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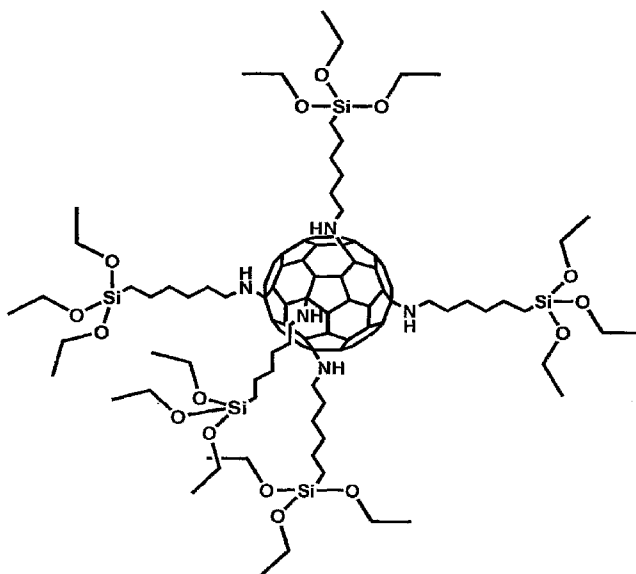
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(54) Title: POROUS MATERIALS DERIVED FROM POLYMER COMPOSITES



(57) Abstract: This disclosure relates generally to networks of polymers in fullerene compounds and polymers, to methods of preparing precursors for such networks, and to their subsequent use as low dielectric constant materials in microelectronic devices.

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## POROUS MATERIALS DERIVED FROM POLYMER COMPOSITES

### BACKGROUND OF THE INVENTION

#### Field of the Invention

[0001] This disclosure relates generally to fullerene-comprising compounds, methods of preparing such compounds, and to their subsequent use as low dielectric constant materials in microelectronic devices.

### BRIEF SUMMARY OF THE INVENTION

[0002] In one embodiment, the present invention provides methods of producing a porous film. In suitable embodiments, a polyfunctional fullerene monomer comprising at least one reactive arm is provided. A composite precursor solution comprising the polyfunctional fullerene monomer and at least one organic polymer porogen is then prepared. The composite is then applied to a substrate and the polyfunctional monomer cured. At least a portion of the porogen is then removed to form the porous film. In exemplary embodiments, the polyfunctional fullerene monomer comprises a fullerene (e.g., C<sub>60</sub>) and at least one reactive arm comprising: a reactive group coupled to the fullerene; an organic spacer portion; and a metal or metalloid alkoxide. Exemplary reactive arms suitably comprise: an amine, an azide, a diene or a carbanion; an alkyl organic spacer portion; and a metal or metalloid alkoxide selected from the group consisting of -Si(OR)<sub>3</sub>, -Ge(OR)<sub>3</sub>, -Ti(OR)<sub>3</sub>, -Zr(OR)<sub>3</sub>, -Sn(OR)<sub>3</sub>, -Al(OR)<sub>2</sub> and -B(OR)<sub>2</sub>. For example, the reactive arms can be 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, diethylenetriaminopropyltrimethoxysilane, hexanediaminomethyltriethoxysilane or 11-aminoundecyltriethoxysilane.

[0003] Exemplary porogens for use in the practice of the present invention include acrylate-based polymers such as poly(methyl methacrylate). Suitably methods for applying the composite include, spin-coating, dip-coating or spray-coating. Suitably, the curing comprises heating to between about 50°C to 120°C in a moist atmosphere. Exemplary methods for removing the porogen include thermal baking, for example, heating to between about 150°C to 350°C in an inert atmosphere.

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[0004] The present invention also provides methods of producing a porous film. For example, a plurality of C<sub>60</sub> fullerenes are provided, and then aminoethyltriethoxysilane is added to the fullerenes, wherein amino groups of the aminoethyltriethoxysilane react with the fullerenes to generate functionalized fullerenes. The functionalized fullerenes are combined with poly(methyl methacrylate) to generate a composite and then applied to a substrate. The polyfunctional monomer is then cured, and at least a portion of the poly(methyl methacrylate) is removed to form a porous film. In further embodiments, films, including films produced by the methods of the present invention, are provided.

### BRIEF DESCRIPTION OF THE DRAWINGS/FIGURES

[0005] FIGURE 1 shows a typical polyfunctional fullerene monomer.

[0006] FIGURE 2 shows a representation of a section of the composite structure of the fullerene cluster polymer and polymer porogen after deposition onto a substrate and initial curing. Fullerene cages are shown as hashed circles, junctions formed by the condensation of terminal groups of the radial arms are shown as black hexagons, the porogen is shown as a dashed solid, and the solid substrate is dotted.

