



(51) International Patent Classification:

H01G 4/33 (2006.01) *C23C 18/12* (2006.01)
C08G 77/04 (2006.01) *H01G 4/018* (2006.01)
C08G 77/26 (2006.01)

(21) International Application Number:

PCT/US2017/032414

(22) International Filing Date:

12 May 2017 (12.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/335,108 12 May 2016 (12.05.2016) US

(71) Applicant: **GEORGIA TECH RESEARCH CORPORATION** [US/US]; 505 Tenth St., NW, Atlanta, Georgia 30332 (US).

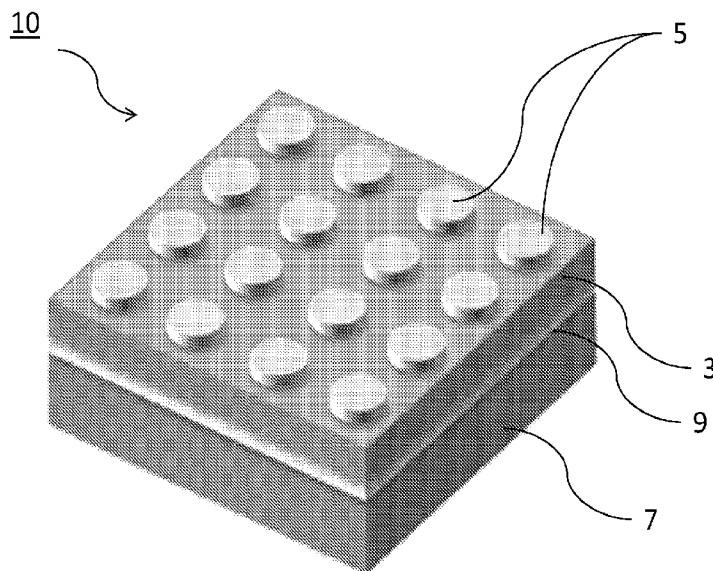
(72) Inventors: **PERRY, Joseph W.**; C/o Georgia Tech Research Corporation, 505 Tenth St., NW, Atlanta, Georgia 30332 (US). **KATHAPERUMAL, Mohanalingam**; C/o Georgia Tech Research Corporation, 505 Tenth St., NW, Atlanta, Georgia 30332 (US). **KIM, Yun Sang**; C/o Georgia Tech Research Corporation, 505 Tenth St., NW, Atlanta, Georgia 30332 (US).

(74) Agent: **SCHNEIDER, Ryan A.** et al.; Troutman Sanders LLP, 600 Peachtree St., NE, Suite 5200, Atlanta, Georgia 30308 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

(54) Title: POLARIZABLE SOL-GEL MATERIALS, METHODS OF PREPARATION AND PROCESSING FOR HIGH ENERGY AND POWER STORAGE DEVICES

FIG. 1



(57) Abstract: A capacitor device with high energy density and high extraction efficiency based on sol-gel films. The films can be formed by use of a single precursor, including siloxane precursors bearing a polar group on a flexible tethering group. The sol-gel compositions used in the formation of films can have high dielectric permittivity, low dielectric loss, high breakdown strength and high-energy storage properties. The forming processing methods described here can be well suited for both high energy density and high power density to provide enhanced energy storage capabilities for discrete, embedded or on-chip integrated capacitor applications, gate dielectrics for transistors and displays, capacitive touch screens, light weight mobile defibrillators, filters for cellular devices, electric propulsion, electric vehicles, power invertors for microgrid storage, load leveling of transients on a wide range of timescales for medium voltage electric grids.



CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

POLARIZABLE SOL-GEL MATERIALS, METHODS OF PREPARATION AND PROCESSING FOR HIGH ENERGY AND POWER STORAGE DEVICES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This Application claims benefit of priority under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application No. 62/335,108, filed May 12, 2016, and titled “POLARIZABLE SOL-GEL MATERIALS, METHODS OF PREPARATION AND PROCESSING FOR HIGH ENERGY AND POWER STORAGE DEVICES,” which is incorporated by reference herein in its entirety as if fully set forth below.

BACKGROUND

[0002] Electrical energy storage devices can be increasingly important as a class of devices for both high-energy density and high-power density to provide enhanced energy storage capabilities for a very wide variety of applications, including but not limited to discrete, embedded or on-chip integrated capacitor applications, gate dielectrics for transistors and displays, capacitive touch screens, filters for cellular devices, defibrillators, electric propulsion, electric vehicles, power invertors, microgrid storage, and load leveling of transients over a wide range of timescales for medium voltage electric grids. Among high-performance energy storage materials and devices, such as capacitors, supercapacitors, batteries, and fuel cells, capacitors can be advantageous for high power density because of their fast electrical charge and discharge responses. The performance of capacitors can be limited by the characteristics of the dielectric storage material. Such limitations can include permittivity, electrical loss, breakdown strength and statistics, and processability. The stored energy density (U) in dielectric films can be generally expressed as shown in Equation (1):

$$U = \int E \, dD \quad (1)$$

where E is the applied electric field and D is the electric displacement.

[0003] In addition to having a high dielectric strength, a large electric displacement that can be obtained through high permittivity can also be desirable to maximize the storage capacity of dielectric materials. A need exists for, among other things, the development of materials that possess high permittivity, large breakdown strength, low loss at high electric field, high reliability, and large energy extraction efficiency.

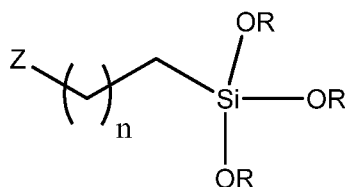
[0004] It is with respect to these and other considerations that the various embodiments described below are presented.

SUMMARY

[0005] In some aspects, high energy and/or power density materials and devices with high energy extraction efficiency derived from organic-inorganic sol-gel film based devices are disclosed and the methods by which they are prepared. The solution of this disclosure further relates to devices derived from sols freshly prepared from the sol-gel precursors and also by the dissolution of the gel/powder formed from the precursors. The sol-gel film based devices herein are useful in various energy storage applications and possess both high energy and power densities.

[0006] In one embodiment, the sol-gel composition that forms the film layer of this disclosure can comprise of a sol-gel material formed from a single precursor. The sol-gel composition can be used in a capacitor for energy storing. The single precursor can contain a hydrolysable and condensable trialkoxysilane group which in the presence of a liquid catalyst undergoes cross-linking to produce a silicate network. In this regard, R may be an alkyl group such as methyl, ethyl, propyl or butyl while Z can be a polar group such as CN, -SCN, -NCO, -NH₂, -CF₃. Finally, n can be selected to be an integer in the range of 0 to about 10.

[0007] In another embodiment, a device for capacitor and energy storage is disclosed. The device includes a composition of a single sol-gel precursor according to formula I:

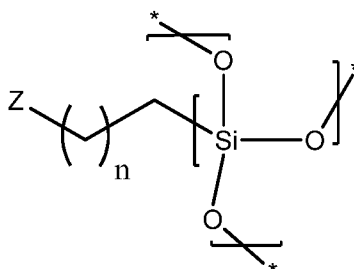


[0008] The composition has an overall weight. In the formula, R is an alkyl group that includes methyl, ethyl, propyl or butyl. Z is a polar group that includes CN, -SCN, -NCO, -NH₂, -CF₃. N is an integer ranging approximately between 0 and 10. In the device, a solvent is provided that accounts for at least 10% of the overall weight. A catalyst is also provided that accounts for at least 10% of the overall weight.

[0009] In other embodiments, the solvent can be methanol, ethanol, isopropyl alcohol, N, N-dimethylformamide, acetonitrile, N, N-dimethylacetamide, or tetrahydrofuran. In other embodiments, the catalyst comprises of 0.1 N hydrochloric acid and water. The catalyst can include 100% 0.1 N hydrochloric acid, ultrapure water, 1 to 99 % of 0.1 N hydrochloric acid, or 1 to 99 % of ultrapure water. The catalyst can include 100% of basic catalysts not limited to sodium hydroxide, ammonium hydroxide and barium hydroxide.

[0010] In other embodiments, the gel further can include of Z groups having a dipole moment of at least 0.25 D. The gel can have a shelf-life of at least a month. In other embodiments, the shelf life of the gel can be at least three months.

[0011] In other embodiments, a capacitor energy and power storage device comprising an inorganic-organic network formed using the sol-gel composition of this disclosure that includes a recurring unit of the following formula:



[0012] In other embodiments, the sol-gel composition is cast into a film and deposited on a substrate which is comprised of a metal or a semiconducting material. The film can include a thickness ranging between 30-4000 nm. A charge-blocking layer can also be deposited on top of the sol-gel film. In other embodiments, the composition can include a charge-blocking layer that includes of a polymer layer with thickness ranging from 5 to 500 nm. In other embodiments, the composition can include a charge-blocking layer that includes of a nanoscale metal oxide layer. The metal of the substrate can be Si, Al, Zn, Zr, and Hf. A thickness of the charge-blocking layer can range between 1 to 200 nm. In other embodiments, the composition can include a charge-blocking layer that comprises of an organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or aryl silanes and alkyl or aryl siloxanes and alkyl or aryl carboxylic acids.

[0013] In other embodiments, the sol-gel film is deposited on a substrate comprising of a charge-blocking layer on a metal or a semiconducting layer. The charge-blocking layer can include of a polymer layer. The charge-blocking layer can include of a nanoscale metal oxide layer where the metal can be Si, Al, Zn, Zr, Hf and the layer thickness can be in the range of 1 to 200 nm. The charge-blocking layer can include of an organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or aryl silanes and alkyl or aryl siloxanes and alkyl or aryl carboxylic acids.

[0014] In other embodiments, the sol-gel film can be sandwiched between two identical polymer layers. The sol-gel film can also be sandwiched between two identical oxide layers. The sol-gel film can be sandwiched between two organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or

aryl silanes and alkyl or aryl siloxanes and alkyl or aryl carboxylic acids. In other embodiments, thin layers of charge blocking layers are formed by dip coating, spin-casting, blade casting and spray casting.

[0015] In other embodiments, a sol-gel thin film device is provided that consists of a sol-gel film between a bottom and a top electrode. The sol-gel film is made of metal or conduction to semi-conducting metal oxides. A top electrode is made of metal or conduction to semi-conducting metal oxides. A first charge blocking layer is disposed between the bottom electrode and the sol-gel film. A second charge blocking layer is between the top electrode and the sol-gel film.

[0016] In other embodiments, a sol-gel thin film device is provided that consists of a sol-gel film between a bottom and a top electrode. The sol-gel film is transparent to opaque semi-conducting metal oxides. A top electrode is made of metal or conduction to semi-conducting metal oxides. A first charge blocking layer is between the bottom electrode and the sol-gel film. A second charge blocking layer is between the top electrode and the sol-gel film.

[0017] In other embodiments, a sol-gel thin film device is provided that consists of a sol-gel film between a bottom electrode made of metal or conduction to semi-conducting metal oxides. A top electrode is also provided that is made of metal or conduction to semi-conducting metal oxides. A first charge blocking layer is between the bottom electrode and the sol-gel film. A second charge blocking layer is between the top electrode and the sol-gel film.

[0018] In other embodiments, a sol-gel thin film device is provided that consists of a sol-gel film between a bottom electrode and transparent to opaque semi-conducting metal oxides. A top electrode is made of metal or conduction to semi-conducting metal oxides. A first charge blocking layer is between the bottom electrode and the sol-gel film. A second charge blocking layer is between top electrode and the sol-gel film.

[0019] In other embodiments, a flexible sol-gel thin film device is disclosed having one or more charge blocking layers. The device also includes a composition of a single sol-gel precursor. The precursor can include a hydrolysable and condensable trialkoxysilane group that undergoes cross-linking in the presence of a catalyst to produce a silicate network. The device also includes sol-gel dielectric films formed from the composition. The films are combined with the one or more charge blocking layers. In other embodiments, the sol-gel dielectric films are formed on a substrate. The substrate can include a glass or different metal

layers of varying thickness. The device can also include an ultrathin layer of a polymer having a permittivity greater than 2, the ultrathin layer being disposed between the substrate and the sol-gel dielectric films. The substrate can also include a flexible substrate.

[0020] In other embodiments, the device can include an electrode positioned on the one or more charge blocking layers. The one or more charge blocking layers can be disposed on top of and/or below the sol-gel dielectric films. A glass layer can be disposed in communication with the one or more charge blocking layers and the film.

[0021] In other embodiments, the device can include a top electrode. At least one of the one or more charge blocking layers can be disposed between the sol-gel dielectric films and the top electrode. In other embodiments, the device can include a bottom electrode, wherein at least one of the one or more charge blocking layers can be between the bottom electrode and the sol-gel dielectric films. In other embodiments, the device can include a bottom electrode and a top electrode, wherein the one or more charge blocking layer can be between the bottom electrode, the top electrode, and the sol-gel dielectric films.

[0022] In other embodiments, the single sol-gel precursor of the device can include a trialkoxysilane having a cyanoalkyl polar group and water is the catalyst for hydrolysis. The cross-linked network of this embodiment exhibits higher extractable energy density and energy extraction efficiency.

[0023] In other embodiments, the single sol-gel precursor of the device can include a trialkoxysilane having a cyanoalkyl polar group and a mixture of water and hydrochloric acid is the catalyst. The cross-linked network of this embodiment exhibits higher extractable energy density and energy extraction efficiency.

[0024] In other embodiments, a method of processing a capacitor and energy storage device is disclosed. The method can include: mixing a sol-gel material with liquid catalyst, the sol-gel material being formed from a composition formed from a single precursor; heating or drying the sol-gel material to remove a solvent thereby forming a dry powder; dissolving the powder with a solvent to form a solution; and casting the sol-gel material into a film. The sol-gel material processed in this method can have a shelf-life of at least one month.

[0025] In other embodiments, the method can also include sandwiching the film between two identical polymer layers; sandwiching the film between two identical oxide layers; and/or sandwiching the film between two organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or aryl silanes and alkyl or aryl siloxanes.

