CROSSLINKED POLYMERIC DIELECTRIC MATERIALS AND ELECTRONIC DEVICES INCORPORATING SAME

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See application file for complete search history.

FOREIGN PATENT DOCUMENTS
EP 1 494 298 A2 1/2005
GB 7,605,394 B2 1/2005

OTHER PUBLICATIONS

* cited by examiner

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ABSTRACT

Solution-processable dielectric materials are provided, along with precursor compositions and processes for preparing the same. Composites and electronic devices including the dielectric materials also are provided.
Figure 3

Figure 4
Figure 5
Figure 6
Figure 7

Figure 8
Figure 9

Figure 10A

Figure 10B
Figure 11A

Figure 11B
Figure 12
CROSS LINKED POLYMERIC DIELECTRIC MATERIALS AND ELECTRONIC DEVICES INCORPORATING SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of U.S. patent application Ser. No. 11/823,859, filed on Jun. 28, 2007, which claims priority to and the benefit of U.S. Provisional Patent Application Ser. No. 60/816,952, filed on Jun. 28, 2006, the disclosure of each of which is incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under Grant No. N00014-02-1-0909 awarded by the Office of Naval Research, Grant No. DMR-0076097 awarded by the National Science Foundation, and Grant No. NCC-2-1363 awarded by the National Aeronautics and Space Administration (NASA). The government has certain rights in the invention.

BACKGROUND

The development of polymeric dielectric materials has been fundamental for the progress of both traditional and organic electronic devices. In particular, emerging display and labeling technologies based on organic thin-film transistors (OTFTs), such as electronic paper and radiofrequency identification (RFID) cards, require fabrication of OTFTs on flexible plastic substrates over very large areas and via high throughput processes. Therefore, there has been considerable effort in developing new materials for OTFT components (semiconductor, dielectric, and contacts) that can be deposited via solution-processing methods such as spin-coating, casting, and printing.

Many organic semiconductors are readily deposited from solution either directly or as molecular/polymeric soluble precursors which are then converted into the insoluble form. Doped conjugated polymers and nanoparticle-based conductive inks allow solution fabrication of sufficiently low resistivity lines for source/drain and gate contact applications.

Although various polymers have been employed as dielectrics for OTFTs, two major limitations with current-generation polymeric dielectric-based OTFTs exist. First, OTFTs function at relatively large operating voltages due to the intrinsically low (compared to crystalline semiconductors) semiconductor charge carrier mobilities. Second, because very few polymeric dielectric materials can perform optimally with a wide range of both hole-transporting (p-type) and electron-transporting (n-type) organic semiconductors, there has been limited complementary circuit application. These problems are exacerbated when printed dielectric/circuit fabrics are fabricated.

In a typical organic field effect transistor (OFET), the conductance of the source-drain channel region is modulated by the source-gate electric field (E_G). When the device is in the off-state (E_G<0), the channel conductance is very low (typically ~10^-5 Ω). When the device is in the on-state (E_G>0), a sharp increase in conductance is observed (~10^4 Ω), and the output current flow (in saturation) between the source and the drain (I_DS) is defined by:

\[ I_{DS} = \frac{W}{2L} \mu C_s (V_G - V_T)^2 \]  \hspace{1cm} (Eq. 1)

where W is the width of the channel, L is the length of the channel, \( \mu \) is the semiconductor charge carrier mobility, \( C_s \) is the dielectric capacitance per unit area, \( V_G \) is the source-gate voltage, and \( V_T \) is the threshold voltage. It can be seen that for a given device geometry and semiconductor, equivalent current gains (I_on/I_off) can be achieved at lower operating biases by increasing \( C_s \).

Because

\[ C_s = \varepsilon_0 \frac{k}{d}, \]  \hspace{1cm} (Eq. 2)

where \( k \) is the dielectric constant, \( \varepsilon_0 \) is the vacuum permittivity, and \( d \) is the thickness of the dielectric material. \( C_s \) is increased when \( k \) increases and/or \( d \) decreases. However, \( k \) of most insulating polymers is low (~3-6). Additionally, most insulating polymers need to be quite thick (usually ~1 μm) to avoid considerable current leakage through the gate electrode.

To reduce current leakage for thinner films, polymeric dielectrics such as crosslinked melamine/CR salts-polyvinyl phenol (PVP) and crosslinked benzozylobutene (BCB) have been introduced. However, these polymer films require high annealing temperatures and \( C_s \) values are typically ~<20 nF cm^-2.

Furthermore, the choice of dielectric material can affect \( \mu \), which is an important device parameter. In particular, the gate dielectric permits the creation of the gate field and the establishment of the two-dimensional channel charge sheet. Upon application of a source-drain bias, the accumulated charges move very close to the dielectric-semiconductor interface from the source electrode to the drain electrode. Therefore, the nature of the dielectric-semiconductor interface, more particularly, the dielectric surface morphology prior to the deposition of the semiconductor material, can greatly affect how these charges move within the semiconductor, i.e., the carrier mobility. Moreover, the surface morphology of the dielectric material and variations in its surface energies (e.g., surface treatment via self-assembled monolayers) have been shown to modify the growth, morphology, and microstructure of the vapor/solution-deposited semiconductor, each of these being a factor affecting \( \mu \) and \( I_{on}/I_{off}, \) the latter being the drain-source current ratio between the “on” and “off” states, another important device parameter. The properties of the dielectric material can also affect the density of state distribution for both amorphous and single-crystal semiconductors.

It is also desirable to have dielectric materials that adhere well to diverse substrates, i.e., the dielectric materials do not delaminate easily, to ensure device integrity under operating conditions, and to have dielectric materials that are hydrophobic such that device performance is not affected by humidity.

Accordingly, there is a desire in the art for polymeric dielectric materials that can exhibit relatively high capacitance and low current leakage, that can be prepared from commercially available polymer/molecular precursors via solution processes at low temperatures and atmospheric pressures, that can be compatible with diverse gate materials and
semiconductors, that can adhere well to various substrates, and that can be resistant to the absorption of ambient moisture.

SUMMARY

In light of the foregoing, the present teachings provide dielectric materials and related precursor compositions and/or associated devices that address various deficiencies and shortcomings of the prior art, including some of those outlined above.

In one aspect, the present teachings provide a precursor composition that includes in solution at least one of (i) a polymeric component and a crosslinker component, and (ii) a polymeric crosslinker that includes a pendant group having a thermally curable crosslinking moiety. The composition is adapted to form a dielectric material after crosslinking (e.g., by thermally curing) the precursor composition. The crosslinker component can include a thermally curable crosslinking moiety having the formula:

$$(X)_3_{(Y)}Si -(Z) - Si (X)_{(Y)} (X_{3})_{(Y)}$$

and the polymeric crosslinker can include a thermally curable crosslinking moiety having the formula:

$$Q - Si (Y)_{(X)}(X_{3})_{(Y)}$$

wherein Q, X, Y, Z, and m are as defined herein.

For example, thermally curable crosslinkers of the present teachings can include $[CH_3C(O)O]_3Si -(CH_2)_2-O -(CH_2)_2-Si (CH_3C(O)O)Si]_n$, $ClSi -(CH_2)_2-O -(CH_2)_2-O -(CH_2)_2-SiCl$ or $ClSi -(CH_2)_2-O -(CH_2)_2-CF_2$ and $ClSi -(CH_2)_2-SiCl$ or $ClSi -(CH_2)_2-(CF_2)_2$ and $ClSi -(CH_2)_2-SiCl$, and $[CH_3C(O)O]_3Si -(CH_2)_2(CF_2)_2$ and $[CH_2]_2-Si(CH_3C(O))_3$.

An exemplary polymeric crosslinker having a thermally curable crosslinking moiety according to the present teachings can have the formula:

$$Q - Si (Y)_{(X)}(X_{3})_{(Y)}$$

wherein $R^6$, $R^7$, $R^8$, Q, X, Y, and m are as defined herein.

In certain embodiments, the precursor composition can further include at least one of (i) a crosslinker component comprising a photochemically curable crosslinker and (ii) a photochemically curable polymeric crosslinker. Such photochemically curable crosslinkers typically include an alkenyl group (i.e., one or more double bonds), for example, an allyl group, a phenylethynyl group, or a cinnamyl group.