[0007] FIGURE 3 shows the section of FIG 2, after removal of the polymeric porogen.

[0008] FIGURE 4 shows a representation of the process steps disclosed herein.

### DETAILED DESCRIPTION OF THE INVENTION

[0009] The derivatized fullerene monomers of the present disclosure, used as precursors to matrix-forming polymers, and which are well-suited for forming highly crosslinked three-dimensional networks, include a central core comprising a fullerene that is subsequently derivatized by a plurality of radial arms. Such derivatized fullerene molecules possess a high solubility in common solvents and the ability to form three-dimensional network polymers upon condensation with adjacent clusters. The clusters and polymers prepared according to the present disclosure are largely composed of fragments exhibiting intrinsically low dielectric constants.

[0010] The present invention also relates to methods for combining the monomers with a thermally labile organic polymer porogen to form a composite structure, depositing the composite structure as a film on a desired substrate, polymerizing the fullerene-containing

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matrix material, and subsequently removing the polymer porogen to yield a porous polymer film, especially when such films are used as intra- or interlayer dielectrics for microelectronic devices. Any preparative route that produces a similar soluble, reactive fullerene monomer, where the core is symmetrically surrounded by one or more arms each terminated by a reactive group may be used. One method involves the use of a bifunctional coupling agent to form the arms that contain, at one end an amine group and at the opposite end a metal- or metalloïd-alkoxide. Any coupling agent which is capable of both reacting with a fullerene and undergoing condensation reactions with other identical coupling agents may be used.

**[0011]** The fullerene core of the organic phase precursor monomers includes, but is not limited to one or more of the following: C<sub>60</sub>, C<sub>70</sub>, C<sub>72</sub>, C<sub>74</sub>, C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, C<sub>96</sub>, and higher analogues up to, and beyond, C<sub>184</sub> or mixtures thereof. Commercially available mixtures of C<sub>60</sub> and C<sub>70</sub>, commonly know as Fullerite, fullerene extract, or fullerene soot may also be employed in various embodiments of the present invention.

**[0012]** Many possible compounds that are well-suited to form the reactive arms of the organic phase precursor monomers are readily available. The reactive arms include three general parts; a terminal group known to react with fullerenes, a linear organic spacer, and an opposing terminal group capable of undergoing multiple condensation reactions, or which is cross-linkable, with similar groups.

**[0013]** Any terminal group capable of forming covalent bonds with the fullerene core may be used. For example, terminal groups to couple the arms to the fullerene core include a primary or secondary amine. Amines are known to those skilled in the art to react with fullerenes in a facile manner by nucleophilic addition reactions across one of the many delocalized bonds of the fullerene cage. Anywhere from one to twelve amine molecules may be added to a single C<sub>60</sub> molecule, the actual number depending largely on their steric bulk. One example being six. Other reactive groups, especially other nucleophiles, may be used, which include, but are not limited to azides, dienes, and carbanions.

**[0014]** The organic-spacer portion of the coupling agent may be any spacer group capable of connecting the terminal groups. For example, the spacer groups include, but are not limited to an alkyl chain, a polyether chain, a polyunsaturated alkyl chain, or an amine-containing alkyl chain. In one example, the organic spacer is an alkyl chain 3-20 carbon

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units long, alternatively 3-7 carbon units long. The spacer chain may include one or more heteroatomic groups, such as ether groups or amino groups, and optionally, may further include one or more rigid components, including, but not limited to alkynyl- segments, aryl- segments, or other cyclic segments.

[0015] The opposing terminal reactive group used for linking the organic phase monomers to each other and to the other components of the composite structure may be any cross-linkable group. For example, the cross-linkable terminal group includes, but is not limited to metal- or metalloid-alkoxides. Alkoxides are well known in the art to readily undergo hydrolysis and condensation reactions, forming polymeric oxides, and to bond with, upon hydrolysis, the chemically similar surfaces of solid oxides. Any one of numerous possible alkoxide groups may be used according to the present disclosure, including, but not limited to,  $-\text{Si}(\text{OR})_3$ ,  $-\text{Ge}(\text{OR})_3$ ,  $-\text{Ti}(\text{OR})_3$ ,  $-\text{Zr}(\text{OR})_3$ ,  $-\text{Sn}(\text{OR})_3$ ,  $-\text{Al}(\text{OR})_2$ ,  $-\text{B}(\text{OR})_2$ . In one embodiment, as silica is a well known dielectric material, an example of a terminal group is  $-\text{Si}(\text{OR})_3$ .

