Table 1.

Table 1

	Amount of Added Nanoparticles (wt%)	Dielectric Constant	Diameter of a Pore (nm)	Others
Example 1	10	1.800±0.010	7.3	-
Example 2	20	1.740±0.020	7.1	-
Example 3	30	1.650±0.030	6.9	-
Example 4	40	1.440±0.050	7.1	-
Comparative Example 1	10	2.764±0.050	N.A.	Phase Separation
Comparative Example 2	20	2.660±0.050	N.A.	Phase Separation
Comparative Example 3	30	2.714±0.050	N.A.	Phase Separation
Comparative Example 4	40	2.750±0.050	N.A.	Phase Separation

5 As shown in the above Table 1, low dielectric insulation films prepared according to Examples 1 to 4 of the present invention had uniformly and minutely formed pores and low dielectric constants. However, those prepared according to Comparative Examples 1 to 4 showed phase separation and high dielectric constants.

10 In conclusion, according to embodiments of the present invention, a nanoparticle of core-shell type comprises an organic polymer core particle, with a silsesquioxane prepolymer with hydroxyl, methoxy, and ethoxy end groups surrounding it. The nanoparticle can advantageously work as a pore formation material for evenly forming a pore having a size (diameter) of less than 10 nm inside the silsesquioxane polymer material due to its high compatibility with a silicate polymer. This may result in a silsesquioxane insulation film with an ultra-low dielectric constant. Therefore, according to embodiments of the present invention, a silsesquioxane polymer insulation film with minute pores inside can be variously applied as an insulation material for semi-conductors and electronic parts due to its high dielectric rate and much improved insulation.

WHAT IS CLAIMED IS:

1. A nanoparticle of core-shell type comprising:
an organic polymer core particle with a network structure; and a shell-layer comprising a silsesquioxane prepolymer and surrounding the core particle.
- 5 2. The nanoparticle of core-shell type of claim 1, wherein a diameter of the nanoparticle is in a range from 2 nm to 120 nm.
3. The nanoparticle of core-shell type of claim 1, wherein a diameter of the organic polymer core particle is in a range from 1 nm to 100 nm.
- 10 4. The nanoparticle of core-shell type of claim 1, wherein the organic polymer core particle is prepared by polymerizing i) a multifunctional unsaturated monomer with more than two vinyl groups (a first unsaturated monomer), or ii) a mixture of a multifunctional unsaturated monomer with more than two vinyl groups and an unsaturated monomer with one vinyl group (a second unsaturated monomer).
- 15 5. The nanoparticle of core-shell type of claim 4, wherein the first unsaturated monomer is at least one selected from the group consisting of divinyl benzene, trivinyl benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane, allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, trimethylol propane trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, bisphenol-A diacrylate ethyl ester, bisphenol-A dimethacrylate ethyl ester, polyethylene glycol 600 dimethacrylate, polybutanediol diacrylate, pentaerythritol triacrylate, trimethylol propane triethoxy triacrylate, glycerylpropyloxytriacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxy pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxide siloxane, and polyphenyl vinyl siloxane.
- 20 6. The nanoparticle of core-shell type of claim 4, wherein the second unsaturated monomer is at least one selected from the group consisting of methacrylic acid, methacryl amide, methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene, vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-

methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, and vinyl piperidine.

5 7. The nanoparticle of core-shell type of claim 1, wherein the silsesquioxane prepolymer is prepared by using at least one silsesquioxane monomer selected from the group consisting of trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, 10 bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethyl benzene, and bis(trimethoxy silyl)ethyl benzene.

8. A method of preparing a nanoparticle of core-shell type comprising:

15 a) preparing a micro-emulsion by providing: i) a multifunctional unsaturated monomer with more than two vinyl groups (a first unsaturated monomer) or ii) a multifunctional unsaturated monomer with more than two vinyl groups and a unsaturated monomer with one vinyl group (a second unsaturated monomer), into a surfactant solution including a surfactant and a co-surfactant;

 b) preparing an organic polymer core particle with a network structure by adding an initiator into the micro-emulsion and reacting them with the monomer; and

20 c) preparing a silsesquioxane prepolymer shell-layer on the surface of the organic polymer core particle with a network structure by adding a silsesquioxane monomer and catalyst into the micro-emulsion and reacting them.

9. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the surfactant of a) is at least one cationic surfactant selected from the group consisting of: 25 sodium dodecyl sulfate (SDS), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), dodecyl benzene sulfonic acid, sodium dioctyl sulfosuccinate, sodium alkyl phenol ether sulfonate, and sodium alkyl sulfonate.

10. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the surfactant solution of the step a) comprises a surfactant in a range from 0.1 M to 10 M.

30 11. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the first unsaturated monomer is at least one selected from the group consisting of divinylbenzene, trivinylbenzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane, allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, 35 trimethylol propane trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene

glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, bisphenol-A diacrylate ethylester, bisphenol-A dimethacrylate ethylester, polyethylene glycol 600 dimethacrylate, polybutandiol diacrylate, pentaerythritol triacrylate, trimethylolpropane triethoxy triacrylate, glycerylpropyloxytriacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxy pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxide siloxane, and polyphenyl vinyl siloxane.

12. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the second unsaturated monomer is at least one selected from the group consisting of methacrylic acid, methacryl amide, methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene, vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, and vinyl piperidine.

13. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the weight ratio of the mixture between the surfactant and i) the first unsaturated monomer or ii) the mixture of the first unsaturated monomer and the second unsaturated monomer in the step a) is in a range from 1:100 to 100:1.

14. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the weight ratio of the silsesquioxane monomer and i) the first unsaturated monomer or ii) the mixture of the first unsaturated monomer and the second unsaturated monomer is in a range from 1:100 to 100:1.

15. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the catalyst used in c) is more than one base catalyst selected from the group consisting of sodium hydroxide, potassium hydroxide, potassium carbonate, and sodium carbonate.

16. The method of preparing a nanoparticle of core-shell type of claim 8, wherein the catalyst used in c) is at least one acid catalyst selected from the group consisting of hydrochloric acid, sulfuric acid, acetic acid, citric acid, and lactic acid.

17. A method of preparing a low dielectric insulation film comprising:

a) mixing a nanoparticle of core-shell type and a silicate polymer to form a mixture;
b) reacting the mixture of the nanoparticle of core-shell type and the silicate polymer by sol-gel reaction; and

c) heat-treating the reacted mixture such that minute pores are formed.

18. The method of preparing a low dielectric insulation film of claim 17, wherein the

nanoparticle of core-shell type and silicate polymer mixture is mixed such that the weight ratio of the mixture is in a range from 1:99 to 50:50.

5 19. The method of preparing a low dielectric insulation film of claim 17, wherein the heat treatment is performed at a temperature in a range between 200 °C to 500 °C, in a nitrogen atmosphere or a vacuum.

20. The method of preparing a low dielectric insulation film of claim 17, wherein the silicate polymer is at least one selected from the group consisting of methyl silsesquioxane, ethyl silsesquioxane, and hydrogen silsesquioxane.

10 21. The method of preparing a low dielectric insulation film of claim 20, wherein the silicate polymer comprises a repeating unit induced from at least one monomer selected from the group consisting of trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethylbenzene, and bis(trimethoxy silyl)ethylbenzene.

15 22. A low dielectric insulation film prepared by the method of claim 17, comprising the complex of the silsesquioxane prepolymer and the silicate polymer, with minute pores formed therein.

20 23. The low dielectric insulation film of claim 22, wherein a size of at least some of the pores is less than or equal to 100 nm.

AMENDED CLAIMS

[received by the International Bureau on 02 September 2005 (02.09.2005);
original claims 1-18 amended; remaining claims unchanged (4 pages)]

WHAT IS CLAIMED IS:

1. **(Amended)** A pore forming material comprising:
 an organic polymer core particle with a network structure; and a shell-layer
 comprising a silsesquioxane prepolymer and surrounding the core particle.
- 5 2. **(Amended)** The pore forming material of claim 1, wherein a diameter of the
 nanoparticle is in a range from 2 nm to 120 nm.
3. **(Amended)** The pore forming material of claim 1, wherein a diameter of the
 organic polymer core particle is in a range from 1 nm to 100 nm.
4. **(Amended)** The pore forming material of claim 1, wherein the organic polymer
 10 core particle is prepared by polymerizing i) a multifunctional unsaturated monomer with more
 than two vinyl groups (a first unsaturated monomer), or ii) a mixture of a multifunctional
 unsaturated monomer with more than two vinyl groups and an unsaturated monomer with
 one vinyl group (a second unsaturated monomer).
5. **(Amended)** The pore forming material of claim 4, wherein the first unsaturated
 15 monomer is at least one selected from the group consisting of divinyl benzene, trivinyl
 benzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol
 diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane,
 allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate,
 propylene glycol dimethacrylate, propylene glycol diacrylate, trimethylol propane
 20 trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene
 glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene
 glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate,
 tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol
 diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate,
 25 polyethylene glycol dimethacrylate, bisphenol-A diacrylate ethyl ester, bisphenol-A
 dimethacrylate ethyl ester, polyethylene glycol 600 dimethacrylate, polybutanediol diacrylate,
 pentaerythritol triacrylate, trimethylol propane triethoxy triacrylate,
 glycerylpropyloxytriacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate,
 dipentaerythritol monohydroxy pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl
 30 silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl
 silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl
 disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxide siloxane, and polyphenyl vinyl
 siloxane.
6. **(Amended)** The pore forming material of claim 4, wherein the second
 35 unsaturated monomer is at least one selected from the group consisting of methacrylic acid,
 methacryl amide, methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl
 acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl

styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene, vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl
 5 imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, and vinyl piperidine.

7. **(Amended)** The pore forming material of claim 1, wherein the silsesquioxane prepolymer is prepared by using at least one silsesquioxane monomer selected from the group consisting of trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl
 10 diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethyl benzene, and bis(trimethoxy silyl)ethyl benzene.

8. **(Amended)** A method of preparing a pore forming material comprising :
 15 a) preparing a micro-emulsion by providing: i) a multifunctional unsaturated monomer with more than two vinyl groups (a first unsaturated monomer) or ii) a multifunctional unsaturated monomer with more than two vinyl groups and a unsaturated monomer with one vinyl group (a second unsaturated monomer), into a surfactant solution including a surfactant and a co-surfactant;

20 b) preparing an organic polymer core particle with a network structure by adding an initiator into the micro-emulsion and reacting them with the monomer; and

c) preparing a silsesquioxane prepolymer shell-layer on the surface of the organic polymer core particle with a network structure by adding a silsesquioxane monomer and catalyst into the micro-emulsion and reacting them.

25 9. **(Amended)** The method of claim 8, wherein the surfactant of a) is at least one anionic surfactant selected from the group consisting of: sodium dodecyl sulfate (SDS), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), dodecyl benzene sulfonic acid, sodium dioctyl sulfosuccinate, sodium alkyl phenol ether sulfonate, and sodium alkyl sulfonate.

30 10. **(Amended)** The method of claim 8, wherein the surfactant solution of the step a) comprises a surfactant in a range from 0.1 M to 10 M.

11. **(Amended)** The method of claim 8, wherein the first unsaturated monomer is at least one selected from the group consisting of divinylbenzene, trivinylbenzene, divinyl pyridine, divinyl naphthalene, divinyl xylene, methyl silsesquioxane glycol diacrylate, trimethylol propane triacrylate, diethylene glycol divinyl ether, trivinyl cyclohexane, allyl
 35 methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, trimethylol propane trimethacrylate, glycidyl methacrylate, 2,2-dimethyl propane 1,3-diacrylate, 1,3-butylene glycol diacrylate,

1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 5 bisphenol-A diacrylate ethylester, bisphenol-A dimethacrylate ethylester, polyethylene glycol 600 dimethacrylate, polybutanediol diacrylate, pentaerythritol triacrylate, trimethylolpropane triethoxy triacrylate, glycerylpropyloxytriacylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxy pentaacrylate, divinyl silane, trivinyl silane, dimethyl vinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, 10 divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, polymethyl vinyl siloxane, polyvinyl hydroxide siloxane, and polyphenyl vinyl siloxane.