In some embodiments, the polymeric component of the composition can include a polymer selected from a polyalkylene, a substituted polyalkylene, a siloxane polymer and a copolymer thereof. Examples of polyalkylenes and substituted polyalkylenes include, but are not limited to, polyethylenes, polypropylenes, polyvinylalcohols, polyesters, ring-functionalized derivatives of polyesters (e.g. polyvinylphenol (PVP)), and polyacrylates (e.g., polymethylmethacrylates (PMMA)).

At least one of the polymeric component and the crosslinker component typically is dissolved in an anhydrous solvent. The anhydrous solvent can be selected from ethyl acetate, dioxane, bis(2-methoxyethyl)ether (diglyme), tetrahydrofuran, toluene, xylene, various alcohols including methanol and ethanol, and various ketones including acetone, cyclopentanone (CP), methyltetrahydrofuran, and the like.

In some embodiments, the precursor composition can further include a metal oxide component, for example, to increase the dielectric constant (k) of a dielectric formed from the composition. The metal oxide component can be in particular form and can be blended, mixed and/or incorporated in the composition. The metal oxide component can include a metal component selected from a Group I metal, a Group II metal, a Group III metal, a Group IV metal, a transition metal, and combinations thereof.

In another aspect, the present teachings provide dielectric materials that include a crosslinked polymeric material that is a thermally cured product and/or a photochemically cured product of any of the precursor compositions described above. Also embraced with the scope of the present teachings are various compositions, composites, and articles of manufacture (e.g., electronic devices) that incorporate the dielectric materials disclosed herein. Examples of electronic devices that can incorporate one or more dielectric materials of the present teachings include, but are not limited to, organic thin film transistors (OTFTs) (e.g., organic field effect transistors (OFETs)) and capacitors. In addition to a dielectric component, these devices can include, for example, a substrate component, a semiconductor component, and/or one or more metallic contact components.

In a further aspect, the present teachings provide various methods for preparing a dielectric material. The methods can include applying a precursor composition of the present teachings onto a substrate, and thermally curing the precursor composition (i.e., the coated substrate) to provide a dielectric material. The applying step can be performed by, for example, spin-coating, printing, spraying, or casting. In some embodiments, the curing step can include heating at a temperature within a range of about 70°C to about 150°C in a high humidity atmosphere. In embodiments in which the precursor composition includes a photochemically curable crosslinker, the curing step can include exposing the precursor composition (i.e., the coated substrate) to ultraviolet light, e.g., by irradiation at a wavelength of about 245 nm. For a dielectric precursor composition that includes both a thermally curable crosslinker and a photochemically curable crosslinker, the curing step can include first heating at a temperature within a range of about 70°C to about 150°C in a high humidity atmosphere, followed by irradiation with a wavelength of about 245 nm, or vice versa. In some embodiments, the crosslinking reaction can be achieved by electron beam irradiation.

The foregoing as well as other features and advantages of the present teachings, will be more fully understood from the following figures, description, and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

It should be understood that the drawings described below are for illustration purposes only and are not necessarily to scale. The drawings are not intended to limit the scope of the present teachings in any way.

FIG. 1 is a schematic representation of different crosslinking strategies that can be employed using dielectric precursor compositions of the present teachings.

FIG. 2 is a schematic representation of a crosslinking-patterning process, illustrating in order: depositing a dielectric precursor composition onto a substrate, photochemically
The present teachings provide crosslinked polymeric dielectric materials that can exhibit good insulating properties as well as structural robustness. These materials can be used in various applications, such as organic thin film transistors (OTFTs) and organic light-emitting diodes (OLEDs). The crosslinked polymeric matrices can be fabricated using a variety of methods, including spin-coating and printing. The crosslinking process involves the use of different crosslinkers, such as C6C11C6OAc, EGOAc, and C6NMe2. The dielectric materials of the present teachings can operate at low biases, reducing power consumption and improving overall efficiency. The materials can also be combined with different semiconductors, such as pentacene, to enhance performance. The crosslinked polymeric matrices can be used in capacitor structures as well, providing high capacitance values (e.g., 300 nF cm−2). The use of crosslinked polymeric matrices in dielectric applications offers a promising solution for low-power and high-performance electronic devices.
As used herein, "alkoxy" refers to —O-alkyl group. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy (e.g., n-propoxy and isopropoxy), t-butoxy groups, and the like.

As used herein, "alkyl" refers to a straight-chain or branched saturated hydrocarbon group. Examples of alkyl groups include methyl (Me), ethyl (Et), propyl (e.g., n-propyl and isopropyl), butyl (e.g., n-butyl, isobutyl, s-butyl, t-butyl), pentyl groups (e.g., n-pentyl, isopentyl, neopentyl), and the like. A lower alkyl group typically has up to 4 carbon atoms. Examples of lower alkyl groups include methyl, ethyl, propyl (e.g., n-propyl and isopropyl), and butyl groups (e.g., n-butyl, isobutyl, s-butyl, t-butyl).

As used herein, "haloalkyl" refers to an alkyl group having one or more halogen substituents. Examples of haloalkyl groups include CF₃, CF₂Cl, CH₂F, CCl₃, CHCl₂, CH₂Cl₂, and the like. Perhaloalkyl groups, i.e., alkyl groups wherein all of the hydrogen atoms are replaced with halogen atoms (e.g., CF₃ and C₂F₆), are included within the definition of "haloalkyl." For example, a C₁₋₂₀ haloalkyl group can have the formula —CX₂a₋₁ or —CX₃₋₀, wherein X is F, Cl, Br, or I, a is an integer in the range of 1 to 20, and b is an integer in the range of 0 to 40, provided that b ≤ 2a + 1.

As used herein, "arylkyl" refers to an -alkyl-aryl group, wherein the arylkyl group is covalently linked to the defined chemical structure via the alkyl group. An arylkyl group is within the definition of an L-C₆₋₁₄ aryl group, wherein L is as defined herein. An example of an arylkyl group is a benzyl group (—CH₂—C₆H₅). An arylkyl group can be optionally substituted, i.e., the aryl group and/or the alkyl group can be substituted as disclosed herein.

As used herein, "alkenyl" refers to a straight-chain or branched alkyl group having one or more carbon-carbon double bonds. Examples of alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, butadienyl, pentadienyl, hexadienyl groups, and the like. The one or more carbon-carbon double bonds can be internal (such as in 2-butene) or terminal (such as in 1-butene).

As used herein, "cycloalkyl" refers to a non-aromatic carbocyclic group including cyclized alkyl, alkenyl, and alkynyl groups. A cycloalkyl group can be monocyclic (e.g., cyclohexyl) or polycyclic (e.g., containing fused, bridged, and/or spiro ring systems), wherein the carbon atoms are located inside or outside of the ring system. Any suitable ring position of the cycloalkyl group can be covalently linked to the defined chemical structure. Examples of cycloalkyl groups include, but are not limited to, cyclopentyl, cyclopropylmethyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexymethyl, cyclohexylethyl, cycloheptyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cycloheptatrienyl, norbornyl, norpinyl, norcaryl, adamantyl, and spiro[4.5]decanyl groups, as well as their homologs, isomers, and the like. In some embodiments, cycloalkyl groups can be substituted as disclosed herein.

As used herein, "heteroaryl" refers to an aromatic monocyclic ring system containing at least 1 ring heteroatom selected from O, N and S, and optionally contains one or more double or triple bonds. One or more N or S atoms in a cyclohetoroalkyl group may be oxidized (e.g., morpholine N-oxide, thiophenol S-oxide, thiophenone S,S-dioxide). In some embodiments, nitrogen atoms of cyclohetoroalkyl groups can bear a substituent, for example, a hydro- gen atom, an alkyl group, or other substituents as described herein. Cyclohetoroalkyl groups can also contain one or more oxo groups, such as piperidino, oxazolidinyl, pyrimidin-2(1H)-dione, pyridin(2(1H)-one, and the like. Examples of cyclohetoroalkyl groups include, among others, morpholine, thiomorpholine, pyridan, imidazolidine, imidazoline, oxazolidine, pyrazolidine, pyrrolidine, pyr- rolone, tetrahydrofururan, tetrahydrothiophene, piperidine, pip- erazine, and the like. In some embodiments, cyclohetoroalkyl groups can be substituted as disclosed herein.