[0016] The following are non-limiting examples of commercially available coupling agents which can be used in the practice of the present invention; 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, diethylenetriamino-propyltrimethoxysilane, hexanediaminomethyltriethoxysilane, 11-aminoundecyltriethoxysilane. However, numerous additional compounds may prove useful.

[0017] The preparation of the polyfunctional fullerene monomer may be readily achieved. The desired amount of the selected fullerene core is added to a large excess of the selected coupling agent. Initially, the fullerene is insoluble in the coupling agent and is present as a fine black suspension. Reaction of the amine group of the coupling agent with the fullerene occurs readily at ambient temperature. However, heating the mixture to 50-60 °C allows the reaction to proceed at a more desirable rate. As the reaction proceeds, the partially derivatized fullerenes exhibit increased solubility in the coupling agent and the mixture exists as a dark brown solution. After approximately 18 hours, the formation of the organic phase precursor monomer is complete, with the maximum number of coupling agents, typically six, being added to the fullerene core. The unreacted coupling agent is removed using vacuum-distillation and recovered for use in future

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preparations, leaving a deep brown-black residue containing the organic phase precursor monomer. An example of such a compound, derived from C<sub>60</sub> and 6-aminohexyltriethoxysilane is shown in FIG. 1.

- [0018] The derivatized fullerene monomers possesses a high solubility in many common organic solvents, including alkanes, toluene, benzene, ketones, and alcohols. Examples of alcohols for use in the present invention include, but are not limited to ethanol and 2-propanol, which are solvents employed for the deposition of spin-on inorganic films in the microelectronics industry. The residue prepared as above may be redissolved in a solvent suitable for application to the desired substrate, such as ethanol.
- [0019] The fullerene monomers may form network polymers through condensation reactions with adjacent monomers or clusters of monomers. With multiple reactive arms surrounding each monomer fullerene core, each monomer can form several strong links with neighboring monomers. Highly-crosslinked polymers show significant increases in both thermal stability and mechanical strength relative to similar polymers that are less crosslinked. Both of these qualities are important for a material that is intended for use in microelectronic devices, where temperatures of 400 °C as well as strong mechanical forces are common during processing.
- [0020] The polyfunctional fullerene monomers may also form strong bonds to common substrates encountered in microelectronic structures. These substrates include, but are not limited to oxides and metals, two classes of materials that form strong bonds to films containing alkoxides. Excellent film adhesion is a property that a successful dielectric material should possess to achieve use in practice. With multiple reactive groups per cluster, the fullerene monomer may form strong bonds to a desired substrate, especially relative to other organic polymers found in the art.
- [0021] The matrix-forming polyfunctional fullerene monomer may be combined with an organic polymeric porogen material in a suitable solvent, to form a precursor solution for the composite structure used to form the final porous film. The material for the porogen phase is suitably thermally or chemically removable under conditions that do not degrade the fullerene-containing matrix. In addition, the material suitably will be adequately soluble in a solvent, or mixture of solvents that also show good solvating ability towards the matrix-forming fullerene monomers. The porogen is suitably miscible with the matrix-forming monomer in proportions adequate to yield the desired amount of final

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film porosity, and it should be available in a suitable range of molecular weights to form pores of the desired size.

[0022] Examples of porogens for use in the present invention include acrylate-based polymer porogens. One example of a porogen for use includes, but is not limited to, poly(methyl methacrylate). This polymer is widely available in various desirable molecular weights, shows good solubility in useful solvents such as ketones and ethers, and is easily thermally depolymerized with the onset occurring above 150 °C. These may be derived from copolymers of methyl methacrylate with other acrylate esters, from direct polymerization of other acrylate monomers, or from copolymers with other monomers such as styrene. Currently available examples of other useful acrylate-based polymer porogens include, but are not limited to, poly(methyl methacrylate-co-ethyl acrylate), poly(methyl methacrylate-co-ethylene glycol dimethacrylate), poly(methyl methacrylate-co-butyl methacrylate), poly(styrene-co-methyl methacrylate), or poly(styrene-co-butadiene-co-methyl methacrylate). Alternatively, the polymeric porogen may include either a linear polymer or a crosslinked polymer formed by any common crosslinking agent including, but not limited to, allylmethacrylate or 1,3,5-trivinylbenzene.

[0023] The ratio of the matrix-forming monomer and the porogen is chosen such that each phase exists as a continuous network conterminous with the other phase. This provides a free path for the subsequent removal of the porogen, to avoid the formation of pores larger than about 20 nm in diameter, and to leave a strong, continuous matrix after the porogen has been removed. Additionally, the amount of porogen is suitably sufficient to ensure that the desired level of porosity of the final film is achieved, with a corresponding lowering of the film's dielectric constant. In one example, the porogen occupies between about 30% and 60% of the volume of the dried composite film after deposition onto the desired substrate. Other compositions that yield a suitably strong porous film may also be used.