[0026] In other embodiments, the method can also include positioning an electrode and a charge blocking layer on top of and/or below the film; providing a glass layer in communication with the one or more charge blocking layers and the film; and depositing the bottom conducting layer on top of the glass layer.

[0027] In other embodiments, the method can also include selecting the liquid catalyst from a plurality of liquid catalysts to hydrolyze and condense the single precursor; and maintaining relatively high permittivity in the sol-gel film by reducing leakage current of the film.

[0028] In other embodiments, the method can also include casting the sol-gel material into the film by spin, blade, or spray coating; scratching the film thereby obtaining the powder; re-dissolving the sol-gel material in the same or a different solvent; and/or applying the sol-gel material on one or more polymer layers for one or more predetermined electrical applications.

[0029] Other aspects and features of the present disclosure will become apparent to those of ordinary skill in the art, upon reviewing the following detailed description in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] Reference will now be made to the accompanying drawings, which are not necessarily drawn to scale.

[0031] Fig. 1 depicts an example embodiment of a capacitor device of this disclosure.

[0032] Fig. 2 depicts an example wafer for use in a capacitor device of this disclosure.

[0033] Fig. 3 depicts an example wafer for use in a capacitor device of this disclosure.

[0034] Fig. 4 depicts an example wafer for use in a capacitor device of this disclosure.

[0035] Fig. 5 depicts an example wafer for use in a capacitor device of this disclosure.

[0036] Fig. 6 depicts leakage current measurements on cyanoethyltrimethoxysilane (CNETMS) films processed at different pH.

[0037] Fig. 7 depicts breakdown measurements on CNETMS films processed at different pH.

[0038] Fig. 8 depicts Weibull modulus measurements on CNETMS films processed at different pH.

[0039] Fig. 9 depicts discharged energy density of CNETMS films processed at different pH.

[0040] Fig. 10 depicts an example method of manufacturing a capacitor having a sol-gel material of this disclosure.

[0041] Fig. 11 depicts extractable energy density and energy extraction efficiency of CNETMS films processed at different pH.

[0042] Fig. 12 depicts chemical structures of sol-gel precursors described in this disclosure.

[0043] Fig. 13 depicts example chemical structures of polymers used as charge-blocking layers.

[0044] Fig. 14 depicts example chemical structures used as charge-blocking self-assembled monolayers.

[0045] Fig. 15 depicts extractable energy density and energy extraction efficiency of CNETMS films with self-assembled monolayer of n-octylphosphonic acid as a charge-blocking layer.

[0046] Fig. 16 depicts extractable energy density and energy extraction efficiency of 300 nm CNETMS films with and without an octylphosphonic acid charge blocking layer.

[0047] Fig. 17 depicts extractable energy density and energy extraction efficiency of 200 nm CNETMS films without a charge-blocking layer.

[0048] Fig. 18 depicts extractable energy density and energy extraction efficiency of 85 nm CNETMS films with and without an octylphosphonic acid charge blocking layer.

DETAILED DESCRIPTION

[0049] The subject matter of the various embodiments is described with specificity to meet statutory requirements. However, the description itself is not intended to limit the scope of the embodiments recited in the claims. Rather, it has been contemplated that the claimed devices and methods can be embodied in other ways, to include different steps or elements similar to the ones described in this document, in conjunction with other present or future technologies. Although the term “step” can be used herein to connote different aspects of methods employed, the term should not be interpreted as implying any particular order among or between various steps herein disclosed unless and except when the order of individual steps is explicitly required. The following description is illustrative and non-limiting to any one aspect.

[0050] It should also be noted that, as used in the specification and the claims, the singular forms “a,” “an” and “the” include plural references unless the context clearly dictates

otherwise. For example, reference to a component is intended to also include composition of a plurality of components. References to a composition containing “a” constituent are intended to include other constituents in addition to the one named. Also, in describing preferred embodiments, terminology will be resorted to for the sake of clarity. It is intended that each term contemplates its broadest meaning as understood by those skilled in the art and includes all technical equivalents that operate in a similar manner to accomplish a similar purpose.

[0051] Ranges can be expressed herein as from “about” or “approximately” one particular value and/or to “about” or “approximately” another particular value. When such a range is expressed, other exemplary embodiments include from the one particular value and/or to the other particular value. The terms “comprising” or “containing” or “including” mean that at least the named component, element, particle, or method step is present in the system or article or method, but does not exclude the presence of other components, materials, particles, or method steps, even if the other such components, material, particles, and method steps have the same function as what is named.

[0052] It is also to be understood that the mention of one or more method steps does not preclude the presence of additional method steps or intervening method steps between those steps expressly identified. Similarly, it is also to be understood that the mention of one or more components in a system or composition does not preclude the presence of additional components than those expressly identified. To facilitate an understanding of the principles and features of the present disclosure, embodiments are explained hereinafter with reference to implementation in illustrative embodiments.

[0053] The solution of this disclosure generally relates to capacitor, energy storing devices derived from sol-gels freshly prepared from one or more sol-gel precursors and also by the dissolution of the gel formed from the precursors. The sol-gel film based devices of this disclosure are useful in various energy storage applications and possess both high energy and power densities.

[0054] There is a critical need for materials and material compositions for energy and power storage that have high dielectric constant, low dielectric loss, and breakdown strength, as well as high extractable energy/power density and energy/power extraction efficiency. Because of the need to satisfy multiple device properties including reliability of device breakdown, it is often difficult to find a suitable material for efficient, high energy density storage. The present disclosure provides compositions and processing methods for sol-gel

materials suited for energy storage applications. Specifically, this disclosure can be tuned and/or tailored to improve the properties the sol-gel material such as, for example, dielectric permittivity, breakdown strength, and energy density and energy extraction efficiency of the devices. Embodiments of the sol-gel based materials of this disclosure demonstrate the role of the processing methods to improve energy storage characteristics of sol-gel materials.

[0055] The gel/powders in this disclosure obtained from the compositions can be redissolved in certain solvents that allow obtaining thin films, increasing the shelf-life of the otherwise short-lived sol-gel sols. Furthermore, use of specific nanoscale and monolayer blocking layers, including various metal oxides, alkyl phosphonic acids, alkylthiols, and polymeric layers, in combination with sol-gel dielectric films lead to enhanced energy storage properties. Turning to Fig. 1, an example embodiment of a capacitor device 10 of this disclosure is shown. Specifically, Fig. 1 shows a schematic representation of an example thin-film capacitor device 10 of this disclosure that employs a bi-layer dielectric that can be formed by a monolayer 3, a sol-gel film 9, and one or more electrode layers 5. As shown, the electrode layers 5 can be formed from a metal, such as Aluminum. Layer 7 can be formed from a glass or ITO (indium tin oxide). It is also understood that device 10 depicted in Fig. 1 is not necessarily drawn to scale and is strictly for schematic purposes. The bilayer structure of device 10 can block the injection of electrons into the sol-gel film 9, providing low leakage current, high breakdown strength, and high energy extraction efficiency.

[0056] In one embodiment, the sol-gel composition that forms the film layer of this disclosure can comprise of a sol-gel material formed from a single precursor. The sol-gel composition can be used in a capacitor for energy storing. The single precursor can contain a hydrolysable and condensable trialkoxysilane group which in the presence of a liquid catalyst undergoes cross-linking to produce a silicate network. In this regard, R may be an alkyl group such as methyl, ethyl, propyl or butyl while Z can be a polar group such as CN, -SCN, -NCO, -NH₂, -CF₃. Finally, n can be selected to be an integer in the range of 0 to about 10.

[0057] In a certain embodiments, a trialkoxysilane having a cyanoalkyl polar group is used as a precursor and water is used as the catalyst for hydrolysis. In this respect, the cross-linked network exhibits higher extractable energy density and energy extraction efficiency. In other embodiments, the catalyst used can include a mixture of water and hydrochloric acid. In another embodiment, the sol-gel composition can be used for energy storage with a high dielectric strength and high dielectric constant thin film device. This provides a high permittivity dielectric solid which can be also re-dissolved in different solvents to apply on

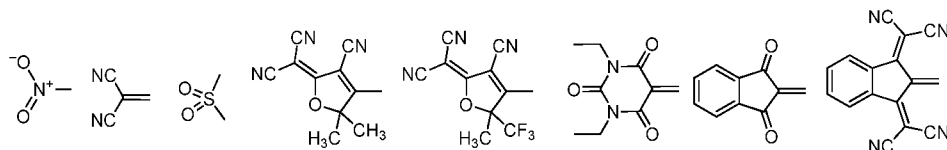
other polymer layers for different electrical applications. Moreover, the gel produced in certain embodiments using water as a catalyst can be heated to remove the solvent thereby obtaining a dry powder. A solution can be prepared from the dry powder which can be coated as a film of desired thickness. Processes that can be used include spin, blade or spray coating. In another embodiment, the thickness of the ranges between 30 nm to 10,000 nm.

[0058] In certain embodiments, a method for further improving the energy storage capability of the sol-gel composition is disclosed. The method utilizes a charge blocking nano- or mono-layer of polymer, organic and inorganic metal oxide. The method can also utilize ultrahigh breakdown strength material as a charge blocking layer. The ultrahigh breakdown material can include a diamond or hexagonal boron nitride deposited by chemical vapor deposition or other deposition methods. In another embodiment, the ultrahigh breakdown material can include a wide band gap (e.g. hexagonal boron nitride (ca. 6 eV)).

[0059] In other embodiments, a method for improving the energy/power storage capability of the sol-gel composition is disclosed. In this method, the sol-gel can be used as a host material for inorganic fillers that include barium titanate, strontium titanate, barium strontium titanate and/or related high dielectric materials. In another embodiment, the inorganic fillers are different sized nanoparticles. In another embodiment, the inorganic fillers can be functionalized on their surface with suitable groups that will help disperse them in the sol-gel host.

[0060] In some embodiments, a charge blocking nano/mono-layer can be disposed between the sol-gel dielectric layer and the top metal electrode. In another embodiment, the charge blocking layer is between the bottom electrode and the sol-gel dielectric layer. The charge blocking layer can be present between both the bottom electrode and sol-gel layer as well as between the sol-gel layer and the top electrode.

[0061] A sol-gel precursor of the composition of this disclosure can include a monomer according to the structural formula (I), as described earlier. The R group can be an alkyl linker of varying lengths, such as a methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, dodecyl and/or undecyl group. In one embodiment, the Z group can be substituted with a halogen atom, or cyano group. Non-limiting examples of substituent groups can include F, Cl, Br, I, CN or any group in Scheme 1, wherein n can be selected to be an integer in the range of 0 to 10.



Scheme 1. Polar (Z) groups in formula (I).

[0062] In another embodiment, a sol-gel precursor is provided that includes a monomer according to the structural formula (II). The R group in this respect is an alkyl group that can include a methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and/or undecyl group. Similar to other embodiments, n can be an integer in the range of 0 to 10. R2 can be a hydrogen atom or an alkyl group which could be a methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and/or undecyl group.

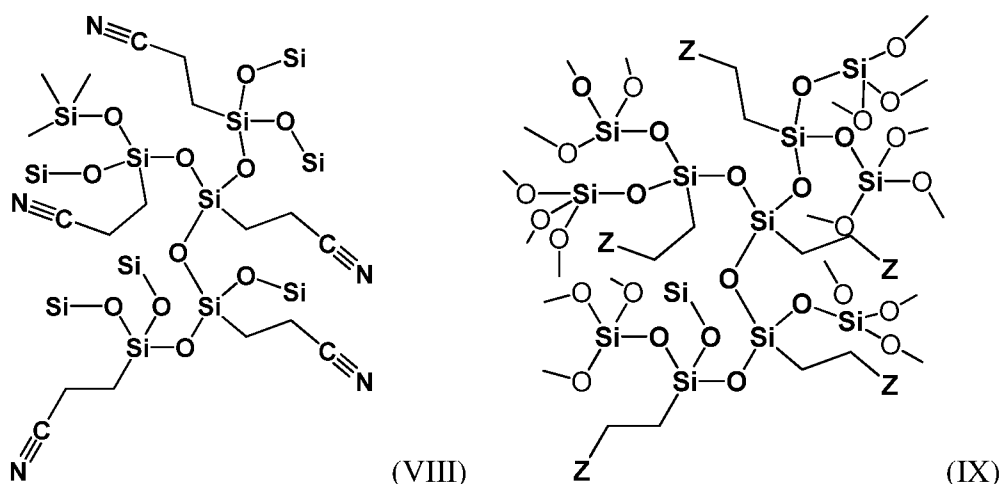
[0063] In another embodiment, two hydrogen atoms attached to an alkyl group can be replaced with Z group which could be a F, Cl, Br, I and -CN group. This is advantageous as it increases the polar nature of the moiety as in the formula given in formulas III, IV and V.

[0064] In another embodiment, a substituted ethyl group of the sol-gel precursor can include a Z group of F, Cl, Br, I or —CN. In those embodiments according to the structural formula (III), the number of electronegative groups can vary from 1 to 3. In another embodiment according to structural formula (IV), the number of electronegative groups can be one or two. In another embodiment according to structural formula (V), the number of electronegative groups can vary from 1 to 5. In another embodiment, polymerizable (e.g., acrylate, epoxy, vinyl or the like) moieties are attached to the alkyl groups which are a part of the trialkoxysilane.

[0065] In another embodiment, the hydrolysis followed by condensation of structural formulas (VI) or (VII) will provide a relatively high dielectric film which can further be cross-linked by illuminating with UV light. In this regards, structures similar to structural formulas (VI) and (VII) can produce films that can be patterned to any required shape or form on different substrates that can include ITO, Al, Ti, Ti-Au, Au, and flexible substrates such as Al-Mylar, ITO-PEN, ITO-polyester.