As used herein, "arly" refers to an aromatic monocyclic hydrocarbon ring system or a polycyclic ring system in which two or more aromatic hydrocarbon rings are fused (i.e., having a bond in common with) together or at least one aromatic monocyclic hydrocarbon ring is fused to one or more cycloalkyl and/or cyclohetoroalkyl rings. An arly group can have from 6 to 14 carbon atoms in its ring system, which can include multiple fused rings. In some embodiments, a polycyclic arly group can have from 8 to 14 carbon atoms. Any suitable ring position of the arly group can be covalently linked to the defined chemical structure. Examples of arly groups having only aromatic carbocyclic ring(s) include, but are not limited to, phenyl, 1-naphthyl (bicyclic), 2-naphthyl (bicyclic), anthracenyl (tricyclic), phenanthrenyl(tricyclic) and like groups. Examples of polycyclic arly rings in which at least one aromatic carbocyclic ring is fused to one or more cycloalkyl and/or cyclohetoroalkyl rings include, among others, benzo derivatives of cyclopentane (i.e., an indanyl group, which is a 5,6-bicyclic cycloalkyl/aromatic ring system), cyclohexane (i.e., a tetrahydrocyclohexyl group, which is a 6,6-bicyclic cycloalkyl/aromatic ring system), imidazoline (i.e., a benzimidazolinyl group, which is a 5,6-bicyclic cyclohetoroalkyl/aromatic ring system), and pyran (i.e., a chromenyl group, which is a 6,6-bicyclic cyclohetoroalkyl/ aromatic ring system). Other examples of arly groups include, but are not limited to, benzoxyoxanil, benzdioxanil, chromanil, indolinyl groups, and the like. In some embodiments, arly groups can be substituted as disclosed herein.

As used herein, "heteroary" refers to an aromatic monocyclic ring system containing at least 1 ring heteroatom selected from oxygen (O), nitrogen (N) and sulfur (S) or a polycyclic ring system where at least one of the rings present in the ring system is aromatic and contains at least 1 ring heteroatom. Polycyclic heteroaryl groups include two or more heteroaryl rings fused together and monocyclic heteroaryl rings fused to one or more aromatic carbocyclic rings, non-aromatic carbocyclic rings, and/or non-aromatic cyclohetoroalkyl rings. A heteroaryl group, as a whole, can have, for example, from 5 to 14 ring atoms and contain 1-5 ring heteroatoms. The heteroaryl group can be attached to the defined chemical structure at any heteroatom or carbon atom that results in a stable structure. Generally, heteroaryl rings do not contain O—O, S—S, or S—O bonds. However, one or more N or S atoms in a heteroaryl group can be oxidized (e.g., pyridine N-oxide, thiophene S-oxide, thiophene S,S-dioxide). Examples of heteroaryl groups include, for example, the 5-membered monocyclic and 5-6 bicyclic ring systems shown below.
Throughout the specification, structures may or may not be presented with chemical names. Where any question arises as to nomenclature, the structure prevails.

The present teachings provide precursor compositions including one or more polymers (i.e., a polymeric component) and one or more crosslinking moieties or crosslinkers (i.e., a crosslinker component) which, upon crosslinking (e.g., by thermally curing or photochemically curing), can provide crosslinked polymeric materials that are suitable for use as dielectric materials. In some embodiments, the precursor composition can include the polymeric component and the crosslinker component as separate chemical moieties. For example, the crosslinker component can include one or more crosslinkers that are small molecule compounds having one or more crosslinking groups. In other embodiments, the polymeric component and the crosslinker component can be chemically combined in the form of a polymeric crosslinker, specifically, a polymer having one or more pendant crosslinking groups on its backbone. The precursor composition can include one or more solvents in which at least one of the polymeric component and the crosslinker component is substantially soluble.

In some embodiments, the crosslinker component of the precursor composition can include thermally curable crosslinkers that include two or more silyl groups. These silyl groups can include one or more (e.g., one, two, or three) hydrolyzable moieties such as halo groups, amino groups, alkoxy groups, and carboxylate groups that can react with OH groups and induce crosslinking. For example, the thermally curable crosslinkers can have the formula:

\[(X)_{2}---Y---Z---Si(OM)_{3}\]

and (ii) a polymeric crosslinker comprising a pendant group, the pendant group comprising a thermally curable crosslinking moiety having the formula:

\[-Q-Si(OM)_{3}\]

wherein:

- m, at each occurrence, is independently selected from 0, 1, and 2;
- X, at each occurrence, is independently selected from a halogen, --NR^{1}R^{2}, --OR^{3}, and --OC(0)R^{3};
- Y, at each occurrence, is independently selected from H, a C_{1-6} alkyl group, and a C_{1-6} haloalkyl group;
- Z is Q-W-Q; and
- Q, at each occurrence, is independently selected from --O--, --O-4-L, --L-O--, --NR^{4}--, --NR^{4}-L, --L-NR^{4}--, and a covalent bond;

wherein:

- L, at each occurrence, is independently a divalent C_{1-10} alkyl group or a divalent C_{1-10} haloalkyl group, each of which is optionally substituted with 1-4 R^{4} groups;
- W is selected from --SiXX--, --SiXY--, --SiYY--, --SiXX--, --SiXY--, --SiYY--; --O--[(CR^{4})_{2}---O]_{p}[(CR^{4})_{2}---O]_{q}, a divalent C_{6-14} aryl group, a divalent 5-14 membered heteroaryl group, and a covalent bond, wherein each of the divalent C_{6-14} aryl group and the divalent 5-14 membered heteroaryl group is optionally substituted with 1-4 R^{4} groups;
- R^{1} and R^{2} are independently selected from H, a C_{1-6} alkyl group, a C_{6-14} aryl group, a 5-14 membered heteroaryl group, a --C_{6-14} alkyl-C_{6-14} aryl group, and a --C_{6-14} alkyl-C_{6-14} haloalkyl group;
- R^{3} is selected from H, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{2-6} alkynyl group, a C_{2-6} alkynyl group, a
C_{6-14} aryl group, a 5-14 membered heteroaryl group, a \text{C}_{1-6} \text{alkyl-C}_{6-14} \text{aryl group, and a } \text{C}_{1-6} \text{alkyl-5-14 membered heteroaryl group.}

R^4 and R^5, at each occurrence, are independently selected from H, a halogen, a \text{C}_{1-6} \text{alkyl group, a } \text{C}_{6-14} \text{haloalkyl group, a } \text{C}_{1-6} \text{aryl group, a } \text{C}_{6-14} \text{aryl group, a 5-14 membered heteroaryl group, a } \text{C}_{1-6} \text{alkyl-5-14 membered heteroaryl group, and } \text{SiX}_3 \text{ groups, wherein } X \text{ is selected from Cl, OCH}_3, \text{OCH}_2 \text{CH}_3, \text{N(CH}_3)_2, \text{N(CH}_2 \text{CH}_3)_2, \text{OC(0)CH}_3, \text{and OC(0)CH}_2 \text{CH}_3.}

In some embodiments, Z can be a divalent linker that can be symmetrical or asymmetrical. In certain embodiments, Q, at each occurrence, can be independently selected from \text{O}, a \text{C}_{1-6} \text{alkyl group (e.g., (CH}_2)_t \text{), a divalent } \text{C}_{1-6} \text{alkyl group (e.g., (CF}_2)_t \text{), and a covalent bond; and W can be selected from } \text{O} \text{ and } \text{CF}_2 \text{, a methyl group, and an ethyl group. For example, the thermally curable crosslinkers can be bis-functionalized with SiXs groups, wherein X is selected from Cl, OCH}_3, \text{OCH}_2 \text{CH}_3, \text{N(CH}_3)_2, \text{N(CH}_2 \text{CH}_3)_2, \text{OC(0)CH}_3, \text{and OC(0)CH}_2 \text{CH}_3.}

It should be understood that the linker Z, as defined above, can exclude certain combinations of Q-W-Q. For example, it should be understood that Z cannot be \text{O} or a divalent C_{1-20} alkyl group, or a covalent bond.