[0024] A solution of the matrix-forming fullerene monomer may be combined with a solution of the chosen porogen, forming a composite film precursor solution. This solution is applied to the desired substrate by any method commonly employed in the art, such as spin-coating, dip-coating, or spray-coating. A subsequent initial thermo-chemical curing step removes residual solvent and initiates the hydrolysis and condensation reactions of the terminal alkoxide groups of the radial arms in the matrix-forming phase,

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crosslinking fullerene-containing monomers and bonding the entire composite structure to the solid substrate. This step is performed at a temperature and under an atmosphere sufficient to hydrolyze and condense the alkoxide groups of the matrix-forming monomers, but which will leave the porogen phase unaffected. The initial curing step is suitably performed between about 50 °C and about 120 °C under an atmosphere of moist air. A section of such a composite structure on a solid substrate is shown in FIG. 2. Fullerene cages are shown as hashed circles, junctions formed by the condensation of terminal groups of the radial arms are shown as black hexagons, the porogen is shown as a dashed solid, and the solid substrate is dotted.

**[0025]** The porogen phase may be removed during a subsequent thermal bake. This step is generally performed at a temperature, and under an atmosphere, which will depolymerize and volatilize the porogen, but leave the polymerized fullerene matrix unaffected. This typically requires an inert atmosphere, typically oxygen-free argon or nitrogen, and at temperatures in the range between about 150 and about 350 °C, though temperatures outside of this range may be employed without departing from the methods of the present disclosure. FIGURE 3 shows a representation of such a porous film after removal of the porogen. The film includes fullerenes (hashed circles) linked in a three-dimensional network by the condensation of the terminal groups of the reactive arms (black hexagons).

**[0026]** Alternatively, a portion or all of the porogen phase may be extracted from the composite film prior to the thermal cure. This is typically accomplished by contacting the film with a solvent capable of dissolving the porogen while leaving the fullerene polymer matrix unaffected.

**[0027]** The matrix materials of the films prepared as disclosed above possess both an intrinsically low dielectric constant, due to the low silica content of the fullerene polymer, and a controllable amount of porosity. The low dielectric constant of the fullerene polymer allows for a lower amount of porosity to be used when a certain dielectric constant is desired, relative to commonly used porous matrices with higher dielectric constants, such as silica.

**[0028]** A summary of the process steps typically contemplated according to the present disclosure is shown in FIG. 4.

### Examples

- [0029]** The following non-limiting example demonstrates the experimental conditions suitable to prepare a microporous films of polymerized fullerene monomers, useful as low dielectric constant materials, according to the methods described hereinabove.
- [0030]** A porous, three-dimensional polymeric network of linked fullerenes with a low dielectric constant was prepared according to the processes of the present disclosure. A solution of a polyfunctional starburst-shaped fullerene molecule to be used as a monomer for said polymer was prepared as follows. About 0.50 grams of C<sub>60</sub> was mixed with about 20 mL of 6-aminohexyltriethoxysilane in a 100-mL Schlenk flask. The flask was flushed with dry nitrogen, and the mixture heated to about 60 °C for about 24 hours. During that time the mixture slowly changed from a clear liquid containing a fine black suspended powder to a dark brown solution with a moderate amount of a thick brown precipitate. The remaining 6-aminohexyltriethoxysilane was removed by vacuum distillation. This should be accomplished at the lowest possible pressure so that lower distillation temperatures may be employed. After the brown-black residue was dry, about a 0.250-gram portion was removed and dissolved in about 10 mL of anhydrous ethanol/10mL of acetone. This solution was filtered to remove any undissolved material and reserved for use in the next step.
- [0031]** The above solution was mixed with a second solution of about 0.150 grams of poly(methylmethacrylate) (MW is about 50,000 g/mol) in methylisobutyl ketone. The composite precursor solution was coated onto a 2 x 2-cm section of silicon wafer and allowed to air dry. The coated substrate was then heated to about 60 °C for about 30 minutes to remove residual solvent. The temperature was then increased to about 90 °C and the substrate was held at that temperature under an atmosphere of moist air for about 120 minutes. The atmosphere was then exchanged for dry argon, and the temperature above the coated substrate was increased at a rate of about 5 °C/min to about 200 °C and held at that temperature for about 60 minutes. A continued increase at about 5 °C/min to about 350 °C and an isothermal bake at that temperature for about 30 minutes completed the removal of the porogen and the curing process. The resulting brown film contained approximately 50% porosity and exhibited excellent adhesion and scratch resistance and is well-suited for use as a low dielectric constant material.