[0066] In another embodiment, the sol-gel precursor after hydrolysis is cast into films and dried at 130 °C for 3 hours. The dried film can be scratched to obtain cross-linked powders

(e.g. those of structures VIII and IX). The cross-linked powders of the sol-gel precursor can be re-dissolved in a variety of solvents. In an embodiment, the powder dissolved in a solvent is spin- or blade-cast into films of high dielectric constant and low dielectric loss on substrates such as ITO, Al, Ti, Ti-Au, Au deposited glass or silicon wafer. However, flexible substrates can also be used, such as Al-Mylar, ITO-PEN, ITO-polyester as shown in Figs. 2-5:



EXAMPLES

[0067] Various aspects of the disclosed devices and methods may be still more fully understood from the following description of some example implementations and corresponding results. Some experimental data is presented herein for purposes of illustration and should not be construed as limiting the scope of the disclosed technology in any way or excluding any alternative or additional embodiments.

[0068] Fig. 6 shows a plot of the leakage current measured as a function of voltage (I-V measurements). The measured current density is relatively high when the pH of the catalyst is 1.5. When the pH of the catalyst used was changed from 1.5 to 3, the current decreases by nearly an order of magnitude and any further increase in pH to 4.8 and 6.5 does not change the current significantly. This capability of selecting a particular catalyst to hydrolyze and condense sol-gel precursor to facilitate a reduction in leakage current while maintaining high permittivity of films, makes a broad range of device applications feasible. The possible sources of current in these films are the ions (H^+ , OH^- , MeO^- and Cl^-) generated from the catalyst used for the sol-gel hydrolysis and condensation. For example, 0.1 N HCl (at pH 1.5), a mixture of 0.1 N HCl and water (at pH 3 and pH 4.8) and only water (at pH 6.5). Based on the current values obtained from

Fig. 6, it is possible that the main contribution to the current is from Cl⁻ ions (Cl⁻ ion concentration change as follows; pH 1.5 > pH 3 > pH 4.5 > pH 6.5 and considering the other factors constant at different pH). Additional evidence of this trend has also been obtained from energy dispersive spectroscopy-SEM data and chlorine elemental map on the films processed at different pH. It is evident from the Fig.6 that the newly developed processing methods lead to highly improved dielectric properties and a variety of device applications of the CNETMS sol-gel films.

[0069] The dielectric breakdown strengths of the CNETMS films were determined and analyzed using the Weibull method, as has been discussed elsewhere. The Weibull cumulative failure probability distribution (PF) is expressed by the following formula:

$$P_F(E) = 1 - \exp \left[- \left\{ \frac{(E-\gamma)}{\alpha} \right\}^\beta \right] \quad (2)$$

[0070] In the Weibull formula, E is the applied electric field, a is the "scale" parameter, 13 is the "shape" parameter or Weibull modulus that represents dispersion of the breakdown field, and y is the electric field breakdown threshold parameter that represents the field below which no observable failure occurs. Conventionally, the characteristic breakdown strength, E_{BD}, is defined as the field where P_F is 63.2%. The failure probability of the CNETMS films and the reliability parameter of devices fabricated from different pH as a function of the applied electric field are shown in Fig. 7 and Fig. 8 respectively. In general, the narrower the cumulative distribution function (CDF) with respect to electric field, the more reliable the material is for high dielectric strength applications. Breakdown measurements and Weibull analysis have been carried out on the films prepared from different pH are shown in Fig. 7. As evident from Figs. 7 and 8, the increase in pH leads to a decrease in the breakdown voltage spread or narrower distribution of α and also an increase in the reliability parameter. β, the Weibull modulus, increases from about 5 to 11 when the pH was increased from 1.5 to 11. This increase in β, can be attributed to the decrease in chloride ion from pH 1.5 to pH 4.8 and then further to the complete absence of chloride ions at pH 6.5. The presences of ions/ionic species in films generally contribute to increase the conductivity/current.

[0071] In other embodiments, as shown in Fig. 10, a method 100 is disclosed of processing a capacitor and energy storage device of this disclosure. The method 100 can include a first step, 105, mixing a sol-gel material with liquid catalyst, the sol-gel material

being formed from a composition formed from a single precursor. A second step 110 includes heating or drying the sol-gel material to remove a solvent thereby forming a dry powder. A third step includes 115 dissolving the powder with a solvent to form a solution. A fourth step 120 includes casting the sol-gel material into a film. The sol-gel material processed in this method can have a shelf-life of at least one month.

[0072] Other steps are also contemplated in this method. For example, the method can also include sandwiching the film between two identical polymer layers; sandwiching the film between two identical oxide layers; and/or sandwiching the film between two organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or aryl silanes and alkyl or aryl siloxanes. In other embodiments, the method can also include positioning an electrode and a charge blocking layer on top of and/or below the film; providing a glass layer in communication with the one or more charge blocking layers and the film; and depositing the bottom conducting layer on top of the glass layer. In other embodiments, the method can also include selecting the liquid catalyst from a plurality of liquid catalysts to hydrolyze and condense the single precursor; and maintaining relatively high permittivity in the sol-gel film by reducing leakage current of the film. In other embodiments, the method can also include casting the sol-gel material into the film by spin, blade, or spray coating; scratching the film thereby obtaining the powder; re-dissolving the sol-gel material in the same or a different solvent; and/ or applying the sol-gel material on one or more polymer layers for one or more predetermined electrical applications.

[0073] Turning to the examples, the field dependent $U_{\max}$ of CNETMS films processed at different pH from CD and PE measurements is shown in Fig. 9 and Fig. 11, respectively. Energy density measurements from charge-discharge methods show a large value of about 34 J/cm^3 . The improved processing method wherein the films were prepared by redissolving the gel in DMF exhibit energy density values of about 25 to 30 J/cm^3 with an extraction efficiency of about 80%. This enhanced energy extraction efficiency has been achieved by improved processing methods via the use of ultrapure water for hydrolysis and thereby eliminating the presence of chloride ions during the sol and film formation.

[0074] In another embodiment, the sol-gel film can be with and without a charge blocking layer of any polymer or a monolayer of small to long-alkyl chain containing molecules may be formed by dissolving a powder of a dimer, trimer, tetramer, oligomer or polymer derived from sol-gel precursors. The dissolved sol-gel polymer may have a thickness of 25 to 100,000 nm as formed as well as be in the dried form.

[0075] In another embodiment, the sol-gel dielectric films, with and without the charge blocking layer can be formed on various types of substrates, as shown in Figs. 2-5. The substrate can be comprised of glass or different metal layers of varying thickness (30 nm to 500 nm). Example metal layers include, but are not limited to, indium tin oxide (ITO), Al, Au, Ag, Cu, Ti, Cr, Mo and combinations of alloys thereof. The substrate can also be comprised of flexible substrate, including formed from Al-mylar, ITO-polyester, ITO-polyethylenenaphthalate and/or ITO-polysulfone. In certain embodiments, the top electrode to complete the device fabrication can include, but are not limited to indium tin oxide (ITO), Al, Au, Ag, Cu, Ti, Cr, Mo and combinations of alloys thereof. In one embodiment, the bottom conducting layer is ITO or Al deposited on top of glass and the top electrode is Al.

[0076] In another embodiment, the energy storage device is comprised of an ultrathin layer of a polymer having a permittivity of > 2 between the substrate with the metal electrode and the sol-gel dielectric layer. The thickness of the polymer layer is typically between 5 to 500 nm. In one embodiment, the ultrathin layer can comprise of an alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane. The thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer comprise of 0.2 to 10 nm. In another embodiment, the thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer is > 10 nm. The alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane in ethanol layer can be coated by dip-, spin-, drop-, blade- or spray coating or by slot die coating.

[0077] In another embodiment, the energy storage device is comprised of a thin layer of a polymer having a permittivity of > 1 between the sol-gel dielectric layer and the top metal or semiconducting electrode. The thickness of the polymer layer can typically range between 5 to 500 nm. The thin layer can include of an alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane. The thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer can range between 0.2 to 10 nm. In another embodiment, the thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer may be less or greater than 10 nm. The alkylthiol, alkyl phosphonic acid or alkylsiloxane in ethanol layer is coated by dip-, spin-, drop-, blade- or spray- coating or slot die coating. In another embodiment, the energy storage device can include a thin layer of a polymer having a permittivity of greater than 1 between the top electrode and the sol-gel dielectric layer and also between the metal or semiconducting bottom electrodes.

[0078] In another embodiment, thickness of the polymer layer can range between 5 to 500 nm. The thin layer can comprise of an alkyl thiol, alkyl phosphonic acid or alkyl siloxane. The thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer can comprise of 0.2 to 10 nm. In another embodiment, the thickness of the alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane layer can be greater than 10 nm. The alkylthiol, alkylphosphonic acid, alkyl carboxylic acid or alkylsiloxane in ethanol layer is coated by dip-, spin-, drop-, blade- or spray- coating or slot die coating.

[0079] Summaries of other example implementations and related data will now be discussed.

Example 1 (pH 1.5 sol and film fabrication)

[0080] A sol-gel composition was prepared by mixing 1 g of 2-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 2 (pH 3 sol and film fabrication)

[0081] A sol-gel composition was prepared by mixing 1 g of 2-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of an aqueous hydrochloric acid (pH 3) solution and stirring the resulting mixture for 12 hours at ambient conditions. The reaction mixture yielded a gel after 12 hours of stirring. The solvent/supernatant solution was decanted. The gel was heated to 80 °C for 30 minutes to remove any remaining methanol solvent. The dried gel was dissolved by 30 s sonication followed by stirring after addition of 1 mL of solvent such as dimethylformamide or acetone or acetonitrile or dimethylacetamide or propylene carbonate under ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films.

Typically 1 μm thick films were obtained by using a spin-speed of 2000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 3 (pH 4.8 sol and film fabrication)

[0082] A sol-gel composition was prepared by mixing 1 g of 2-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of an aqueous hydrochloric acid (pH 4.8) solution and stirring the resulting mixture for 12 hours at ambient conditions. The reaction mixture yielded a gel after 12 hours of stirring. The solvent/supernatant solution was decanted. The gel was heated to 80 °C for 30 minutes to remove any remaining methanol solvent. The dried gel was dissolved by 30 s sonication followed by stirring after addition of 1 mL of solvent such as dimethylformamide or acetone or acetonitrile or dimethylacetamide or propylene carbonate under ambient conditions. The sol was filtered using a 0.1 μm prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained by using a spin-speed of 2000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 4 (pH 6.5 sol and film fabrication)

[0083] A sol-gel composition was prepared by mixing 1 g of 2-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of an ultrapure water (pH 6.5) solution and stirring the resulting mixture for 12 hours at ambient conditions. The reaction mixture yielded a gel after 12 hours of stirring. The solvent/supernatant solution was decanted. The gel was heated to 80 °C for 30 minutes to remove any remaining methanol solvent. The dried gel was dissolved by 30 s sonication followed by stirring after addition of 1 mL of solvent such as dimethylformamide or acetone or acetonitrile or dimethylacetamide or propylene carbonate under ambient conditions. The sol was filtered using a 0.1 μm prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained

by using a spin-speed of 2000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 5

[0084] A sol-gel composition was prepared by mixing 1 g of 3-thiocyanatopropyltriethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μm prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 6

[0085] A sol-gel composition was prepared by mixing 1 g of 3-isocyanatopropyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μm prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 7

[0086] A sol-gel composition was prepared by mixing 1 g of 3-aminopropyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μm prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained by using a spin-

speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 8

[0087] A sol-gel composition was prepared by mixing 1 g of triethoxysilylbutyraldehyde in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 9

[0088] A sol-gel composition was prepared by mixing 1 g of 3-cyanopropyltriethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 10

[0089] A sol-gel composition was prepared by mixing 1 g of N-(3-Methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-

speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 11

[0090] A mixed sol-gel composition was prepared by mixing 0.5 g of 3-aminopropyltrimethoxysilane along with 0.5 g of 3-isocyanatopropyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 12

[0091] A mixed sol-gel composition was prepared by mixing 0.5 g of 3-aminopropyltrimethoxysilane along with 0.5 g of 3-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of 0.1 N hydrochloric acid (pH 1.5) and stirring the resulting mixture for 12 hours at ambient conditions. The sol was filtered using a 0.1 μ m prior to spin coating. The sols were spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μ m thick films were obtained by using a spin-speed of 5000 rpm for 30 s. Films were cured at 130 °C for hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds.

Example 13

[0092] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of propylphosphonic acid in absolute ethanol at 70 °C for 19 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 14

[0093] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of propylphosphonic acid in absolute ethanol at 70 °C for 3 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 15

[0094] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of propylphosphonic acid in absolute ethanol at 70 °C for 10 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 16

[0095] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octylphosphonic acid in absolute ethanol at 70 °C for 19 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 17

[0096] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octylphosphonic acid in absolute ethanol at 70 °C for 3 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 18

[0097] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octylphosphonic acid in absolute ethanol at 70 °C for 10 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator. The measured energy density and energy extraction efficiency are shown in Fig. 15. More specifically, Fig. 15 depicts the extractable energy

density and energy extraction efficiency of CNETMS films with self-assembled monolayer of n-octylphosphonic acid as a charge-blocking layer.

[0098] Similarly, Figs. 16-18 depict extractable energy density and energy extraction efficiency of 85 nm CNETMS films with and without an octylphosphonic acid charge blocking layer. Specifically, Fig. 16 depicts extractable energy density and energy extraction efficiency of 300 nm CNETMS films without a charge-blocking layer. The sol-gel dielectric film shown in Fig. 16 can include a thickness of 300 nm as fabricated. The field dependent U_{max} of CNETMS processed at a thickness of 300 nm is shown in Fig. 16.

[0099] Fig. 17 depicts extractable energy density and energy extraction efficiency of 200 nm CNETMS films with and without self-assembled monolayer of n-octylphosphonic acid as a charge-blocking layer. The sol-gel dielectric film of this example as shown in Fig. 17 can include a thickness of 200 nm as fabricated. The field dependent U_{max} of CNETMS processed at a thickness of 200 nm is shown in Fig. 17.

[00100] Fig. 18 depicts extractable energy density and energy extraction efficiency of 84 nm CNETMS films with and without self-assembled monolayer of n-octylphosphonic acid as a charge-blocking layer. The sol-gel dielectric film of this example as shown in Fig. 18 can include a thickness of 85 nm as fabricated. The field dependent U_{max} of CNETMS processed at a thickness of 85 nm is shown in Fig. 18.