In some embodiments, Z can include one or more \text{Q-Si(X)_y(O)}_z \text{ groups to provide additional groups for crosslinking. For example, Z can be Q-W-Q, wherein Q, at each occurrence, can be independently a divalent C_{1-10} alkyl group or a divalent C_{1-14} haloalkyl group, and W can be selected from \text{O} \text{ and } \text{CF}_2 \text{, a divalent phenyl group, wherein the divalent C}_{1-10} \text{alkyl group, the divalent C}_{1-14} \text{haloalkyl group, and the divalent phenyl group can be substituted with 1-4 -Q-Si(X)_y(O)}_z \text{ groups (thereby creating a higher order valency group, e.g., a trivalent or tetravalent phenyl group), R^4 and R^5 can be independently H, F, or } \text{Q-Si(X)_y(O)}_z \text{, and Q, X, Y, m, p, q, and t are as defined herein. A non-limiting example of these embodiments is a crosslinker having the formula:}

\text{As aforementioned, the precursor composition can include a polymeric crosslinker, i.e., a polymer having one or more crosslinking pendant groups. For example, the pendant group can include a thermally curable crosslinking moiety having the formula:}

\text{wherein Q, X, Y, and m are as defined herein. In certain embodiments, the thermally curable polymeric crosslinker can have the formula:}

\text{wherein R^6, at each occurrence, is independently H, a halogen, or a } \text{C}_{1-6} \text{alkyl group; R^7 is selected from H, OH, a halogen, C(0)O—R^7, a } \text{C}_{1-6} \text{alkyl group, a } \text{C}_{6-14} \text{haloalkyl group, a } \text{C}_{6-14} \text{aryloxy group, a } \text{C}_{6-14} \text{alkyl-C}_{6-14} \text{aryl group, a } \text{C}_{6-14} \text{alkyl-5-14 membered heteroaryl group, a } \text{C}_{6-14} \text{alkyl-5-14 membered heteroaryl group, and a } \text{C}_{6-14} \text{alkyl-5-14 membered heteroaryl group, wherein each of the } \text{C}_{6-14} \text{aryloxy groups, the } \text{5-14 membered heteroaryl groups, and the } \text{5-14 membered cyclo-heteroaryl groups is optionally substituted with 1-5 substituents independently selected from a halogen, an } \text{oxo group, OH, CN, NO}_2, \text{C(0)O—C}_{1-6} \text{alkyl, a } \text{C}_{1-6} \text{alkyl group, a } \text{C}_{1-6} \text{alkoxy group, and a } \text{C}_{1-6} \text{haloalkyl group; R^8 is selected from } \text{O—}, \text{—C(0)O—}, \text{a divalent } \text{C}_{1-6} \text{alkyl group, and a divalent phenyl group; x and y are independently a real number, wherein } x+y<1, \text{or } x+y=1; \text{and Q, X, Y, and m are as defined herein. In some embodiments of the polymeric crosslinker having the formula described above, R^4, at each occurrence, can be H.}
or a methyl group; \( R^7 \) can be selected from H, OH, a methyl group, C(O)O—C_{1-6} alkyl, and a phenyl group optionally substituted with OH or —O—C_{1-6} alkyl; \( R^8 \) can be selected from —O—, —C(O)O—, a divalent C_{1-6} alkyl group, and a divalent phenyl group; and \( Q \) can be selected from —L—, —O—L—, and a covalent bond, wherein \( L \) is as defined herein. A non-limiting example of such a thermally curable polymeric crosslinker is

\[
\text{(AcO)}_{2}\text{Si}
\]

wherein Ac is an acetyl group (i.e., CH\(_3\)C(O)—), and \( x \) and \( y \) are as defined herein.

Without wishing to be bound to any particular theory, the crosslinking chemistry involving these photochemically curable crosslinkers can consist of a 2+2 photo-stimulated cycloaddition that provides stable cyclobutane moieties. The crosslinking chemistry can also involve free radical additions.

The polymeric component of the precursor compositions described above can include various electrically non-conducting polymers, including those that have been used as dielectric materials. Examples include, but are not limited to, polyalkylenes, substituted polyalkylenes, siloxane polymers, and copolymers of polyalkylenes, substituted polyalkylenes, and/or siloxane polymers.

More specifically, polyalkylenes and substituted polyalkylenes can include, but are not limited to, polyethylenes (PE), polypropylenes (PP), polyvinylalcohols (PVA), polystyrenes (PS), ring-functionalized derivatives of polystyrenes (e.g., polyvinylphenols (PVP)), and polymeric esters (e.g., polymethyl methacrylates (PMMA)).

Siloxane polymers can have a repeating unit of the formula:

\[
\text{R}_9/\text{O}/\text{Si}/y
\]

wherein \( R^9 \), at each occurrence, is independently selected from H, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{6-14} aryl group, a 5-14 membered heteroaryl group, wherein each of the C_{1-6} alkyl group, the C_{6-14} aryl group, the 5-14 membered heteroaryl group can be optionally substituted with 1-5 substituents independently selected from a halogen, CN, OH, and a C_{1-6} haloalkyl group. For example, the siloxane polymer can have the formula:

\[
\text{CH}_3/\text{O}/\text{Si}/y
\]

wherein \( x \) and \( y \) are as defined herein.

The precursor compositions described above can include a metal oxide component. The metal oxide component typically has a high dielectric constant (\( k \)). Therefore, the incorporation of such a metal oxide component into a precursor composition can help increase the dielectric constant of the resulting dielectric material. The metal oxide component can be in particulate form and can be blended, mixed and/or otherwise incorporated in the composition. The metal oxide component can include a metal component selected from a Group I metal, a Group II metal, a Group III metal, a Group IV metal, a transition metal, and combinations thereof.

To provide desirable processing advantages, the various crosslinkers and polymers described above typically are somewhat soluble, and preferably highly soluble, in various solvents (e.g., various anhydrous solvents). The crosslinker component and the polymeric component can be dissolved in the same solvent or in different solvents before combining with each other to provide the precursor compositions of the
The present teachings. As used herein, a compound can be considered soluble in a solvent when at least 1 mg of the compound is soluble in 1 mL of the solvent. Examples of common solvents include petroleum ethers; acetone; aromatic hydrocarbons such as benzene, toluene, xylene, and mesitylene; ketones such as acetone, cyclopentanone (CP), methyl ethyl ketone, and 2-butanone; ethers such as tetrahydrofuran (THF), dioxane, bis(2-methoxyethyl)ether (diglyme), diethyl ether, di-isopropyl ether, and t-butyl methyl ether; alcohols such as methanol, ethanol, butanol, and isopropyl alcohol; aliphatic hydrocarbons such as hexanes; acetates such as methyl acetate, ethyl acetate (EtOAc), methyle formate, ethyl formate, isopropyl acetate; and halogenated aliphatic and aromatic hydrocarbons such as dichloromethane, chloroform, ethylene chloride, chlorobenzene, dichlorobenzene, and trichlorobenzene.

The precursor compositions are adapted to form dielectric materials that can exhibit a wide range of desirable properties and characteristics. For example, the dielectric materials prepared from the precursor compositions described above can be very thin and pinhole-free, can have a high breakdown voltage and good long-term stability, can exhibit high capacitance and low current leakage, can show good adhesion to various substrates, and can be patterned using conventional techniques without delamination. The present dielectric materials can also demonstrate other advantageous characteristics such as, but not limited to, solution-processability, fabricability at low temperatures and/or atmospheric pressures, and compatibility with a diverse range of materials used in fabricating various electronic devices (e.g., thin film transistors, field-effect devices, organic light emitting diodes (OLEDs), organic photovoltaics, photodetectors, capacitors, and sensors.

To prepare a dielectric material in the form of a film using the precursor compositions of the present teachings, various film deposition techniques can be used. These techniques include casting (e.g., drop-casting), dip coating, blade coating, spraying, printing, and spin-coating. Spin-coating involves applying an excess amount of a precursor composition (e.g., a solution of a polymeric component and a crosslinker component) onto a substrate, then rotating the substrate at high speed to spread the fluid by centrifugal force. The thickness and the surface morphology of the resulting dielectric film prepared by this technique is dependent on the spin-coating rate, the concentration of the solution, as well as the solvent used. Printing can be performed, for example, with a rotogravure printing press, a flexo printing press, or an inkjet printer. The thickness of the dielectric film in these cases will similarly be dependent on the concentration of the solution, the choice of solvent, and the number of printing repetitions. Many of the printed electronics technology has focused on inkjet printing, primarily because this technique allows greater control over feature position and multilayer registration. Inkjet printing is a noncontact process, which offers the benefits of not requiring a preformed master (compared to contact printing techniques), as well as digital control of ink ejection, thereby providing drop-on-demand printing. However, contact printing techniques have the key advantage of being well-suited for very fast roll-to-roll processing. Exemplary contact printing techniques include screen-printing, gravure, offset, and microcontact printing.

The thickness of the dielectric materials of the present teachings can be controlled, and can be made as thin as 10 nm to several microns as established by profilometry and/or atomic force microscopy (AFM). For example, dielectric films prepared according to the present teachings can have a thickness range from about 10 nm to about 20 nm and up to 10 µm or more. Films of greater thicknesses, if desired or required, can be obtained by 1) multiple spin-on depositions/printing repetitions before curing, as the dielectric materials of the present teachings can be stable to and not adversely affected by precursor or processing solutions; or 2) adjusting and/or increasing the polymer precursor concentration(s).