12. **(Amended)** The method of claim 8, wherein the second unsaturated monomer is at least one selected from the group consisting of methacrylic acid, methacryl amide, 15 methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl methacrylate, cyclohexyl methacrylate, styrene, α -methyl styrene, vinyl toluene, p-methyl styrene, ethyl vinyl benzene, vinyl benzene, vinyl naphthalene, vinyl xylene, 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, methyl 20 quinolin, isoquinolin, N-vinyl caprolactam, N-vinyl pyrrolidone, vinyl imidazole, N-vinyl carbazole, maleimide, N-vinyl oxazolidone, N-vinyl phthalimide, vinyl pyrrole, vinyl aniline, and vinyl piperidine.

13. **(Amended)** The method of claim 8, wherein the weight ratio of the mixture between the surfactant and i) the first unsaturated monomer or ii) the mixture of the first 25 unsaturated monomer and the second unsaturated monomer in the step a) is in a range from 1:100 to 100:1.

14. **(Amended)** The method of claim 8, wherein the weight ratio of the silsesquioxane monomer and i) the first unsaturated monomer or ii) the mixture of the first 30 unsaturated monomer and the second unsaturated monomer is in a range from 1:100 to 100:1.

15. **(Amended)** The method of claim 8, wherein the catalyst used in c) is more than one base catalyst selected from the group consisting of sodium hydroxide, potassium hydroxide, potassium carbonate, and sodium carbonate.

16. **(Amended)** The method of claim 8, wherein the catalyst used in c) is at least 35 one acid catalyst selected from the group consisting of hydrochloric acid, sulfuric acid, acetic acid, citric acid, and lactic acid.

17. **(Amended)** A method of preparing a low dielectric insulation film comprising:

a) mixing a pore forming material of claim 1 and a silicate polymer to form a mixture;

b) reacting the mixture of the pore forming material and the silicate polymer by sol-gel reaction; and

5 c) heat-treating the reacted mixture such that minute pores are formed.

18. **(Amended)** The method of preparing a low dielectric insulation film of claim 17, wherein the pore forming material and silicate polymer mixture is mixed such that the weight ratio of the mixture is in a range from 1:99 to 50:50.

10 19. The method of preparing a low dielectric insulation film of claim 17, wherein the heat treatment is performed at a temperature in a range between 200 °C to 500 °C, in a nitrogen atmosphere or a vacuum.

20. The method of preparing a low dielectric insulation film of claim 17, wherein the silicate polymer is at least one selected from the group consisting of methyl silsesquioxane, ethyl silsesquioxane, and hydrogen silsesquioxane.

15 21. The method of preparing a low dielectric insulation film of claim 20, wherein the silicate polymer comprises a repeating unit induced from at least one monomer selected from the group consisting of trichlorosilane, methyl triethoxy silane, methyl trimethoxy silane, methyl diethoxy silane, methyl dimethoxy silane, ethyl triethoxy silane, ethyl trimethoxy silane, ethyl diethoxy silane, ethyl dimethoxy silane, bis(trimethoxy silyl)ethane, bis(triethoxy silyl)ethane, bis(triethoxy silyl)methane, bis(triethoxy silyl)octane, bis(trimethoxy silyl)hexane, bis(triethoxy silyl)ethylbenzene, and bis(trimethoxy silyl)ethylbenzene.

22. A low dielectric insulation film prepared by the method of claim 17, comprising the complex of the silsesquioxane prepolymer and the silicate polymer, with minute pores formed therein.

25 23. The low dielectric insulation film of claim 22, wherein a size of at least some of the pores is less than or equal to 100 nm.