[0032] Exemplary embodiments of the present invention have been presented. The invention is not limited to these examples. These examples are presented herein for purposes of illustration, and not limitation. Alternatives (including equivalents, extensions, variations, deviations, etc., of those described herein) will be apparent to persons skilled in the relevant art(s) based on the teachings contained herein. Such alternatives fall within the scope and spirit of the invention.

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## WHAT IS CLAIMED IS:

1. A method of producing a porous film, comprising:
  - (a) providing a polyfunctional fullerene monomer comprising at least one reactive arm;
  - (b) preparing a composite precursor solution comprising the polyfunctional fullerene monomer and at least one organic polymer porogen;
  - (c) applying the composite precursor solution to a substrate;
  - (d) curing the polyfunctional monomer; and
  - (e) removing at least a portion of the at least one porogen to form a porous film.
2. The method of claim 1, wherein the polyfunctional fullerene monomer comprises a fullerene and at least one reactive arm, wherein the at least one reactive arm comprises: a reactive group coupled to the fullerene; an organic spacer portion; and a metal or metalloid alkoxide.
3. The method of claim 2, wherein the fullerene comprises a C<sub>60</sub> fullerene.
4. The method of claim 2, wherein the at least one reactive arm comprises: an amine, an azide, a diene or a carbanion; an alkyl organic spacer portion; and a metal or metalloid alkoxide selected from the group consisting of -Si(OR)<sub>3</sub>, -Ge(OR)<sub>3</sub>, -Ti(OR)<sub>3</sub>, -Zr(OR)<sub>3</sub>, -Sn(OR)<sub>3</sub>, -Al(OR)<sub>2</sub> and -B(OR)<sub>2</sub>.
5. The method of claim 2, wherein the at least one reactive arm is selected from the group consisting of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, diethylenetriaminopropyltrimethoxysilane, hexane-diaminomethyltriethoxysilane and 11-aminoundecyltriethoxysilane.
6. The method of claim 1, wherein the composite precursor solution comprises the polyfunctional fullerene monomer and an acrylate-based polymer.

7. The method of claim 6, wherein the composite precursor solution comprises the polyfunctional fullerene monomer and poly(methyl methacrylate).
8. The method of claim 1, wherein the applying comprises spin-coating, dip-coating or spray-coating the composite precursor solution.
9. The method of claim 1, wherein the curing comprises heating the polyfunctional monomer to between about 50°C to 120°C in a moist atmosphere.
10. The method of claim 1, wherein the removing comprises thermal baking, thereby removing at least a portion of the at least one porogen.
11. The method of claim 10, wherein the removing comprises heating to between about 150°C to 350°C in an inert atmosphere, thereby removing at least a portion of the at least one porogen.
12. A method of producing a porous film, comprising:
  - (a) providing a plurality of C<sub>60</sub> fullerenes;
  - (b) adding aminohexyltriethoxysilane to the fullerenes, wherein amino groups of the aminohexyltriethoxysilane react with the fullerenes to generate functionalized fullerenes;
  - (c) combining the functionalized fullerenes with poly(methyl methacrylate) to generate a composite solution;
  - (d) applying the composite solution to a substrate;
  - (e) curing the functionalized fullerenes; and
  - (f) removing at least a portion of the poly(methyl methacrylate) to form a porous film.
13. The method of claim 12, wherein the applying comprises coating the composite solution on a silicon wafer.

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14. The method of claim 12, wherein the curing comprises heating the functionalized fullerenes to greater than about 80°C.
15. The method of claim 12, wherein the removing comprises heating the functionalized fullerenes to greater than about 200°C in an inert atmosphere.
16. A film on a substrate, wherein the film comprises a polyfunctional fullerene monomer and a porogen.
17. The film of claim 16, wherein the polyfunctional fullerene monomer comprises a fullerene and at least one reactive arm, wherein the at least one reactive arm comprises: a reactive group coupled to the fullerene; an organic spacer portion; and a metal or metalloid alkoxide.
18. The film of claim 16, wherein the fullerene comprises a C<sub>60</sub> fullerene.
19. The film of claim 16, wherein the at least one reactive arm comprises: an amine, an azide, a diene or a carbanion; an alkyl organic spacer portion; and a metal or metalloid alkoxide selected from the group consisting of -Si(OR)<sub>3</sub>, -Ge(OR)<sub>3</sub>, -Ti(OR)<sub>3</sub>, -Zr(OR)<sub>3</sub>, -Sn(OR)<sub>3</sub>, -Al(OR)<sub>2</sub> and -B(OR)<sub>2</sub>.
20. The film of claim 16, wherein the at least one reactive arm is selected from the group consisting of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, diethylenetriaminopropyltrimethoxysilane, hexane-diaminomethyltriethoxysilane and 11-aminoundecyltriethoxysilane.
21. The film of claim 16, wherein the porogen comprises an acrylate-based polymer.
22. The film of claim 16, wherein the porogen comprises poly(methyl methacrylate).
23. The film of claim 16, wherein the substrate comprises a metal.
24. The film of claim 16, wherein the substrate comprises an oxide.
25. The film of claim 16, wherein the film comprises between about 30% and about 80% of the porogen.