Generally, dielectric films of the present teachings are relatively thin (e.g., less than about 300 nm), and in some embodiments, ultra-thin (e.g., less than about 50 nm or less than about 30 nm).

Various curing or crosslinking strategies can be employed to form a crosslinked polymeric material from the precursor compositions described above. The crosslinked polymeric material can be a thermally cured product and/or a photochemically cured product of the precursor composition. For example, four different crosslinking strategies can be employed depending on the type and the order of the crosslinking chemistry. Referring to FIG. 1, these processes include: i) thermal/high-humidity curing; ii) photocuring; iii) thermal/high-humidity curing followed by photochemical curing; and iv) photocuring followed by thermal/high-humidity curing. The thermal curing step can include annealing at an elevated temperature range in a high-humidity environment (~70%-90% humidity) for a short period of time (e.g., 5-10 minutes), followed by dry curing (e.g., in a vacuum oven) at a similar temperature range for a longer period of time (e.g., 1-3 hours). The elevated temperature range can be from about 70° C. to about 150° C., from about 90° C. to about 140° C., and from about 100° C. to about 130° C. The photocuring step can include exposure to ultraviolet light (e.g., irradiation with a wavelength of about 245 nm) for about 5-15 minutes depending on the thickness of the film. In some embodiments, crosslinking also can be achieved by electron beam irradiation alone or in conjunction with one or both of the techniques discussed above. Crosslinked polymeric dielectric materials with different and/or complementary properties can be obtained using one or more of these processes. The use of photochemically curable crosslinkers can facilitate patterning, for example, as illustrated in the process in FIG. 2.

Accordingly, fabrication of a dielectric material can be performed in air (e.g., in a simple fume hood) in a controllable manner. Silane hydrolysis, condensation, and/or crosslinking typically occurs within seconds after deposition under ambient conditions. The process can be optimized by using controlled-atmosphere conditions during film deposition and annealing.

The structural integrity of the resulting dielectric material can be evident by its insolubility in the mother solution. The curing temperatures, typically lower than 130° C., are compatible with common plastic substrates employed in organic electronics such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). In addition, the crosslinking chemistry according to the present teachings can ensure strong adhesion to a substrate, for example, a bottom gate electrode, thus preventing delamination upon successive deposition and/or patterning of subsequent device layers, as well as during device operation.

The present teachings further provide an article of manufacture, for example, a composite, that comprises a dielectric material of the present teachings and a substrate component and/or a semiconductor component. The substrate component can be selected from, but is not limited to, a doped silicon, an indium tin oxide (ITO), ITO-coated glass, ITO-coated mylar, aluminum, a doped polythiophene, and the like. The composite can include a semiconductor component. The semiconductor component can be selected from, but is not
limited to, various fused heterocycles, polythiophenes, fused aromatics, and other such semiconductor compounds or materials, whether p-type or n-type, otherwise known or found useful in the art. The semiconductor component also can include inorganic semiconductor materials such as silicon, germanium, gallium arsenide, and the like. One or more of the composites described above can be embodied within an organic electronic device such as an OTFT, specifically, an OFET. Such an OFET can operate at low biases due to the high capacitance of the dielectric materials of the present teachings.

In the following examples, dielectric materials according to the present teachings were prepared and characterized by AFM, metal-insulator-metal (MIM) device and metal-insulator-semiconductor (MIS) device leakage and impedance spectroscopy measurements, to demonstrate, among other things, their compatibility with various p-type and n-type organic semiconductors. Organic electronic devices, e.g., organic thin film transistors (OTFTs), specifically, organic field effect transistors (OFETs), based on these dielectric films also have been fabricated and characterized, data of which are provided below.

The following examples are provided to illustrate further and to facilitate the understanding of the present teachings and are not in any way intended to limit the invention.

**EXAMPLE 1**

**Preparation of 1-trichlorosilyl-3-[2-(3-trichlorosilyl-propoxy)-ethoxy]-propane (EGCl) and 1-triacetoxysilyl-3-[2-(3-triacetoxysilyl-propoxy)-ethoxy]-propane (EGOAc)**

Scheme 1 below depicts an exemplary synthetic route for the preparation of 1-trichlorosilyl-3-[2-(3-trichlorosilyl-propoxy)-ethoxy]-propane (EGCl) and 1-triacetoxysilyl-3-[2-(3-triacetoxysilyl-propoxy)-ethoxy]-propane (EGOAc).

**Step 1: Preparation of 3-(2-Allyloxy-ethoxy)-propene**

Sodium hydride (NaH, 5.0 g, 0.208 mol) was slowly added to a solution of 2-allyloxy-ethanol (20 mL, 0.187 mol) while stirring. Allyl bromide (32 mL, 0.370 mol) was added and the mixture was stirred at 60° C. for 10 hours. After cooling, the reaction mixture was filtered and a dark oil was obtained after solvent evaporation. The oil was fractionally distilled to give 22 grams of 3-(2-Allyloxy-ethoxy)-propene (0.155 mol, yield 85%) as a colorless oil. 1H NMR (400 Mz, CDCl 3 ): δ 3.6 (t, 2H), 4.0 (d, 2H), 5.1 (d 1H), 5.3 (d 1H), 5.9 (q, 1H).

**Step 2: Preparation of 1-trichlorosilyl-3-[2-(3-trichlorosilyl-propoxy)-ethoxy]-propane (EGCl)**

3-(2-Allyloxy-ethoxy)-propene (20 g, 0.141 mol) and 40 mg of hydrogen hexachloroplatinate (IV) hydrate were added to a 250 mL air-free flask with a condenser. Trichlorosilane (40 mL, 0.396 mol) was added dropwise to the stirred solution which was subsequently heated in an oil bath of 80° C. The reaction mixture was heated at reflux for 4 hours and then distilled in vacuum. The fraction containing (3-trichlorosilyl)propyl ethylene ether (39 g, 0.0944 mol) at 90° C. and 20 mtorr was collected with a yield of 70% based on 3-(2-allyloxy-ethoxy)-propene. 1H NMR (400 Mz, CDCl 3 ): δ 1.5 (t, 2H), 1.8 (m, 2H), 3.4 (t, 2H), 3.6 (t, 2H). 29Si NMR (79.6 Mz, CDCl 3 ): 13.4 (s).

**Step 3: Preparation of 1-triacetoxysilyl-3-[2-(3-triacetoxysilyl-propoxy)-ethoxy]-propane (EGOAc)**

Di(3-trichlorosilyl)propyl ethylene ether (10 g, 0.0242 mol) and acetic anhydride (27 mL, 0.048 mol) were slowly added to a 100 mL air-free flask. The reaction solution was stirred at 80° C. for 5 hours. Acetyl chloride was removed by distillation occasionally during the reaction. After all the volatiles were removed (120° C. at 5 mtorr), 13.4 g (0.0241 mol) of di(3-triacetoxysilyl)propyl ethylene ether (EGOAc) were obtained with a yield of 99.6%. 1H NMR (400 Mz, CDCl 3 ): δ 1.1 (t, 2H), 1.7 (m, 2H), 2.0 (s, 9H), 3.3 (t, 2H), 3.5 (t, 2H). 29Si NMR (79.6 Mz, CDCl 3 ): —44.9 (s). Anal. Caled for C 20 H 34 O 4 Si 2 : C, 53.41; H, 11.95; N, 20.76. Found: C, 51.07; H, 11.39; N, 18.11.
Step 1: Preparation of 1,6-bis(trichlorosilyl)-3,3,4,4-tetrafluorohexane (F₄C₆Cl)

1,2-Diethenyltetrafluoroethane (1 g, 6.5 mmol) and 4 mg of hydrogen hexachloroplatinate (IV) hydrate were dissolved in dried CH₂Cl₂ (15 mL). Trichlorosilane (10 mL, 9.9 mmol) was added dropwise to the stirred solution. The reaction mixture was heated at 40° C. overnight, followed by removal of excess HSiCl₃ and solvent by vacuum evaporation. The crude product was recovered in a yield of greater than about 96% (2.6 g). ¹H NMR (400 MHz, CDCl₃): δ 2.4 (m, 4H), 1.4 (m, 4H). ₂⁹Si NMR (CDCl₃): 14.1 (s). ¹⁹F NMR (CDCl₃): -115.1 (t, J=12 Hz, 4F).