Example 19

[00101] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octadecylphosphonic acid in absolute ethanol at 70 °C for 19 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 20

[00102] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octadecylphosphonic acid in absolute ethanol at 70 °C for 3 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 21

[00103] Sol-gel film from Example 1 was immersed into a solution of 0.1 mM of octadecylphosphonic acid in absolute ethanol at 70 °C for 10 hours. After the treatment, bilayer films were rinsed by ultrasonication in absolute ethanol for ten minutes, blown dry with nitrogen, and stored in a desiccator.

Example 22

[00104] A 0.1 mM solution of octylphosphonic acid was spin-coated on top of the sol-gel film from Example 1 at 1000 rpm for 30s. The film was dried at 120 °C for 2 hrs in a vacuum oven and stored in a desiccator.

Example 23

[00105] A 0.1 mM solution of octylphosphonic acid was spin-coated on top of the sol-gel film from Example 1 at 6000 rpm for 30s. The film was dried at 120 °C for 2 hrs in a vacuum oven and stored in a desiccator.

Example 24

[00106] A 1% solution of polyphenyleneoxide was spin-coated on top of the sol-gel film from Example 1 at 5000 rpm for 30s to obtain a thickness of 20 nm of PPO. The film was dried at 130 °C for 3 hrs in a vacuum oven and stored in a desiccator.

Example 25

[00107] A 2% solution of polyphenyleneoxide was spin-coated on top of the sol-gel film from Example 1 at 4000 rpm for 30s to obtain a thickness of 50 nm of PPO. The film was dried at 130 °C for 3 hrs in a vacuum oven and stored in a desiccator.

Example 26

[00108] A 2% solution of polyphenyleneoxide was spin-coated on top of the sol-gel film from Example 1 at 1000 rpm for 30s to obtain a thickness of 100 nm of PPO. The film was dried at 130 °C for 3 hrs in a vacuum oven and stored in a desiccator.

Example 27

[00109] A 5% solution of polyphenyleneoxide was spin-coated on top of the sol-gel film from Example 1 at 3000 rpm for 30s to obtain a thickness of 350 nm of PPO. The film was dried at 130 °C for 3 hrs in a vacuum oven and stored in a desiccator.

Example 28

[00110] A sol-gel composition was prepared by mixing 1 g of 2-cyanoethyltrimethoxysilane in a vial, 0.5 g methanol followed by 0.5 g of an ultrapure water (pH 6.5) solution and stirring the resulting mixture for 12 hours at ambient conditions. The reaction mixture yielded a gel after 12 hours of stirring. The solvent/supernatant solution was decanted. The gel was heated to 80 °C for 30 minutes to remove any remaining methanol solvent. The gel was further dried at 130 °C for 3 hours under vacuum. The dried powder was stored in a desiccator.

Example 29

[00111] 1 gram of the dry powder, on the the same day the powder was produced, from Example 28 was dissolved in 1 mL of dimethylformamide. The sol was filtered using a 0.1 µm prior to spin coating. The resulting solution was spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 µm thick films were obtained by using a spin-speed of 2000 rpm for 30 s. Films were cured at 130 °C for 3 hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds. Aluminum electrodes were deposited by e-beam evaporation on top of the films for performing the energy density and extraction efficiencies.

Example 30

[00112] Sol-gel film from Example 29 was immersed into a solution of 0.2 mM of octylphosphonic acid in methanol (not limited to methanol solvent....other solents such as ethanol, tetrahydrofuran and toluene can also be used) for 1 hour. After the treatment, bilayer films were rinsed by ultrasonication in methanol for ten minutes, blown dry with nitrogen, dried at 120°C for 1 hr on a hot plate and stored in a desiccator.

Example 31

[00113] 1 gram of the dry powder (3 weeks after the powder was produced) from Example 28 was dissolved in 1 mL of dimethylformamide. The sol was filtered using a 0.1 μm prior to spin coating. The resulting solution was spin-coated onto various rigid substrates such as indium tin oxide on glass (ITO/glass) and Aluminum/glass as well as flexible substrates Aluminum/Mylar, ITO/polyester and ITO/Polysulfone to make films. Typically 1 μm thick films were obtained by using a spin-speed of 2000 rpm for 30 s. Films were cured at 130 °C for 3 hours under vacuum. Thickness of the films can be varied by using different spin-casting speeds. Aluminum electrodes were deposited by e-beam evaporation on top of the films for performing the energy density and extraction efficiencies.

Example 32

[00114] Sol-gel film from Example 31 was immersed into a solution of 0.2 mM of octylphosphonic acid acid in methanol for 1 hour. However, this example implementation is not limited and other solvents can be used such as ethanol, tetrahydrofuran and toluene. After the treatment, bilayer films were rinsed by ultrasonication in methanol for ten minutes, blown dry with nitrogen, dried at 120°C for 1 hr on a hot plate and stored in a desiccator.

Table 1: Dielectric properties of sol-gel films described in examples.

<i>Sol-gel precursor</i>	<i>Dipole moment (D)</i>	<i>e (1kHz)</i>	<i>tans</i>	<i>U_{max}^{cp} (Rem')</i>	<i>U_{max}^{PE} (Rem')</i>	<i>Extraction Efficiency (%)</i>	<i>Pore size (nm)</i>
3-Cyanopropyl trimethoxysilane	6.1	30.7	0.04	10.7	3	13	NA
3-thiocyanatopropyl triethoxysilane	3.4	9.5	0.11	36	22.7	44	1.2
3-isocyanatopropyl triethoxysilane	3.75	4.9	0.03	7.2	9	34	1.5
3-aminopropyl trimethoxysilane	3.05	12.3	0.30	Leaky	Leaky	Leaky	0.9
triethoxysilylbutyraldehyde	1.38	6.9	0.01	2.4	2.3	70	

N-(3-Methacryloxy-2-hydroxypropyl)-3-amino propyltriethoxysilane	NA	5.8	0.06	3.7	2	63	NA
--	----	-----	------	-----	---	----	----

Table 2: Dielectric properties of energy storage devices comprising of sol-gel film and a charge-blocking layer.

<i>Sol-gel precursor (pH used for sol-gel film fabrication)</i>	<i>Charge-blocking layer (thickness in nm)</i>	ϵ (1kHz)	$\tan\delta$	U_{max}^{CD} (J/cm ³)	U_{max}^{PE} (J/cm ³)	<i>Extraction Efficiency (%)</i>
2-Cyanoethyl trimethoxysilane (pH 1.5)	Top PPO (75 nm)	17	0.017	16.5	24	42
2-Cyanoethyl trimethoxysilane (pH 1.5)	Bottom PPO (75 nm)	19	0.009	15.5	22.3	75
2-Cyanoethyl trimethoxysilane (pH 1.5)	Top PPO (75 nm) Bottom PPO (75 nm)	15.6	0.006	12	20.3	68
2-Cyanoethyl trimethoxysilane (pH 6.5)	Top PPO (75 nm) Bottom PPO (75 nm)	16.1	0.009	5.5	14.6	68
2-Cyanoethyl trimethoxysilane (pH 6.5)	Top CYTOP (75 nm) Bottom CYTOP (75 nm)	17.5	0.01	5.6	6.1	90
2-Cyanoethyl trimethoxysilane (pH 6.5)	Top FOx17 (600 nm) Bottom FOx17 (600 nm)		NA	11	9.4	48
2-Cyanoethyl trimethoxysilane (pH 1.5)	Cytop (20 nm)	20.2	NA	9.5	16.5	NA
2-Cyanoethyl trimethoxysilane (pH 1.5)	Cytop (175 nm)	11.8	NA		12	NA
2-Cyanoethyl trimethoxysilane (pH 1.5)	Al ₂ O ₃ (50nm)	19.4	NA	7.7	NA	NA
2-Cyanoethyl trimethoxysilane (pH 1.5)	SiO ₂ (50nm)	19.4	NA	4.8	NA	NA
2-Cyanoethyl trimethoxysilane (pH 1.5)	ZrO ₂ (20nm)	22.1	NA	9.5	21	38
2-Cyanoethyl trimethoxysilane	ZrO ₂ (50nm)	22.5	NA	13	17	20

(pH 1.5)						
2-Cyanoethyl trimethoxysilane (pH 1.5)	Propylphosphonic acid monolayer	20.5	0.02	27.5	35	72
2-Cyanoethyl trimethoxysilane (pH 1.5)	Octylphosphonic acid monolayer	21.5	0.02	29	40	72
2-Cyanoethyl trimethoxysilane (pH 1.5)	Octadecylphosphonic acid monolayer	21.2	0.02	15	28	89
300 nm CNETMS film	None	21	0.025	30-35	56	58
200 nm CNETMS film	None	21	0.02		49.3	79.4
85 nm CNETMS film	None	21	0.035		25	71
2-cyanoethyl trimethoxysilane polymer powder (as prepared)	None	20.5	0.015		30-40	80-60
2-cyanoethyl trimethoxysilane polymer powder (3 weeks after the powder was prepared)	21	0.02			39-51	70

Electrical Current Measurement

[00115] The device structure of certain embodiments, including those tested, can include a substrate such as glass, or polymer having a metal or semiconducting oxide (e.g., transparent or non-transparent such as indium tin oxide or indium zinc oxide) deposited thereon. The sol-gel composition can be spin-coated on top of the metal or semiconducting oxide layer and the sol gel films can be cured at 130 °C for 3 hours prior to the conductivity measurements. Then a second metal layer, such as Aluminum or ITO or gold is formed by sputtering over the sol-gel composition. Electrical leads from a voltage meter can be connected to the sample via a metal layer (e.g., bottom electrode) and metal layer (e.g., top electrode). Electrical measurements can be also carried out on the devices using spring-loaded probes on a probe station.

Breakdown Strength and Device Reliability

[00116] Breakdown strength and device reliability were measured by applying a voltage between the top and bottom electrodes of the sol-gel based device with a ramp of 10

V/s using a Lab View program. Typically the voltage at which the measured current exceeds 1-5 μA is recorded as the breakdown voltage which is then subjected to the Weibull analysis. The breakdown measurements are performed at least on 20 devices.

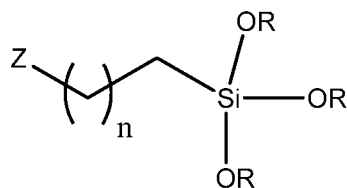
Energy Density by Charge-Discharge (C-D) and Polarization-Electric Field (P-E) Measurements

[00117] Energy densities of the devices were measured by using the pulsed charge-discharge method [Kim, P.; Doss, N. M.; Tillotson, J. P.; Hotchkiss, P. J.; Pan, M.-J.; Marder, S. R.; Li, J.; Calame, J. P.; Perry, J. W., ACS Nano 2009, 3 (9), 2581-2592] with a rise time of ~ 0.5 ms under various field strengths below the breakdown field. Additionally, polarization-electric field (P-E) measurements were performed with a home-built modified Sawyer-Tower circuit. For P-E measurements, samples were subjected to voltages up to 2 kV, which were supplied by a high voltage amplifier (Trek 610-D, Medina, NY). The induced charge on the sample was measured using a charge integrator circuit. The testing was performed using a unipolar sine waveform with a period of 0.01 seconds. As the sample was tested in air (e.g., not immersed in an insulating liquid), special care was taken to maintain appropriate distances (> 1 cm) between probes and cabling to avoid a flash-over.

CLAIMS

What is claimed is:

1. A device for capacitor and energy storage comprising:
a composition of a single sol-gel precursor according to formula I:



- wherein the composition has an overall weight;
 wherein each R is an alkyl group independently chosen from methyl, ethyl, propyl, and butyl;
 wherein Z is a polar group comprising CN, -SCN, -NCO, -NH₂, or -CF₃;
 wherein n is an integer ranging from 0 to 10;
 a solvent comprising at least 10% of the overall weight; and
 a catalyst comprising at least 10% of the overall weight.

2. The sol-gel composition of Claim 1, wherein the solvent comprises methanol, ethanol, isopropyl alcohol, N, N-dimethylformamide, acetonitrile, N, N-dimethylacetamide, tetrahydrofuran, or a combination thereof.

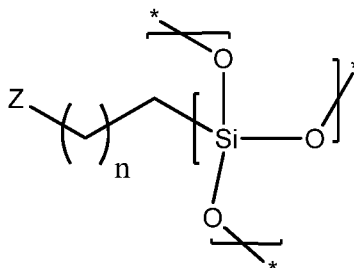
3. The sol-gel composition of Claim 1, wherein the catalyst comprises 0.1 N hydrochloric acid and water.

4. The sol-gel composition of Claim 1, wherein the catalyst comprises 100% 0.1 N hydrochloric acid.

5. The sol-gel composition of Claim 1, wherein the catalyst comprises 100% ultrapure water.

6. The sol-gel composition of Claim 1, wherein the catalyst comprises from 1% to 99% of 0.1 N hydrochloric acid.

7. The sol-gel composition of Claim 1, wherein the catalyst comprises from 1% to 99% of ultrapure water.
8. The sol-gel composition of Claim 1, wherein the gel further comprises Z groups having a dipole moment of at least 0.25 D.
9. The sol-gel composition of Claim 1, wherein the gel has a shelf-life of at least a month.
10. A capacitor energy and power storage device comprising an inorganic-organic network formed using the sol-gel composition in Claim 1 that includes a recurring unit of the formula:



11. The device of claim 10, wherein the sol-gel composition is cast into a film and deposited on a substrate comprising a metal or a semiconducting material.
12. The device of Claim 11, wherein the film includes a thickness ranging from 50 nm to 4000 nm.
13. The device of Claim 11, further comprising a charge-blocking layer on top of the sol-gel film.
14. The device of Claim 11, the composition further comprising a charge-blocking layer that comprises a polymer layer with thickness ranging from 5 nm to 500 nm.
15. The device of Claim 11, the composition further comprising a charge-blocking layer that comprises a nanoscale metal oxide layer;
wherein the metal oxide comprises a metal chosen from Si, Al, Zn, Zr, and Hf; and
wherein a thickness of the charge-blocking layer ranges from 1 nm to 200 nm.