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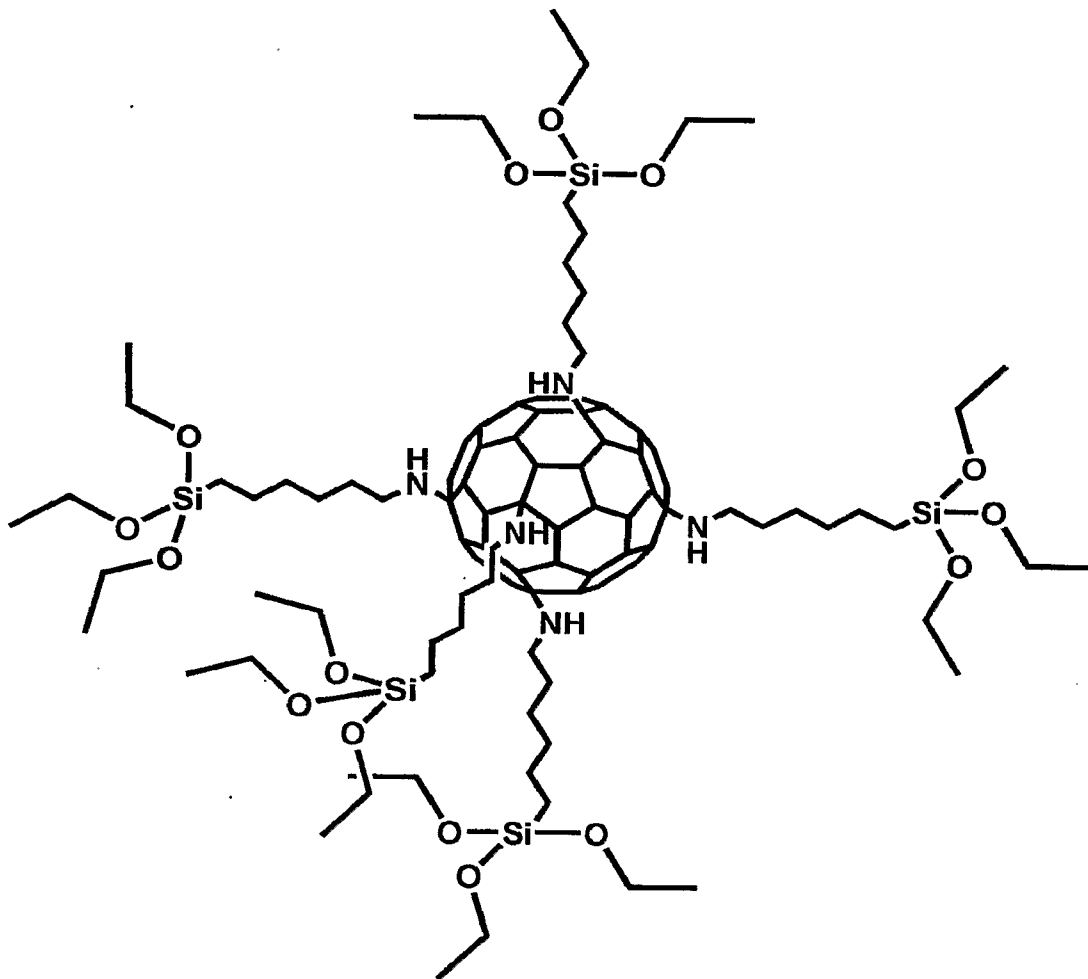
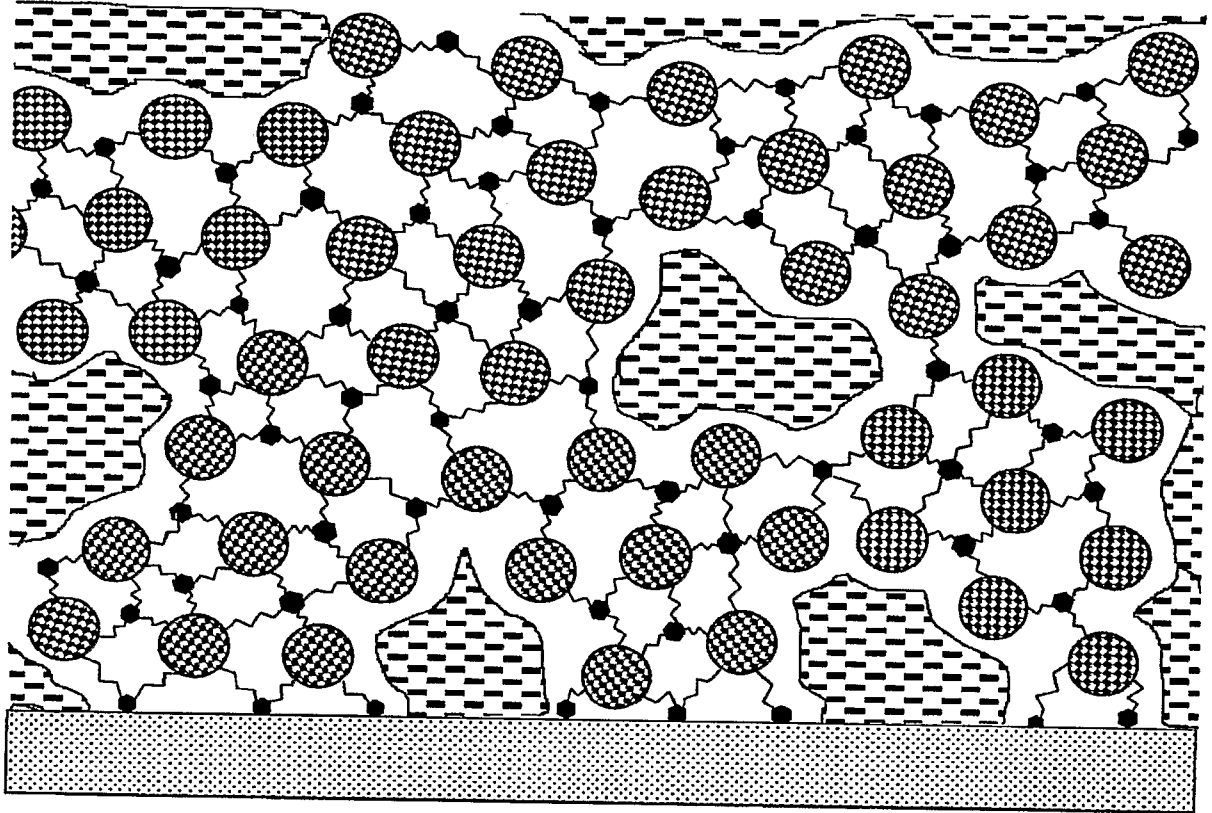