Step 2: Preparation of 1,6-bis(triacetoxysilyl)-3,3,4,4-tetrafluorohexane (F₄C₆OAc)

1,6-Bis(trichlorosilyl)-3,3,4,4-tetrafluorohexane (1 g, 2.35 mmol) and acetic anhydride (4 mL) were added to a 10 mL air-free flask. The reaction solution was stirred at 80° C. for 5 hours. After all the volatiles were removed (120° C. at 5 mtorr), 1.24 g (2.20 mol) of the product were obtained with a yield of 99.6%. ¹H NMR (400 MHz, CDCl₃): δ 2.4 (m, 4H), 1.3 (m, 4H). ₂⁹Si NMR (79.6 MHz, CDCl₃): -45.3 (s). ¹⁹F NMR (CDCl₃): -114.6 (t, J=13 Hz, 4F).

EXAMPLE 4

Preparation of poly[4-methoxystyrene-co-4-(3-triacetoxysilyl propoxystyrene)]

Scheme 3 below depicts an exemplary synthetic route for the preparation of poly[4-methoxystyrene-co-4-(3-triacetoxysilylpropoxystyrene)].
EXAMPLE 5

Preparation of poly(vinylphenol-co-4-cinnamoylstyrene)

Scheme 4 below depicts an exemplary synthetic route for the preparation of poly(vinylphenol-co-4-cinnamoylstyrene).

Poly(4-vinylphenol) (1.0 g, Mw=8,000 g/mol or 20,000 g/mol, hydroxyl group: 8.33 mmol) was dissolved in 20 mL of THF. Cinnamoyl chloride (0.70 g, 4.2 mmol) and triethylamine (1.0 mL, 8.33 mmol) were slowly added to the solution which was subsequently heated to 50°C for 4 hours. The reaction mixture was poured into 500 mL of deionized water. The precipitated solid was filtered, washed with 100 mL of methanol three times and dried in vacuum. 1H NMR verified 50% cinnamation of the poly(vinylphenol). 1H NMR (400 MHz, CDCl3): δ 1.1-2.6 (b), 6.4 (d), 6.5-7.6 (b), 7.7 (d).

EXAMPLE 6

Surface Morphology and Dielectric Properties of Spin-Coated Ultrathin Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Crosslinkers

To assess how the surface morphology and various dielectric characteristics of a CPB dielectric film can be affected by the choice of the polymeric component and the crosslinker component of the precursor composition, precursor compositions were prepared from different combinations of various polymers, thermally curable crosslinkers, and solvents. These precursor compositions were subsequently spin-coated onto silicon substrates to provide ultrathin (<50 nm) dielectric films.
Hexachlorodisiloxane (C₆Cl₆) and 1,6-bis(trichlorosilyl)hexane (C₆Cl₁₂) were purchased from Acros Organics (Geel, Belgium) and Gelest, Inc. (Morrisville, Pa.), respectively, and purified by distillation. 1,12-Bis(trichlorosilyl)dodecane (C₁₂Cl₁₂) was synthesized by hydrosilylation of commercially available 1,11-dodecadiene. 1,6-Bis(trimethoxysilyl)hexane (C₆(O)Me) and 1,6-bis(triacetoxysilyl)hexane (C₆(O)Ac) were synthesized from the chloro precursors C₆Cl₁₂. 1,4-Bis(trimethoxysilyl)ethylnbenzene (Ph(O)Me) was synthesized according to procedures described in Kabeta et al., J. Polym. Sci. A. Polym. Chem., 34(14): 2991-2998 (1996). 1,6-Bis[(dimethylamino)silyl]hexane (C₆(NMe₂)₂), 1,6-bis(trichlorosilyl)-3,3,4,4-tetrafluorohexane (F₄C₆Cl), and 1,6-bis(triacetoxysilyl)-3,3,4,4-tetrafluorohexane (F₄C₆OAc) were prepared as described in Examples 2 and 3.

The solvents used were tetrahydrofuran (THF), dioxane, and ethyl acetate (AcOEt).

The silicon substrates were highly n-doped silicon wafers obtained from Montco Silicon Tech, Inc. (Spring City, Pa.) and cleaned according to standard procedures, e.g., sonication in organic solvent, Piranha solution, and oxygen plasma treatment, before use.

To prepare the precursor composition, solutions of the polymer and the crosslinker were prepared with the selected solvent and the solutions combined in a specific volume ratio. The precursor composition was then spin-coated onto freshly oxygen plasma-treated silicon substrates. The thickness of the film samples was partially controlled by adjusting the spin coating rate between about 1500 rpm and about 5000 rpm (acceleration 60). After the spin-coating step, the resulting dielectric films were annealed (thermally cured) in a high humidity atmosphere (70-90%) at about 100° C. to about 130° C. for 5-10 minutes and then for 1-3 hours in a vacuum oven (dry curing) at the same temperature. Film thickness and surface smoothness (represented by root mean square (RMS)) were determined by profilometry and AFM. MIS capacitor structures were fabricated using the resulting dielectric films, and the capacitance of the dielectric films was measured. The results are summarized in Table 1 below.

**TABLE 1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Crosslinker</th>
<th>Solvent</th>
<th>Ratio</th>
<th>Thickness (nm)</th>
<th>RMS (nm)</th>
<th>εᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVP</td>
<td>C₆Cl</td>
<td>THF</td>
<td>4:4</td>
<td>18-40</td>
<td>6-8</td>
<td>150-305</td>
</tr>
<tr>
<td>2</td>
<td>PVP</td>
<td>C₆Cl</td>
<td>THF</td>
<td>4:4</td>
<td>18-40</td>
<td>1-3</td>
<td>150-300</td>
</tr>
<tr>
<td>3</td>
<td>PVP</td>
<td>C₁₂Cl</td>
<td>THF</td>
<td>4:4</td>
<td>20-40</td>
<td>4-6</td>
<td>150-250</td>
</tr>
<tr>
<td>4</td>
<td>PVP</td>
<td>C₆(OMe)</td>
<td>Dioxane</td>
<td>4:8</td>
<td>17-40</td>
<td>0.5-1</td>
<td>160-250</td>
</tr>
<tr>
<td>5</td>
<td>PVP</td>
<td>Ph(O)Me</td>
<td>Dioxane</td>
<td>4:8</td>
<td>18-40</td>
<td>0.5-1</td>
<td>170-320</td>
</tr>
<tr>
<td>6</td>
<td>PVP</td>
<td>C₆(O)Ac</td>
<td>AcOEt</td>
<td>4:8</td>
<td>17-40</td>
<td>0.4-0.5</td>
<td>150-250</td>
</tr>
<tr>
<td>7</td>
<td>PVP</td>
<td>C₆(O)Ac</td>
<td>AcOEt</td>
<td>4:6</td>
<td>13-35</td>
<td>0.2-0.3</td>
<td>160-300</td>
</tr>
<tr>
<td>8</td>
<td>PVP</td>
<td>C₆(O)Ac</td>
<td>AcOEt</td>
<td>4:4</td>
<td>12-25</td>
<td>0.2-0.3</td>
<td>170-325</td>
</tr>
<tr>
<td>9</td>
<td>PVP</td>
<td>C₆(O)Ac</td>
<td>AcOEt</td>
<td>4:2</td>
<td>10-20</td>
<td>0.2-0.3</td>
<td>180-340</td>
</tr>
<tr>
<td>10</td>
<td>PVP</td>
<td>C₆(NMe₂)</td>
<td>AcOEt</td>
<td>4:6</td>
<td>15-25</td>
<td>0.5-0.9</td>
<td>170-320</td>
</tr>
<tr>
<td>11</td>
<td>PVP</td>
<td>F₄C₆Cl</td>
<td>AcOEt</td>
<td>4:4</td>
<td>13-20</td>
<td>0.4-0.5</td>
<td>180-350</td>
</tr>
<tr>
<td>12</td>
<td>PVP</td>
<td>F₄C₆OAc</td>
<td>AcOEt</td>
<td>4:4</td>
<td>12-18</td>
<td>0.2-0.3</td>
<td>200-360</td>
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<tr>
<td>13</td>
<td>PS</td>
<td>C₆Cl</td>
<td>THF</td>
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<td>8-10</td>
<td>120-220</td>
</tr>
<tr>
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<td>PS</td>
<td>C₆Cl</td>
<td>THF</td>
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<td>10-20</td>
<td>1-2</td>
<td>120-220</td>
</tr>
<tr>
<td>15</td>
<td>PS</td>
<td>C₁₂Cl</td>
<td>THF</td>
<td>4:4</td>
<td>13-30</td>
<td>4-5</td>
<td>100-200</td>
</tr>
<tr>
<td>16</td>
<td>cPVP</td>
<td>C₆(O)Ac</td>
<td>Dioxane</td>
<td>4:4</td>
<td>22-45</td>
<td>0.5-1</td>
<td>130-280</td>
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<tr>
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<td>Dioxane</td>
<td>4:4</td>
<td>10-20</td>
<td>0.5-2</td>
<td>400-600</td>
</tr>
<tr>
<td>18</td>
<td>PMMA</td>
<td>C₆(O)Ac</td>
<td>Dioxane</td>
<td>4:4</td>
<td>19-40</td>
<td>1-2</td>
<td>160-320</td>
</tr>
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</table>
Insulating Properties of Spin-Coated Ultrathin Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers

All of the dielectric films prepared in Example 6 exhibit very low leakage currents, ranging between $10^{-6}$ and $10^{-7}$ A/cm² at 2-4 MV/cm. Representative leakage current-voltage plots are shown in FIG. 3.