16. The device of Claim 11, the composition further comprising a charge-blocking layer comprising organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids, alkyl or aryl carboxylic acids or alkyl or aryl silanes and alkyl or aryl siloxanes.

17. The device of claim 10, wherein the sol-gel film is deposited on a substrate comprising a charge-blocking layer on a metal or a semiconducting layer.

18. The device of claim 17, wherein the charge-blocking layer comprises a polymer layer.

19. The device of claim 17, wherein the charge-blocking layer comprises a nanoscale metal oxide layer where the metal can be Si, Al, Zn, Zr, Hf and the layer thickness can be in the range of 1 to 200 nm.

20. The device of claim 17, wherein the charge-blocking layer comprises of an organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids, alkyl or aryl carboxylic acids or alkyl or aryl silanes and alkyl or aryl siloxanes.

21. The device of claim 10, where the sol-gel film is sandwiched between two identical polymer layers.

22. The device of claim 10, where the sol-gel film is sandwiched between two identical oxide layers.

23. The device of claim 10, where the sol-gel film is sandwiched between two organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids or alkyl or aryl silanes, alkyl or aryl siloxanes, or a combination thereof.

24. The device of claim 10, wherein thin layers of charge blocking layers are formed by dip coating, spin-casting, blade casting, spray casting, or a combination thereof.

25. A sol-gel thin film device consisting of:
- a sol-gel film between a bottom electrode, the sol-gel film being made of metal or conduction to semi-conducting metal oxides;
 - a top electrode made of metal or conduction to semi-conducting metal oxides;
 - a first charge blocking layer between the bottom electrode and the sol-gel film; and
 - a second charge blocking layer between the top electrode and the sol-gel film.
26. A sol-gel thin film device consisting of:
- a sol-gel film between a bottom electrode, the sol-gel film being transparent to opaque semi-conducting metal oxides;
 - a top electrode made of metal or conduction to semi-conducting metal oxides;
 - a first charge blocking layer between the bottom electrode and the sol-gel film; and
 - a second charge blocking layer between the top electrode and the sol-gel film.
27. A flexible sol-gel thin film device consisting of:
- a sol-gel film between a bottom electrode made of metal or conduction to semi-conducting metal oxides;
 - a top electrode made of metal or conduction to semi-conducting metal oxides;
 - a first charge blocking layer between the bottom electrode and the sol-gel film; and
 - a second charge blocking layer between the top electrode and the sol-gel film.
28. A flexible sol-gel thin film device consisting of:
- a sol-gel film between a bottom electrode and transparent to opaque semi-conducting metal oxides;
 - a top electrode made of metal or conduction to semi-conducting metal oxides;
 - a first charge blocking layer between the bottom electrode and the SOL-GEL film;
- and
- a second charge blocking layer between top electrode and the SOL-GEL film.
29. A flexible sol-gel thin film device comprising:
- one or more charge blocking layers;

a composition of a single sol-gel precursor, the precursor containing a hydrolysable and condensable trialkoxysilane group that undergoes cross-linking in the presence of a catalyst to produce a silicate network; and

sol-gel dielectric films formed from the composition, the sol-gel dielectric films being combined with the one or more charge blocking layers.

30. The device of claim 29, wherein the sol-gel dielectric films are formed on a substrate.

31. The device of claim 30, wherein substrate comprises a glass or different metal layers of varying thickness.

32. The device of claim 30, further comprising: an ultrathin layer of a polymer having a permittivity greater than 2, the ultrathin layer being disposed between the substrate and the sol-gel dielectric films.

33. The device of claim 30, wherein the substrate further comprises a flexible substrate.

34. The device of claim 29, further comprising: an electrode positioned on the one or more charge blocking layers, the one or more charge blocking layers being disposed on top of and/or below the sol-gel dielectric films; and

a glass layer disposed in communication with the one or more charge blocking layers and the film.

35. The device of claim 29, further comprising: a top electrode;
wherein at least one of the one or more charge blocking layers is disposed between the sol-gel dielectric films and the top electrode.

36. The device of claim 29, further comprising: a bottom electrode;
wherein at least one of the one or more charge blocking layer is between the bottom electrode and the sol-gel dielectric films.

37. The device of claim 29, further comprising: a bottom electrode and a top electrode;

wherein the one or more charge blocking layer is between the bottom electrode, the top electrode, and the sol-gel dielectric films.

38. The device of claim 29, the single sol-gel precursor comprising a trialkoxysilane having a cyanoalkyl polar group and water is the catalyst for hydrolysis;

wherein the cross-linked network exhibits higher extractable energy density and energy extraction efficiency.

39. The device of claim 29, the single sol-gel precursor comprising a trialkoxysilane having a cyanoalkyl polar group and a mixture of water and hydrochloric acid is the catalyst;

wherein the cross-linked network exhibits higher extractable energy density and energy extraction efficiency.

40. A method of processing a capacitor and energy storage device, the method comprising:

mixing a sol-gel material with liquid catalyst, the sol-gel material being formed from a composition formed from a single precursor;

heating or drying the sol-gel material to remove a solvent thereby forming a dry powder;

dissolving the powder with a solvent to form a solution; and

casting the sol-gel material into a film;

wherein the sol-gel material has a shelf-life of at least one month.

41. The method of claim 40, wherein the liquid catalysis is water.

42. The method of claim 40, further comprising: sandwiching the film between two identical polymer layers.

43. The method of claim 40, further comprising: sandwiching the film between two identical oxide layers.

44. The method of claim 40, further comprising: sandwiching the film between two organic self-assembled monolayers selected from alkyl or aryl thiols, alkyl or aromatic phosphonic acids, alkyl or aryl carboxylic acids or alkyl or aryl silanes, alkyl or aryl siloxanes, or a combination thereof.

45. The method of claim 40, wherein the liquid catalysis is comprised of a mixture of water and hydrochloric acid.

46. The method of claim 40, further comprising: positioning an electrode and a charge blocking layer on top of and/or below the film;
providing a glass layer in communication with the one or more charge blocking layers and the film; and
depositing the bottom conducting layer on top of the glass layer.

47. The method of claim 40, further comprising: selecting the liquid catalyst from a plurality of liquid catalysts to hydrolyze and condense the single precursor; and
maintaining relatively high permittivity in the sol-gel film by reducing leakage current of the film.

48. The method of claim 40, further comprising: casting the sol-gel material into the film by spin, blade, spray coating, or a combination thereof.

49. The method of claim 40, further comprising: scratching the film thereby obtaining the powder.

50. The method of claim 40, further comprising: re-dissolving the sol-gel material in the same or a different solvent; and
applying the sol-gel material on one or more polymer layers for one or more predetermined electrical applications.

51. The method of claim 40, further comprising: coating or casting the film to a predetermined thickness.

52. The method of claim 40, wherein the film includes a thickness ranging from 30 nm to 10,000 nm or from 50 nm to 4,000 nm.

53. The method of claim 40, further comprising: tailoring dielectric permittivity of the powder.

54. The method of claim 40, further comprising: tailoring breakdown strength of the powder.

55. The method of claim 40, further comprising: using the sol-gel material as a host material for an inorganic filler.

56. The method of claim 55, wherein the inorganic filler comprises barium titanate, strontium titanate, barium strontium titanate, or a combination thereof.

57. The method of claim 55, the inorganic filler comprises different sized nanoparticles.

58. The method of claim 55, wherein the inorganic filler is functionalized on its surface with suitable groups to disperse in the sol-gel material.