1/4

Fig.1

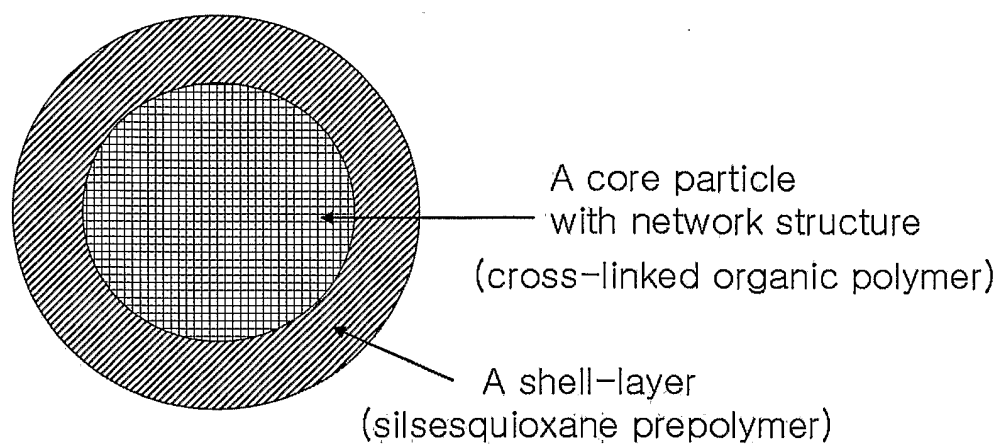
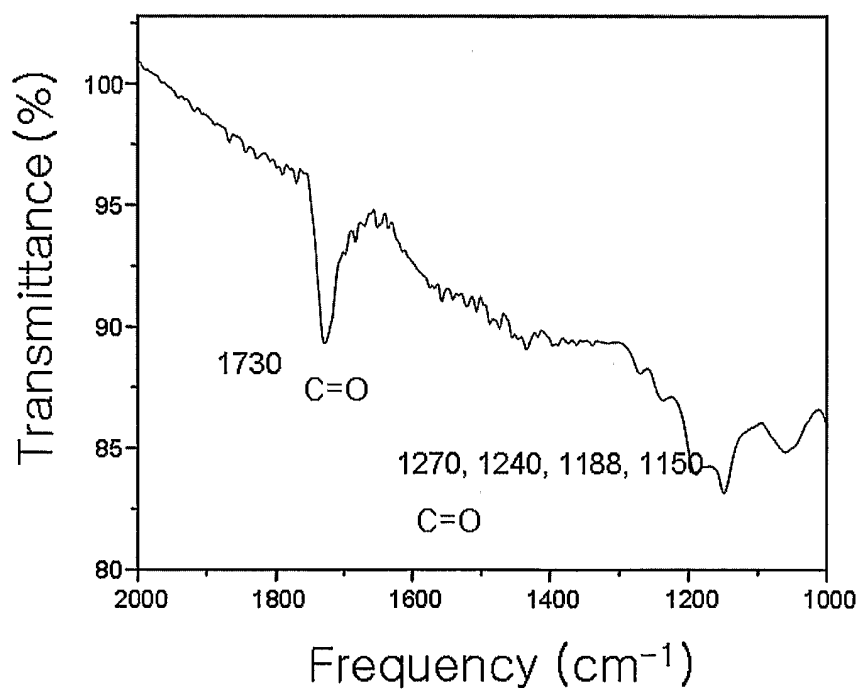