Comparable leakage current densities were obtained using other gate substrates, specifically, Al-PEN and ITO-glass substrates. Al-PEN substrates were prepared according to literature reports; e.g., by sputtering aluminum (about 20-100 nm in thickness) on an O₂-plasma treated commercially-available PEN substrate. ITO-glass substrates were cleaned with an oxygen plasma before use. Representative leakage current-voltage plots are provided in FIG. 4.

**TABLE 2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Gate</th>
<th>Ratio</th>
<th>Thickness (nm)</th>
<th>Cₑ (μF cm⁻²)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>80:80</td>
<td>325</td>
<td>15.25</td>
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<tr>
<td>2</td>
<td>Si</td>
<td>60:60</td>
<td>220</td>
<td>21.0</td>
</tr>
<tr>
<td>3</td>
<td>Si</td>
<td>40:40</td>
<td>145</td>
<td>29.5</td>
</tr>
<tr>
<td>4</td>
<td>Si</td>
<td>30:30</td>
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<td>52.7</td>
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<tr>
<td>5</td>
<td>Si</td>
<td>20:20</td>
<td>40</td>
<td>85.0</td>
</tr>
<tr>
<td>6</td>
<td>Al</td>
<td>80:80</td>
<td>320-330</td>
<td>16.25</td>
</tr>
<tr>
<td>7</td>
<td>Al</td>
<td>60:60</td>
<td>210-230</td>
<td>22.5</td>
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<tr>
<td>8</td>
<td>Al</td>
<td>40:40</td>
<td>140-150</td>
<td>36.0</td>
</tr>
<tr>
<td>9</td>
<td>Al</td>
<td>30:30</td>
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<td>55.75</td>
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<tr>
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<td>20:20</td>
<td>40</td>
<td>80.75</td>
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<tr>
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<td>ITO</td>
<td>80:80</td>
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<tr>
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<td>ITO</td>
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<td>210-230</td>
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<td>ITO</td>
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</tbody>
</table>

Dielectric films prepared with bifunctionalized-silane ethylene glycol crosslinkers exhibited excellent surface smoothness, with an RMS roughness of about 0.3 nm to about 0.7 nm.

**EXAMPLE 8**

Surface Morphology and Dielectric Characteristics of Spin-Coated Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers

Spin-coated dielectric films were prepared using thermally curable precursor compositions containing bifunctionalized triacetoxyalkyl-silane ethylene glycol crosslinkers (EGOAc) following procedures described in Examples 1 and 6. The compositions of the precursor compositions were summarized in Table 2, along with the thickness and the capacitance values of the resulting dielectric films and the substrate used. Both ultrathin (<50 nm) and thin dielectric films (about 50-400 nm) were prepared.

**EXAMPLE 9**

Insulating Properties of Spin-Coated Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers

The dielectric films from Example 8 were used to fabricate capacitor structures and were found to exhibit very large dielectric strength as demonstrated by the current-voltage plots shown in FIG. 5.

**EXAMPLE 10**

Device Performance of OFETs Fabricated with Spin-Coated Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers

Pentacene OFETs were fabricated with dielectric films of Example 8 on both silicon and aluminum gate materials. Specifically, the silicon substrates were highly n-doped silicon wafers obtained from Montco Silicon Tech, Inc. (Spring City, Pa.) and cleaned according to standard procedures, e.g., sonication in organic solvent, Piranha solution, and oxygen plasma treatment, before use. The aluminum substrates were cut from commercially available aluminum foil (Reynolds Wrap®). Pentacene was purchased from Sigma-Aldrich (St. Louis, Mo.) and vacuum-deposited at about 2x10⁻⁶ Torr (500 Å, 0.2 A/s) while maintaining the substrate temperature at about 50°C to about 70°C. Gold electrodes were vacuum-deposited through shadow masks at 3-4x10⁻⁶ Torr (1000 Å, 0.5 A/s). The channel length is 100 µm, and the channel width is 2000 µm.

These OFETs were found to perform very well at variable operating voltages, indicating a high capacitance of the dielectric materials. Representative OFET transfer plots are shown in FIG. 6. The use of thinner dielectric films (20:20) compared to thicker ones (e.g., 60:60) were shown to achieve similar output current. However, the thinner films allowed much lower operating voltages due to their higher capacitance (see Eq. 2). The carrier mobilities of these devices are about 0.5 cm²/Vs to about 3 cm²/Vs, which are typical for pentacene films grown at 50°C. Current modulations ($I_{on}/I_{off}$ ratios) were measured to be >10⁶.

A comparative pentacene OFET device was fabricated using silicon oxide (SiO₂) as the dielectric material. The silicon oxide film has a thickness of 300 nm. The carrier mobilities of this comparative device was found to be about 0.1 cm²/Vs to about 0.3 cm²/Vs at larger operating voltages.

**EXAMPLE 11**

Surface Morphology and Dielectric Properties of Spin-Coated Thin Dielectric Films Prepared from Precursor Compositions Containing Bifunctionalized-Silane Crosslinkers

Thin dielectric films (about 50-300 nm) were prepared using precursor compositions employing PVP as the polymer and $C₆Cl$, $C₆OAc$, $C₆NMe₂$, and $F₆C₆Cl$, respectively as the crosslinker component. The precursor compositions were spin-coated on Si and flexible Al/PEN substrates following procedures described in Example 6. Table 3 summarizes the compositions of the precursor compositions, as well as the electrical and physical properties of the resulting dielectric films on Si substrates.
Thin dielectric films fabricated with crosslinkers C₆Cl and C₆NMe₂ afford ~10 times higher leakage current densities (~1x10⁻⁵ A/cm²) compared to those fabricated with EGOAc and F₄C₆C₁ (-1x10⁻⁶ A/cm²) at an electric field of 2 MV/cm. EGOAc-based dielectric films also afford smoother film morphology (RMS-0.2-0.3 nm) than C₆Cl-based (~0.3-0.4 nm) or C₆NMe₂-based (~2-3 nm) films. While dielectric films fabricated with C₆Cl show relatively smooth film morphology at a small area, the overall film morphology is not as smooth as EGOAc-based films. Compared to films fabricated on Si substrates, dielectric films fabricated on Al/PEN substrates afford relatively rough surface morphologies (RMS-0.5-0.6 nm) and higher leakage current densities (~1x10⁻⁶ A/cm²) at an electric field of 2 MV/cm. Representative leakage current-voltage plots are shown in FIG. 7.

**EXAMPLE 12**

**Fabrication and Performance of Thin Film Transistors Using Ultra-Thin And Thin Spin-Coated Dielectric Films**

Top-contact OFETs were fabricated with ultra-thin (<50 nm) and thin (about 50-300 nm) spin-coated dielectric films prepared with PVP and a crosslinker selected from C₆Cl, C₆OAc, EGOAc, C₆NMe₂ and F₄C₆C₁. Si and Al/PEN substrates were used, along with pentacene (P5) and 5,5''-diphenyl-1,4-phenylene-carbonyl-2,5:2',5'-terthiophene (DFHCO-4T) as the p-type and n-type semiconductor, respectively. P5 was purchased from Sigma-Aldrich (St. Louis, Mo.) and vacuum-deposited at about 2x10⁻⁶ Torr (500 A, 0.5 A/s) while maintaining the substrate temperature at about 50° C. to about 70° C. DFHCO-4T were prepared and deposited as described in U.S. Patent Application Publication No. 2006/0186401, the disclosure of which is incorporated by reference in its entirety. Gold electrodes were vacuum-deposited through shadow masks at 3-4x10⁻⁶ Torr (1000 Å, 0.5 Å/s). The channel length is 100 µm, and the channel width is 2000 µm.