FIG. 1

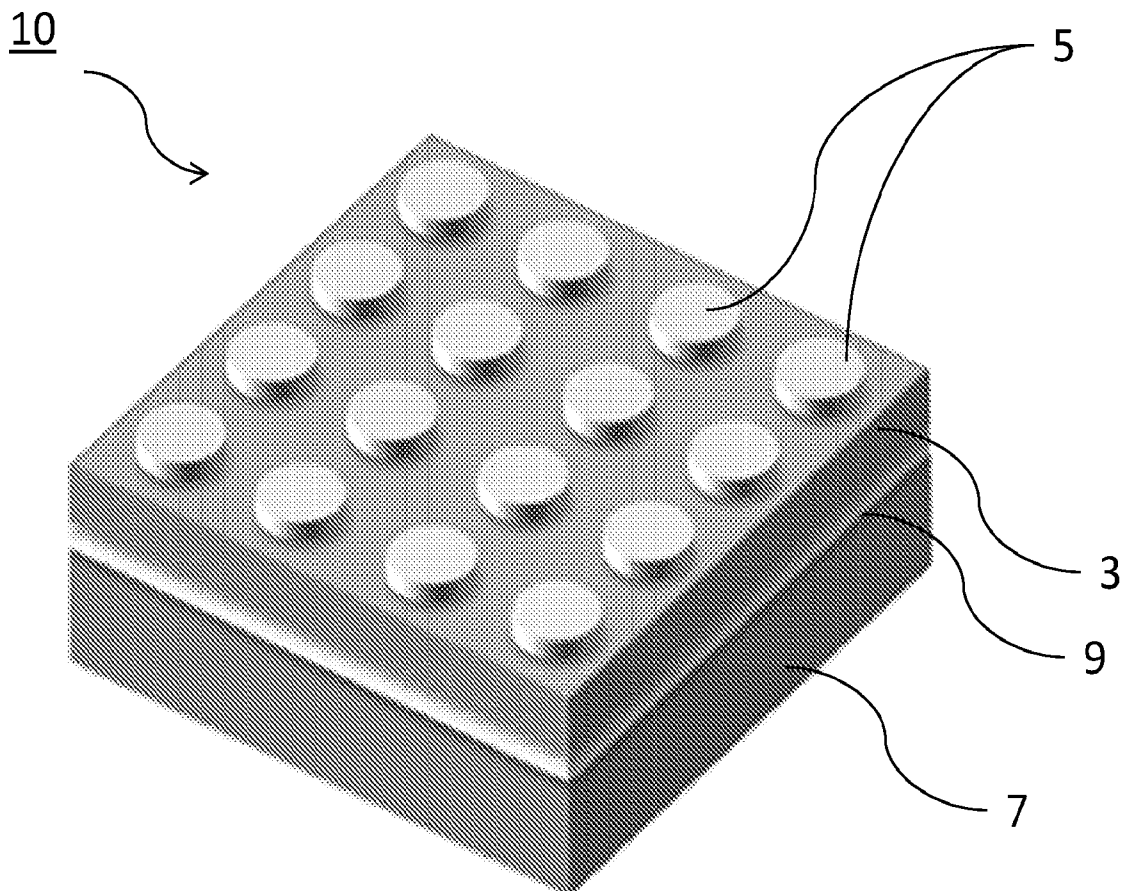


FIG. 2

3" Boron-doped Silicon Wafer

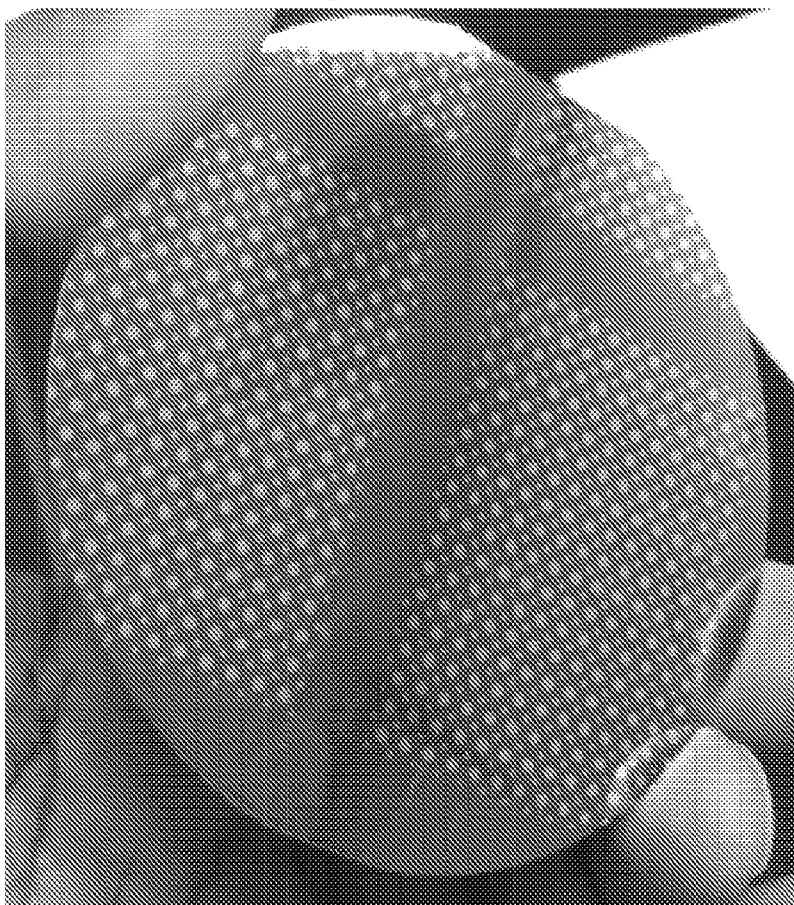


FIG. 3

4" Al-Mylar

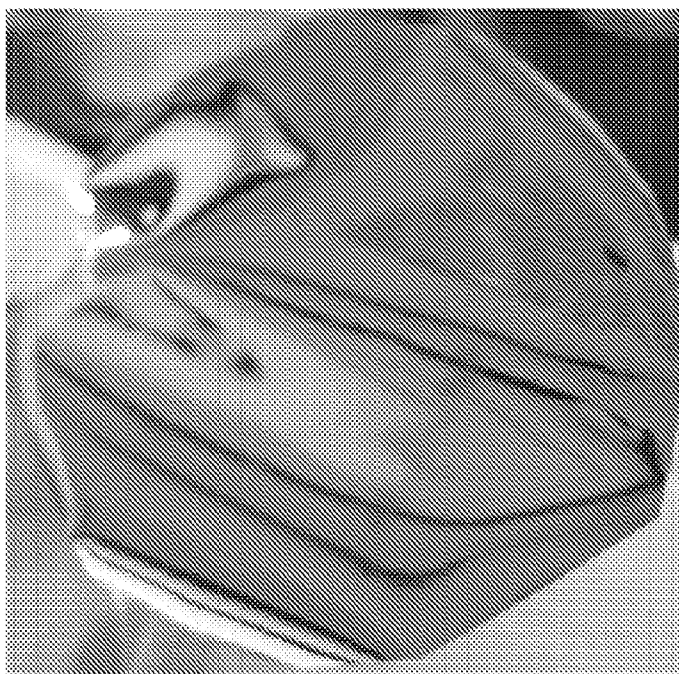


FIG. 4

4" ITO-PSO

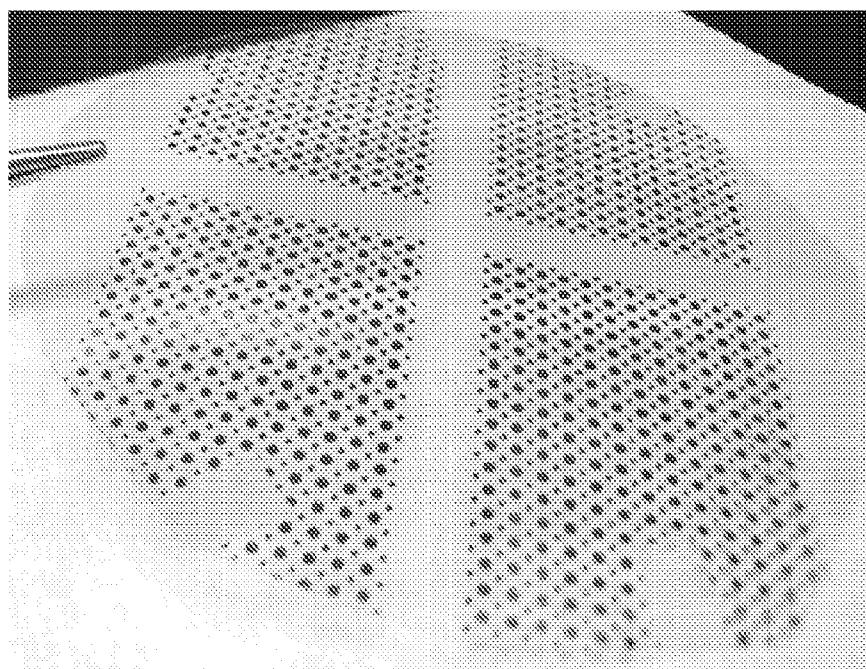


FIG. 5

4" ITO-PET

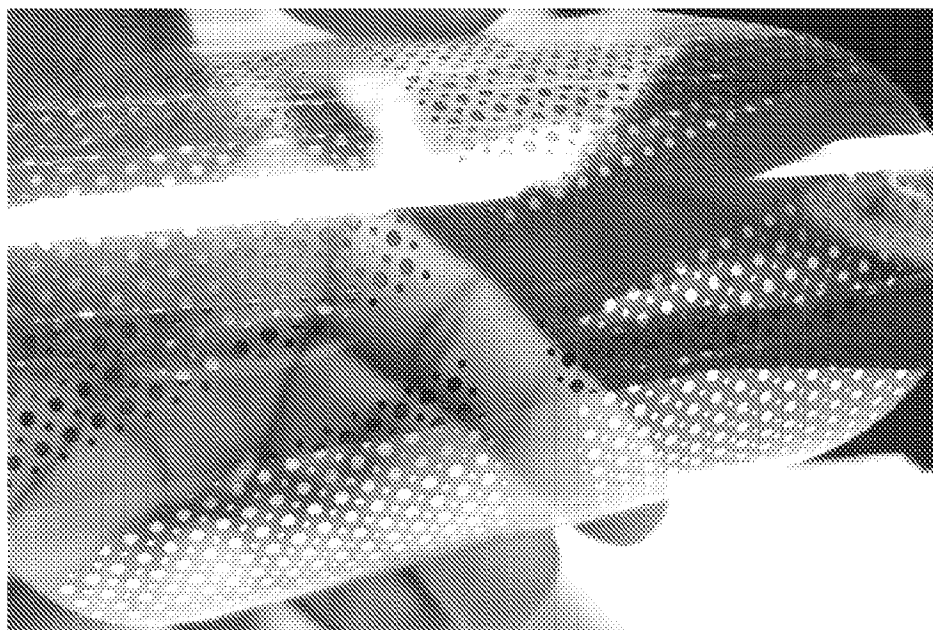


FIG. 6

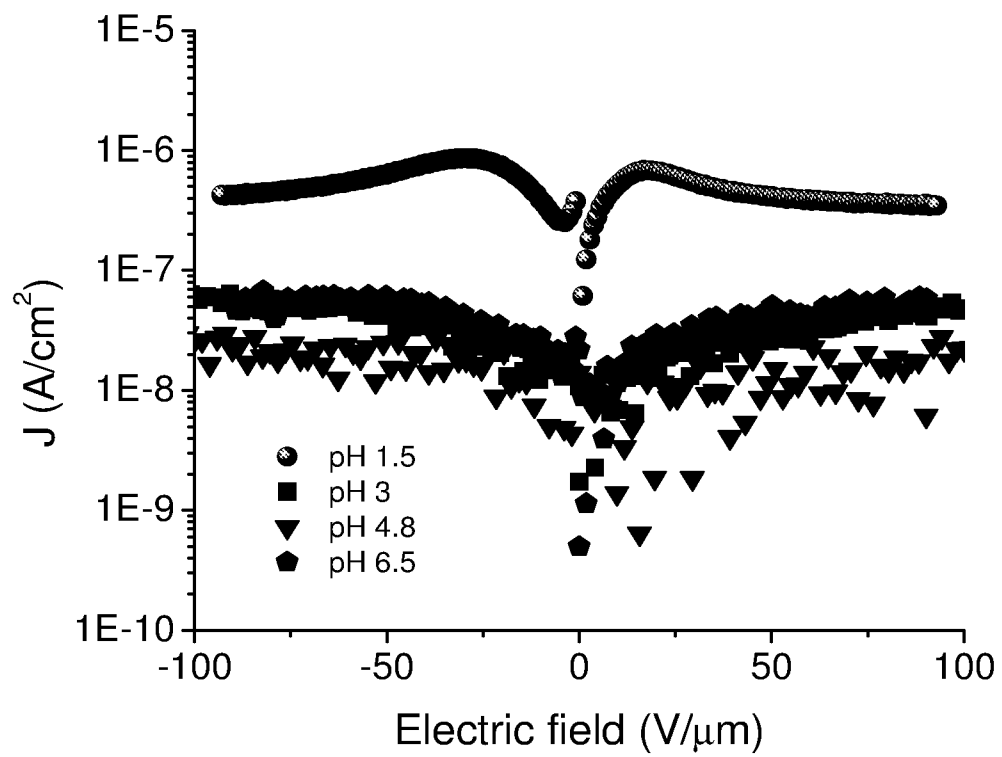


FIG. 7

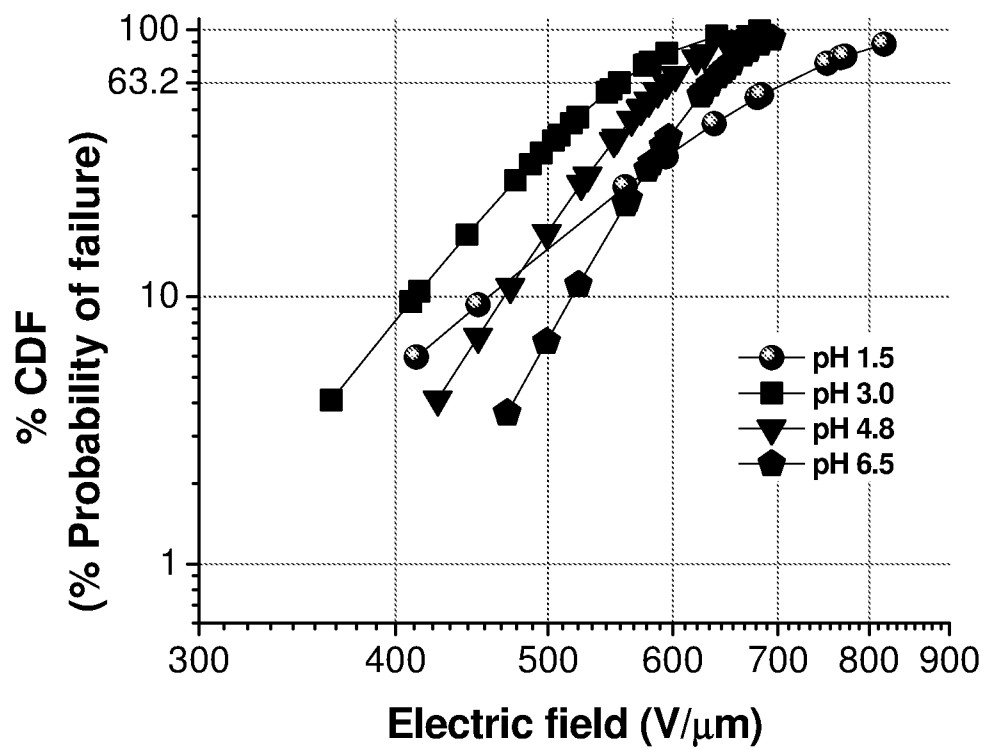


FIG. 8

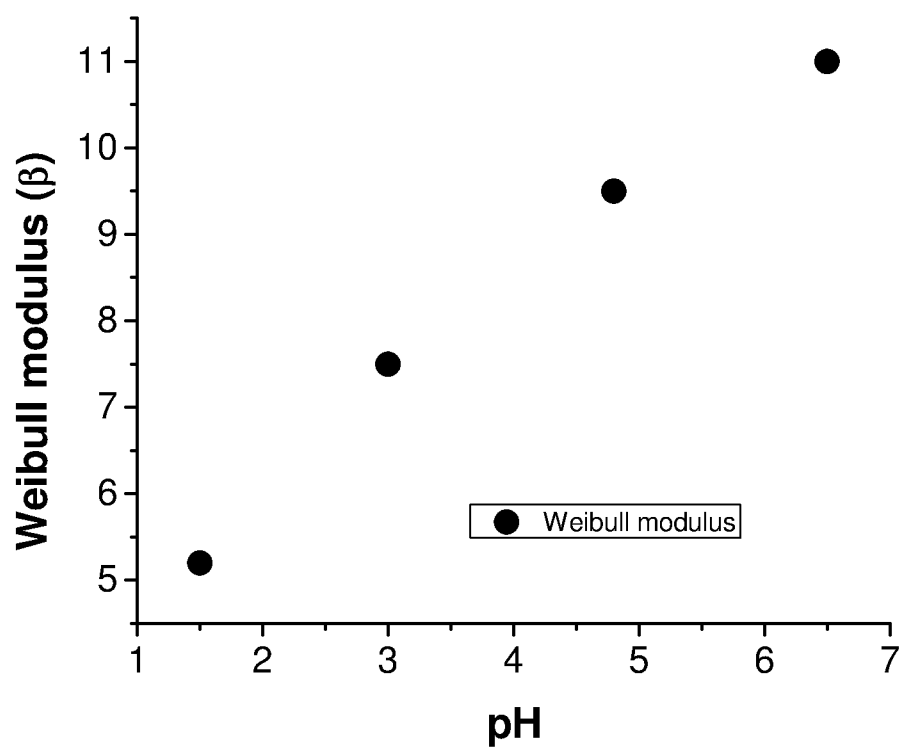
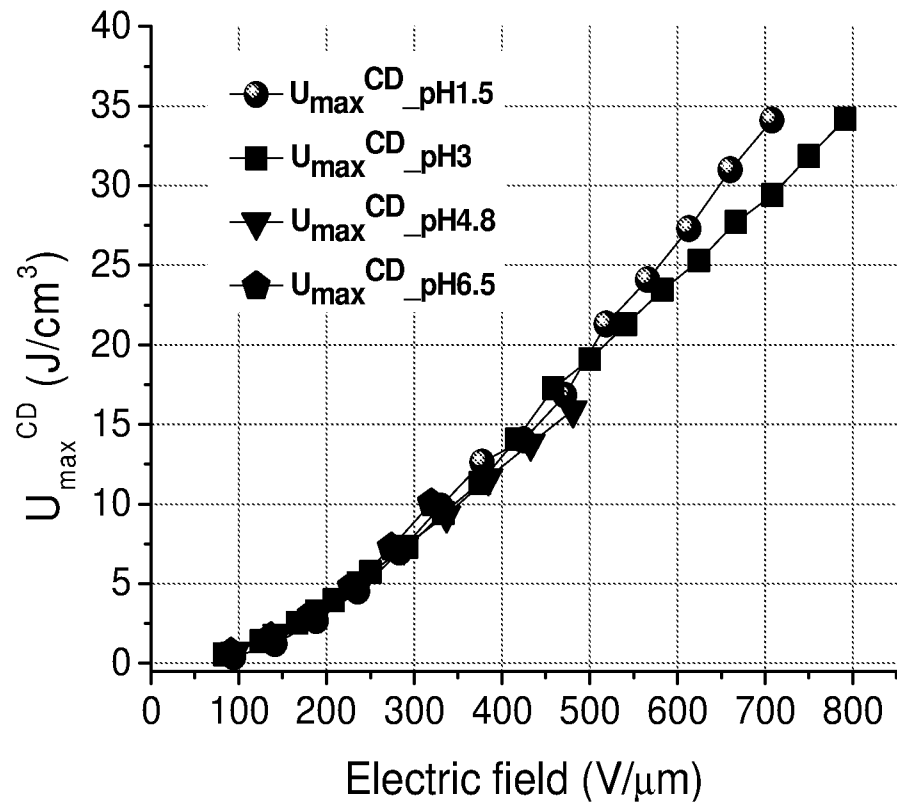