Fig.2



2/4

Fig.3

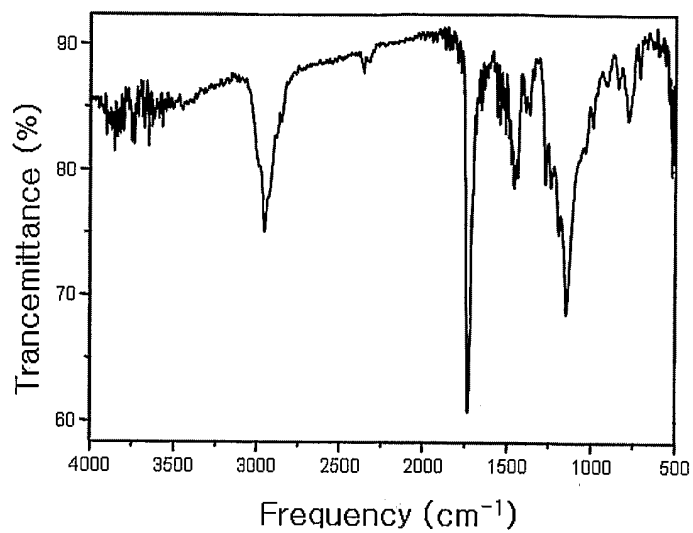
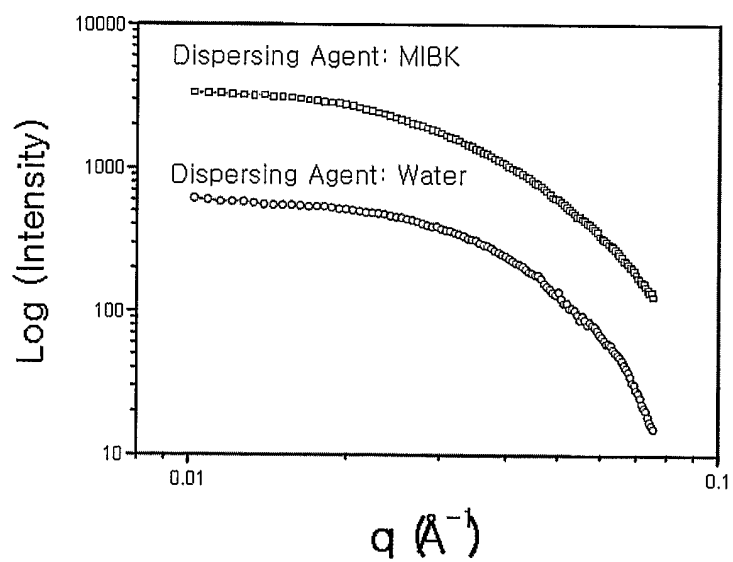
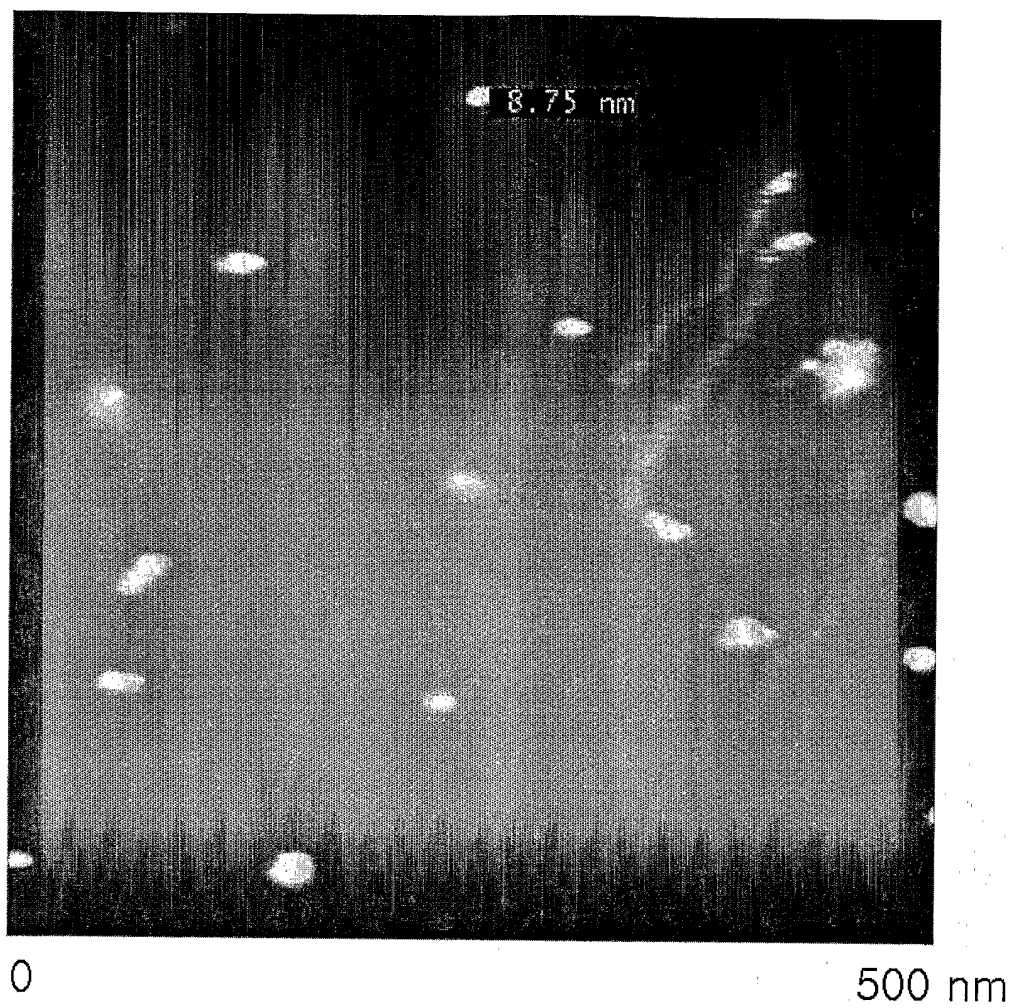