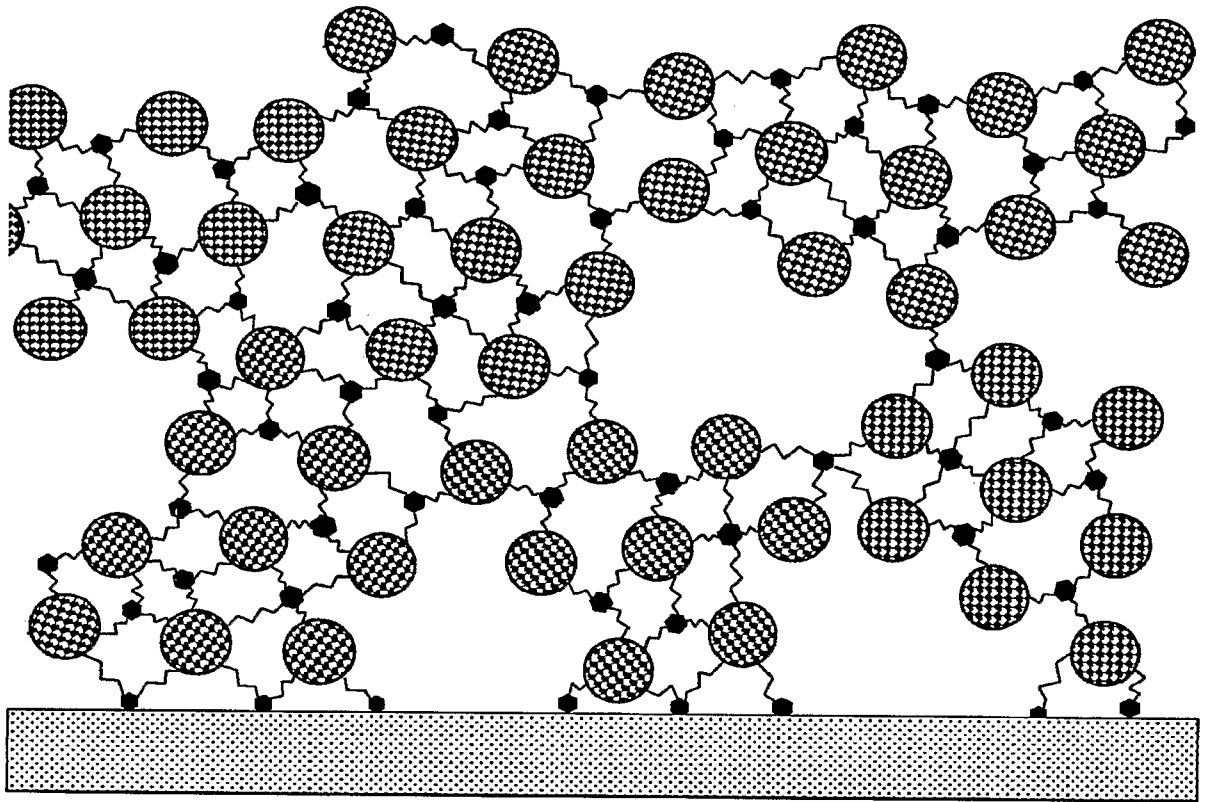
FIGURE 1

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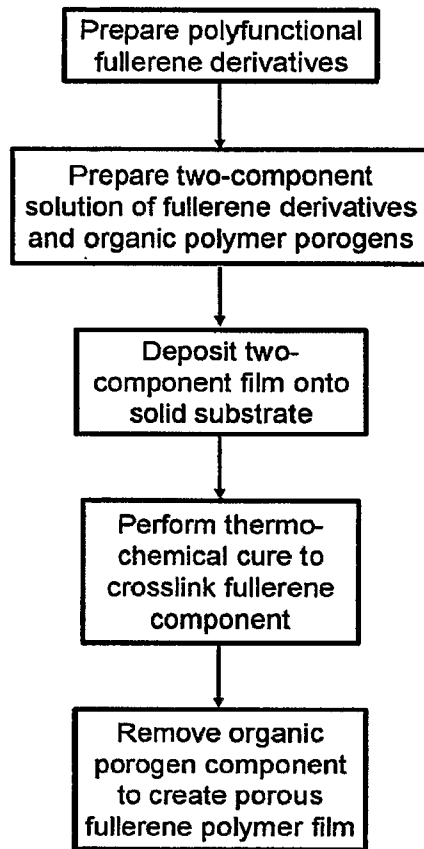
*FIGURE 2*

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*FIGURE 3*

4/4

**FIGURE 4**

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**New International Application  
Inventory of Unscannable or Missing  
Items**

Serial Number PCT/US 07/12836

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✓	Abstract	
✓	Drawings	
	Express Mail Label or Envelope	✓
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✓	Fees Calculation sheet	
	Other (specify)	

## INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC(8) - H01L 21/02, C07C 13/605 (2007.01)  
 USPC - 585/12, 257/632

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)  
 USPC -- 585/12, 257/632

Documentation 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)  
 WEST -- PGPB,USPT,USOC,EPAB,JPAB; Dialog Classic Files 351, 155, 2, 6, 35, 65; Google Patents; USPTO Web Page  
 Search terms -- porous, film, porogen, fullerene, C60, substrate, aminoxytriethoxysilane, polymethyl methacrylate, metal, silica, oxide, 3-aminopropyltrimethoxysilane, spin-coating, heating, wafer, inert atmosphere

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2005/0238889 A1 (IWAMOTO et al.) 27 October 2005 (27.10.2005), para [0004], [0005], [0008], [0011], [0064], [0085], [0086], [0089], [0095], [0105], [0110], [0114], [0134]	16 and 25 ----- 1-15 and 17-24
Y	US 2006/0002875 A1 (WINKLER et al.) 05 January 2006 (05.01.2006), para [0018], [0038], [0039], [0043], [0087], [0089], [0144], [0146], [0357], [0359], [0360], [0376], [0420], [0428]	1-15, 17 and 19-24
Y	US 2004/0121501 A1 (LARGE et al.) 24 June 2004 (24.06.2004), para [0010], [0011]	3, 12-15 and 18
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Further documents are listed in the continuation of Box C.

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Date of the actual completion of the international search

20 September 2007 (20.09.2007)

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