FIG. 9



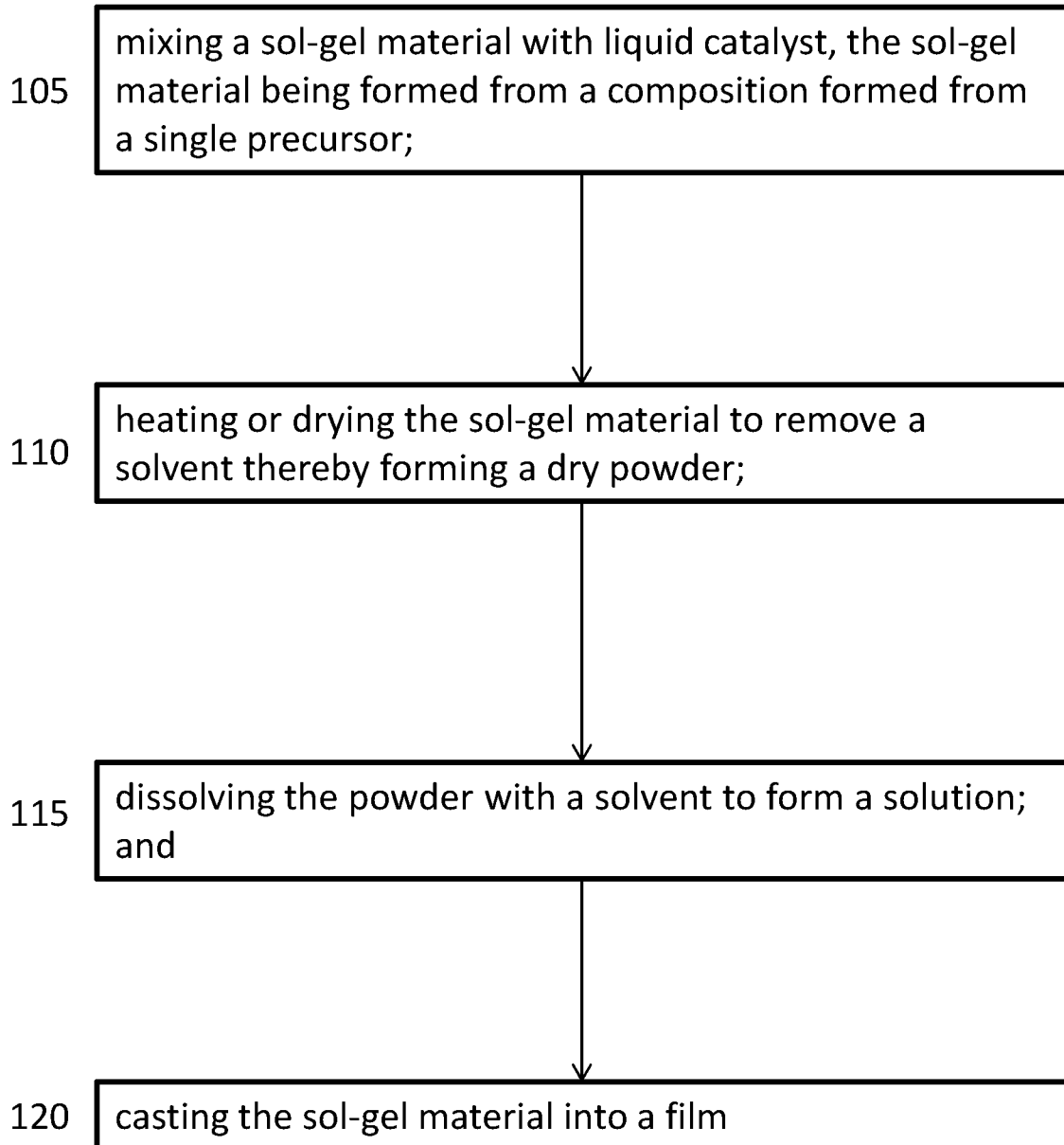
100**FIG. 10**

FIG. 11

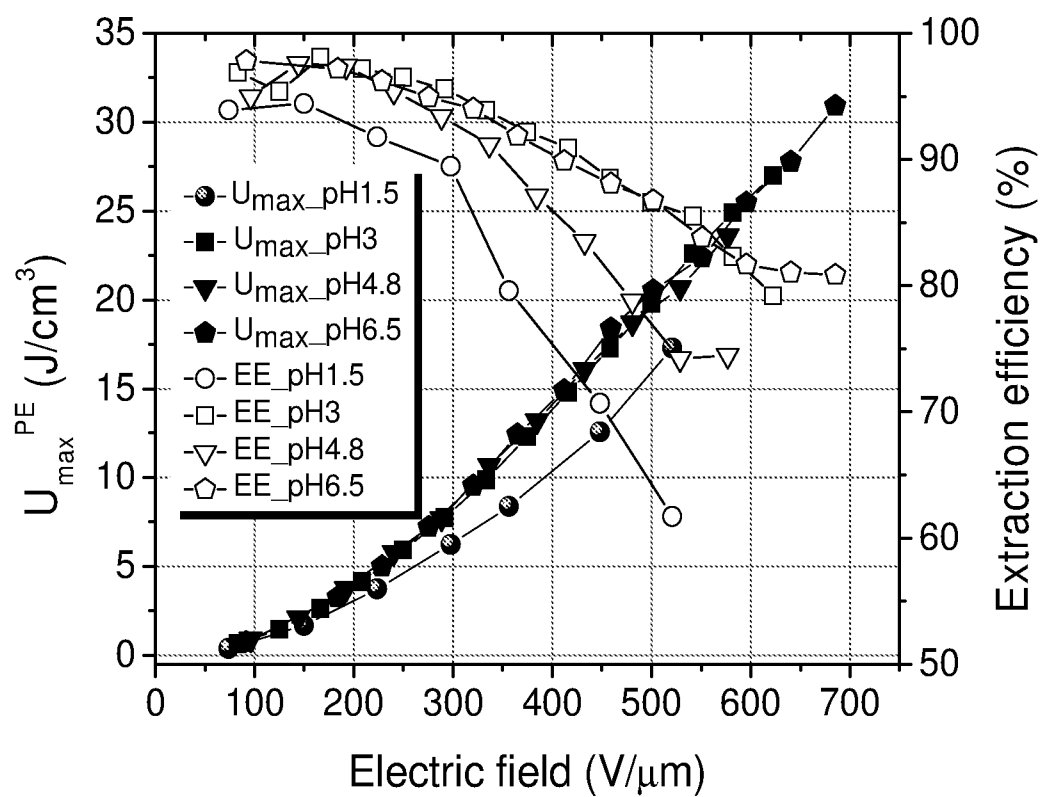


FIG. 12

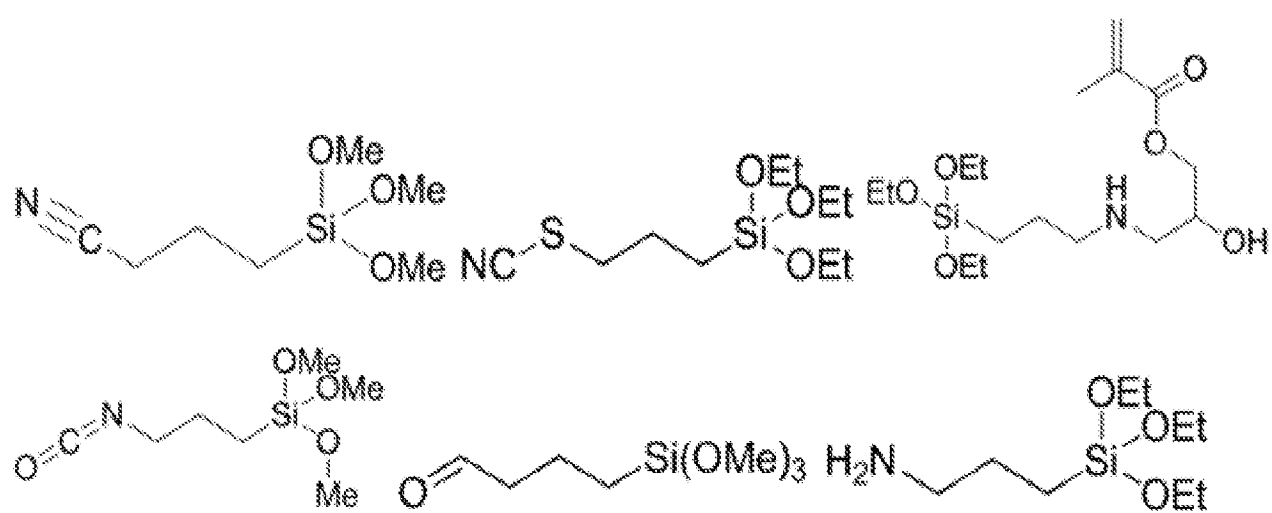


FIG. 13

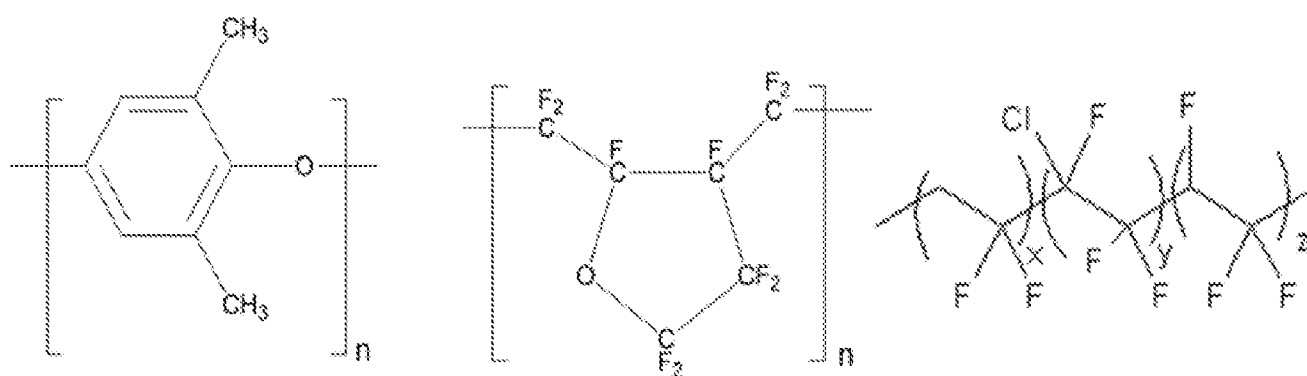


FIG. 14

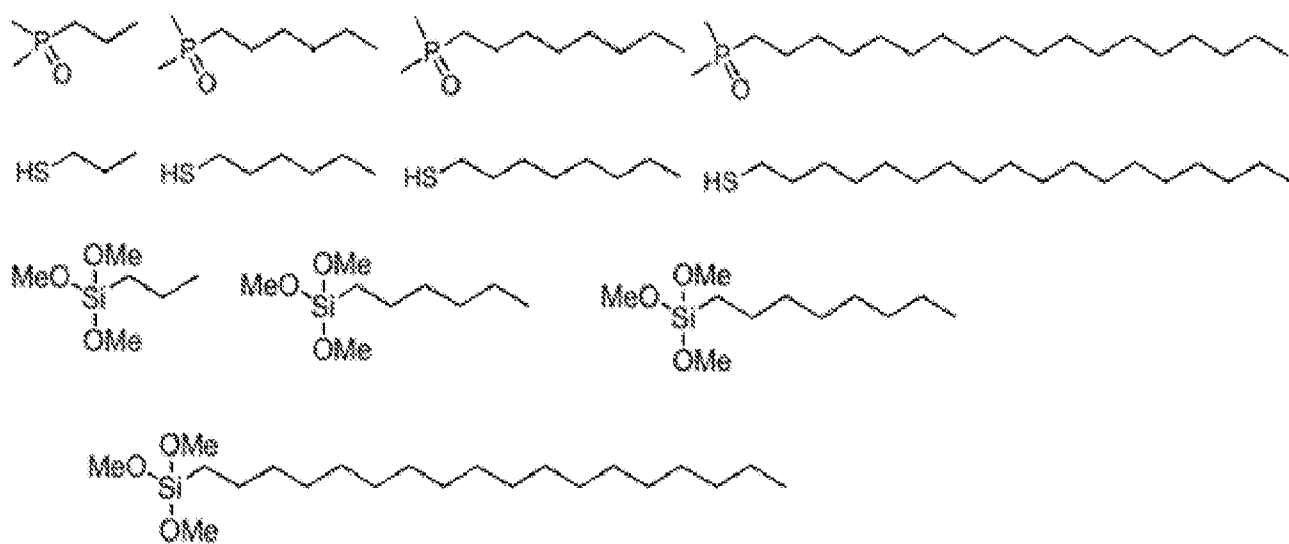


FIG. 15

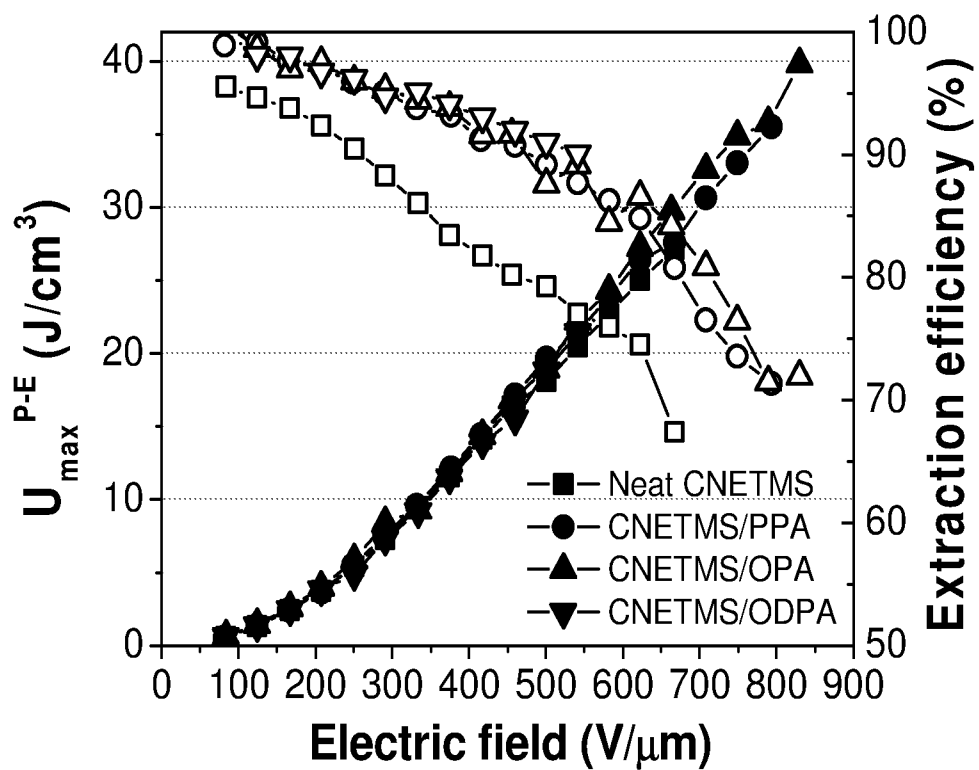


FIG. 16

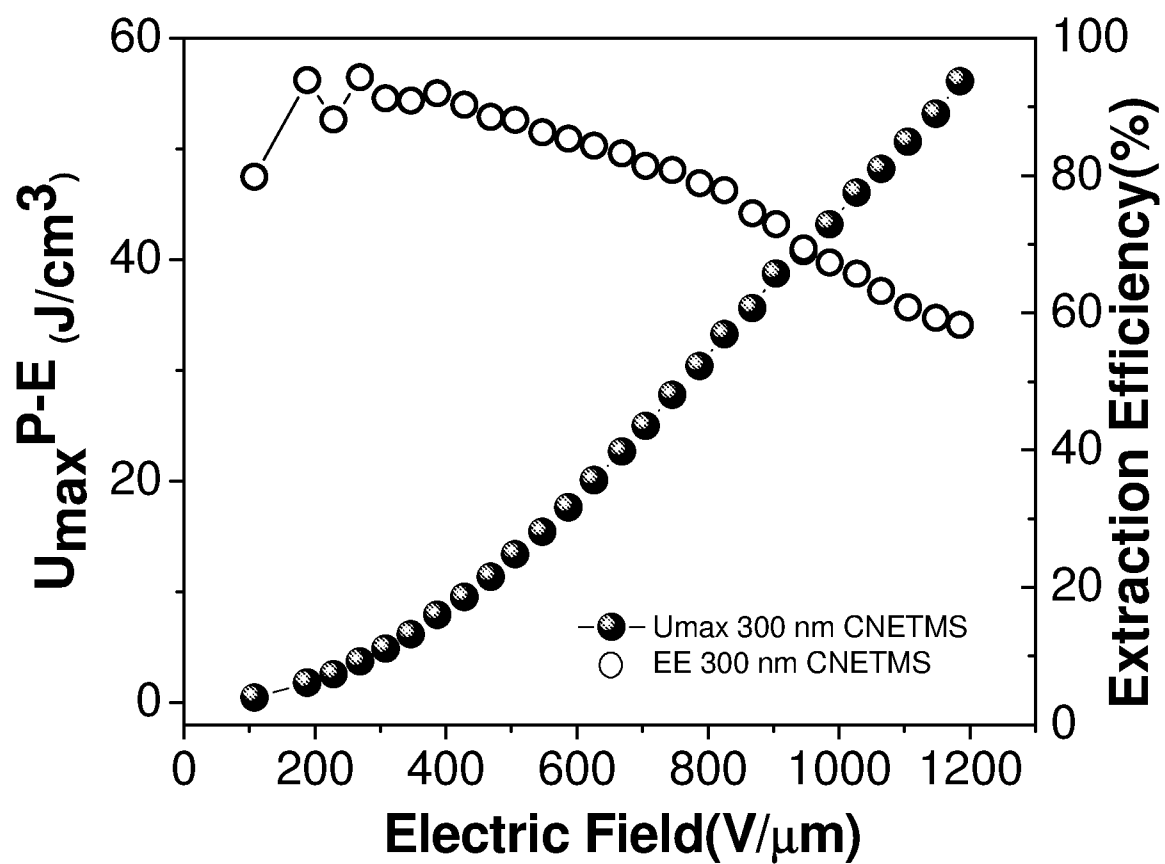


FIG. 17

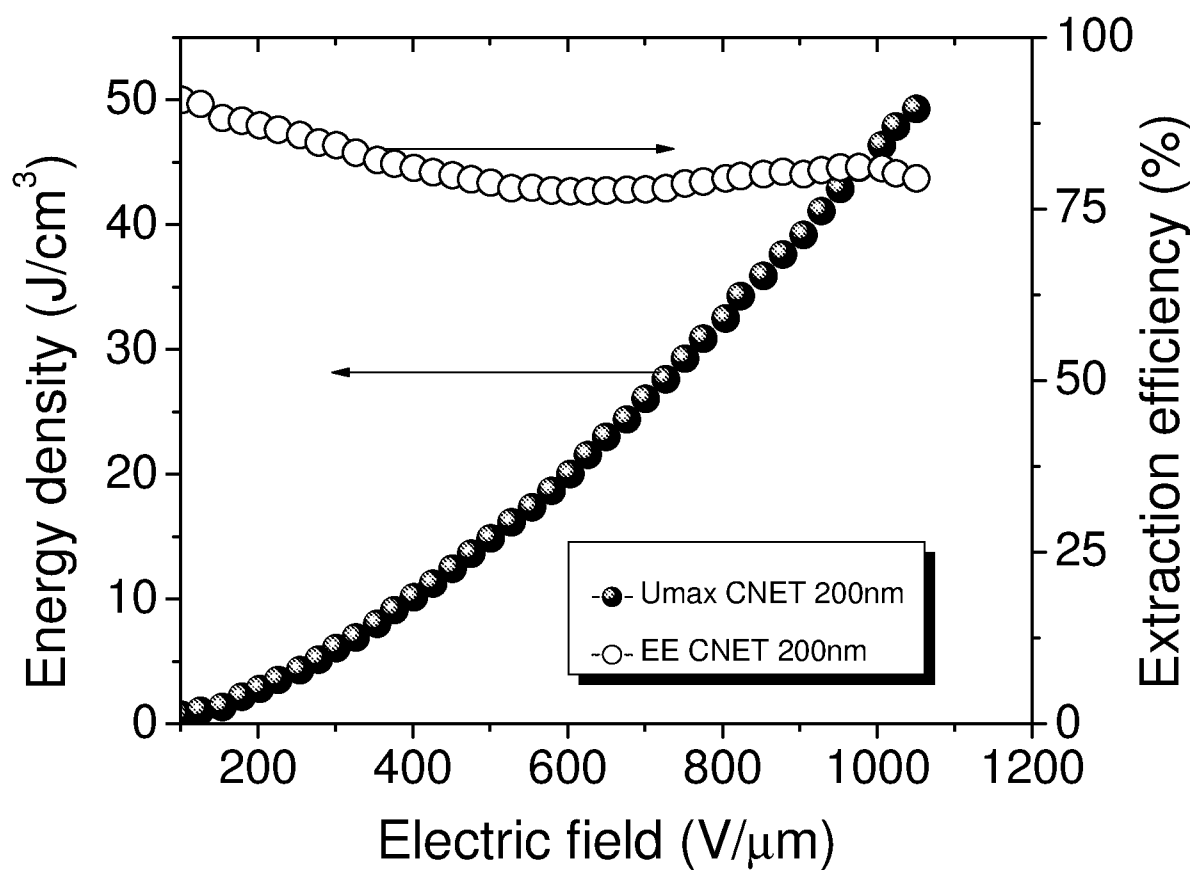
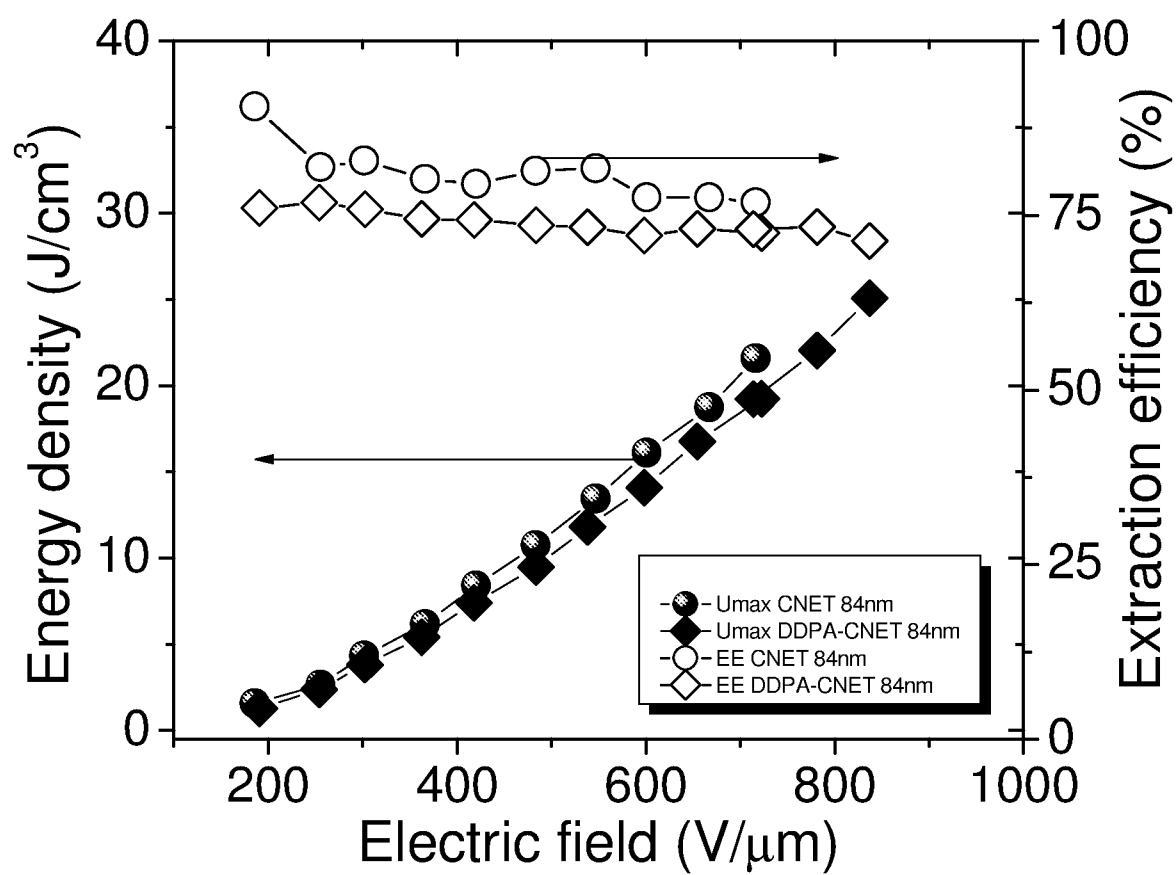


FIG. 18



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/032414

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-39

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/032414

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01G 4/33; C08G 77/04; C08G 77/26; C23C 18/12; H01G 4/018 (2017.01)

CPC - C08G 77/04; C08G 77/26; C23C 18/12; C23C 18/1216; H01G 4/018; H01G 4/33; H01L 28/55 (2017.08)

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)

See Search History document

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)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	KIM et al., Bilayer Structure with Ultrahigh Energy/Power Density Using Hybrid Sol-Gel Dielectric and Charge-Blocking Monolayer, Advanced Energy Materials, July 2015, entire document	1, 2, 4, 6, 8 ----- 3, 5, 7, 9-24, 29-39
Y	US 2010/0035071 A1 (NISHIMI et al) 11 February 2010 (11.02.2010) entire document	3, 5, 38
Y	FIDALGO et al., Role of the Alkyl-Alkoxide Precursor on the Structure and Catalytic Properties of Hybrid Sol-Gel Catalysts, Chemistry of Materials, Vol. 17, No. 26, 24 November 2005, Pgs. 6686-6694	7
Y	US 2015/0210871 A1 (SCHOTT AG) 30 July 2015 (30.07.2015) entire document	9
Y	KIM et al., High-Energy-Density Sol-Gel Thin Film Based on Neat 2-Cyanoethyltrimethoxysilane, ACS Applied Materials & Interfaces, February 2013, entire document	10-24, 29-39