Fig.4



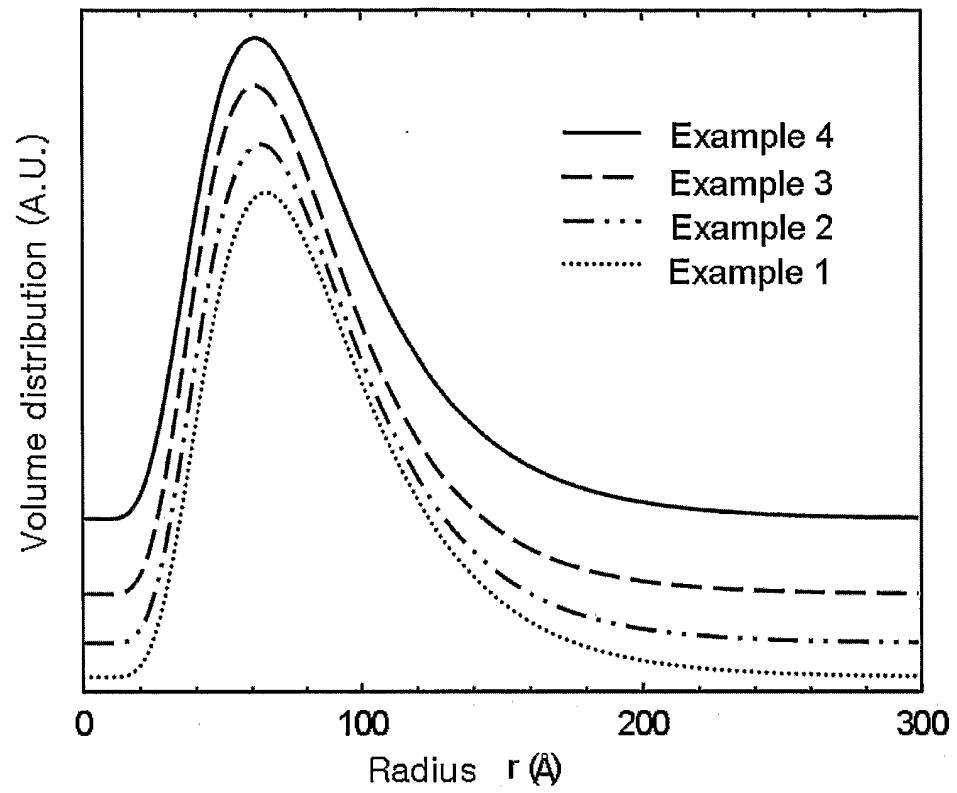
3/4

Fig.5



4/4

Fig.6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 2005/001053

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08F 291/00, C08F 8/42, C09D 183/10, C08G 77/42, C08F 2/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C08F, C08G, C08L, C09DDocumentation searched other than minimum documentation to the extent that such documents are included in the fields searched
----Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPODOC, WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 449263 A2 (JAPAN SYNTHETIC RUBBER CO. LTD.) 2 October 1991 (02.10.1991) <i>claims 1 and 16, abstract, page 3, lines 15-20, page 5, lines 6-15 and lines 52-53, page 6, lines 31-34, pages 9 and 10, table 1, example 10.</i>	1-16

X	US 4859740 A (DAMRATH et al.) 22 August 1989 (22.08.1989) <i>claims 1-4, examples.</i>	1-16

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search
6 June 2005 (06.06.2005)Date of mailing of the international search report
4 July 2005 (04.07.2005)Name and mailing address of the ISA/ AT
Austrian Patent Office
Dresdner Straße 87, A-1200 ViennaAuthorized officer
PUSTERER F.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 2005/001053

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					DE	D1	69120125D	1996-07-18	
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					JP	A	3279244	1991-12-10	