Y	KIM, Ferroelectric Nanocomposite and Polar Hybrid Sol-Gel Materials for Efficient, High Energy Density Capacitors, Georgia Institute of Technology, Ph.D. Dissertation May 2014 [retrieved on 28 August 2017], Retrieved from the Internet: <URL: https://smartech.gatech.edu/handle/1853/51816 >. See Summary, Pgs. 108-124	14, 15, 18, 19, 22, 32



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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 August 2017

Date of mailing of the international search report

25 SEP 2017

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/032414

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/0052403 A1 (TATEMATSU) 01 March 2012 (01.03.2012) entire document	21
A	US 6,133,390 A (KOZLOVSKI et al) 17 October 2000 (17.10.2000) entire document	1-39
A	US 2009/0267058 A1 (NAMDas et al) 29 October 2009 (29.10.2009) entire document	1-39

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/032414

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-39 are drawn to devices for capacitor and energy storage, a capacitor energy and power storage device, and sol-gel thin film devices.

Group II: claims 40-58 are drawn to methods of processing a capacitor and energy storage device.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, devices for capacitor and energy storage, a capacitor energy and power storage device, and sol-gel thin film devices, are not present in Group II; and the special technical features of Group II, methods of processing a capacitor and energy storage device, are not present in Group I.

The Groups I and II share the technical features of a capacitor and energy storage device, comprising a sol-gel material in a thin film. However, these shared technical features do not represent a contribution over the prior art.

Specifically, US 2009/0267058 A1 to Namdas et al. teach a capacitor and energy storage device (Abstract; Claims 16 and 43; Para. [0016]), comprising a sol-gel material in a thin film (Claims 16 and 43).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.