Transfer characteristics of the devices were measured in the saturation regime and transfer plots for 50-nm thick film FETs are shown in FIG. 8. Table 4 summarizes the OFET performance parameters, carrier mobility (µₛst) and current on/off ratio (Iₛst/I₉ff). The charge carrier mobility shows strong correlation with the thickness of the dielectric films. Thin (<50 nm) dielectric films show relatively low mobility of 0.02-0.16 cm²/Vs for both P5 and DFHCO-4T devices, compared to thicker films (~50-300 nm) fabricated with EGOAc (~0.30-0.50 cm²/Vs). For all dielectric films, Iₛst/I₉ff shows comparable values between ~10⁵-10⁶.

**Table 3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Crosslinker</th>
<th>Solvent</th>
<th>Polymer:Crosslinker</th>
<th>Thickness (nm)</th>
<th>RMS (nm)</th>
<th>Cₛst (nF cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVP</td>
<td>C₆Cl</td>
<td>THF</td>
<td>40:40</td>
<td>155</td>
<td>0.3-0.4</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>PVP</td>
<td>C₆OAc</td>
<td>Dioxane</td>
<td>40:20</td>
<td>50</td>
<td>0.2-0.3</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>PVP</td>
<td>EGOAc</td>
<td>Dioxane</td>
<td>60:40</td>
<td>130</td>
<td>0.2-0.3</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>PVP</td>
<td>C₆OAc</td>
<td>Dioxane</td>
<td>60:60</td>
<td>208</td>
<td>0.2-0.3</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>PVP</td>
<td>C₆OAc</td>
<td>Dioxane</td>
<td>80:80</td>
<td>305</td>
<td>0.2-0.3</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>PVP</td>
<td>C₆NMe₂</td>
<td>AcOEt</td>
<td>40:40</td>
<td>90</td>
<td>0.2-0.3</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>PVP</td>
<td>F₄C₆C₁</td>
<td>AcOEt</td>
<td>40:40</td>
<td>115</td>
<td>0.6-0.9</td>
<td>47</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Ratio</th>
<th>µₛst</th>
<th>Iₛst/I₉ff</th>
<th>µₛst</th>
<th>Iₛst/I₉ff</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆Cl</td>
<td>6:6</td>
<td>0.07</td>
<td>10⁶</td>
<td>0.12</td>
<td>10⁴</td>
</tr>
<tr>
<td>C₆OAc</td>
<td>4:6</td>
<td>0.12</td>
<td>10⁵</td>
<td>0.12</td>
<td>10³</td>
</tr>
<tr>
<td>C₆NMe₂</td>
<td>4:6</td>
<td>0.15</td>
<td>10⁴</td>
<td>0.16</td>
<td>10³</td>
</tr>
<tr>
<td>EGOAc</td>
<td>40:40</td>
<td>0.31</td>
<td>10⁶</td>
<td>0.43</td>
<td>10⁶</td>
</tr>
<tr>
<td>F₄C₆C₁</td>
<td>80:80</td>
<td>0.47</td>
<td>10⁴</td>
<td>0.52</td>
<td>10³</td>
</tr>
<tr>
<td>C₆NMe₂</td>
<td>4:6</td>
<td>0.03</td>
<td>10⁵</td>
<td>0.02</td>
<td>10⁵</td>
</tr>
<tr>
<td>DFHCO-4T</td>
<td>4:4</td>
<td>0.04</td>
<td>10⁴</td>
<td>0.09</td>
<td>10³</td>
</tr>
</tbody>
</table>

The trend in mobility values is consistent with the aforementioned dielectric film morphologies. For thin dielectric films, the P5 FET device fabricated with EGOAc, with the smoothest film morphology, afford the highest carrier mobility of 0.15 cm²/Vs among all crosslinkers, followed by C₆OAc (0.12 cm²/Vs), C₆Cl (0.07 cm²/Vs), F₄C₆C₁ (0.04 cm²/Vs), and C₆NMe₂ (0.03 cm²/Vs). Similar trends in charge carrier mobility for n-type semiconductor DFHCO-4T was observed. Because charge transport in OTFT is conrolled by the small region at the semiconductor/dielectric interface, the smoothness of the dielectric film is a prerequisite for improved OTFT performance. It has been reported with pentacene film FETs that rough gate dielectric surfaces afford smaller pentacene grains compared to very smooth substrates, leading to poorer FET performance. Grain boundaries between semiconductor crystallites are considered to be one type of interfacial charge trapping sites, which disrupt charge transport. Pentacene films grown on relatively smooth dielectric films fabricated with C₆OAc and EGOAc afford large, dendritic grains (>3 µm), while very small (<0.3 µm) pentacene grains are grown on C₆Cl-based and C₆NMe₂-based dielectric films.

**EXAMPLE 13**

**Printability of Dielectric Precursor Compositions Containing Thermally Curable Bifunctionalized-Silane Ethylene Glycol Crosslinkers**

Using acetoxy-bisfunctionalized crosslinkers such as C₆OAc from Example 6 and EGOAc from Example 8, printable dielectric materials were fabricated. Experiments were performed to identify the best printing solvent for a certain polymer-crosslinker precursor composition. For instance, in the case of PVP and C₆OAc or EGOAc, the solvents tested are shown in Table 5 below. The experiments were performed using an IGT Reprotest F1 printing press (IGT, Amsterdam, Netherlands) in gravure mode with the following parameters: Anilox force 100 N, printing speed 0.4 m/s, anilox cylinder...
402.206 (copper engraved-chromium plated, stylus 120°, screen angle 45°, volume 7.5 mL/m²). Similar to the procedures described in Example 6, the polymer and the crosslinker were individually dissolved in solvent and combined at a specific volume ratio. The resulting formulation was gravure-printed (also can be flexo printed) onto freshly oxygen plasma-treated ITO-mylar or Al—PEN substrates.

**TABLE 5**

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP (mg)</th>
<th>Crosslinker (mg)</th>
<th>Solvent (0.4 mL)</th>
<th>Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>50</td>
<td>TIF</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>50</td>
<td>Dioxane</td>
<td>Poor</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>50</td>
<td>AcOEt</td>
<td>Excellent</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>50</td>
<td>CP</td>
<td>Poor</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>50</td>
<td>EtOH</td>
<td>Good</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>50</td>
<td>MeOH</td>
<td>Poor</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>40</td>
<td>AcOEt</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

Silane ethylene glycol crosslinkers were obtained (see Tables 5 and 6). These micrographs show that the optimized printed dielectric films exhibit a very smooth surface which is a prerequisite for good OFET charge transport.

**EXAMPLE 15**

**Dielectric Data of Dielectric Films Printed from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers**

In Tables 5 and 6, the dielectric quality was rated from excellent to poor based on the dielectric performance (leakage current, breakdown characteristics) as well as film morphological (roughness) and mechanical (robustness/solubility) characteristics.

In Tables 5 and 6, the dielectric quality was rated from excellent to poor based on the dielectric performance (leakage current, breakdown characteristics) as well as film morphological (roughness) and mechanical (robustness/solubility) characteristics.

**EXAMPLE 14**

**Surface Morphology of Dielectric Films Printed from Precursor Compositions Containing Bifunctionalized-Silane Ethylene Glycol Crosslinkers**

AFM micrographs of dielectric films printed from optimized precursor compositions containing bifunctionalized-

**EXAMPLE 16**

Insulating properties of dielectric films printed from precursor compositions containing thermally curable bifunctionalized-silane ethylene glycol crosslinkers

The leakage current at various operating voltages was measured for the dielectric films of Example 16. FIG. 9 is a representative plot, using dielectric films of Entries 7 and 10 from Example 16. These films were shown to have good insulating properties.
EXAMPLE 17

Device Performance of OFET Fabricated with Dielectric Films Printed From Precursor Compositions Containing Thermally Curable Bifunctionalized-Silane Ethylene Glycol Crosslinkers

Pentacene transistors fabricated on the printed dielectric films from Example 15 were found to exhibit excellent device performance. FIGS. 10A and 10B are representative transfer and output plots for one of the printed PVP-EGOAc formulations (Entry 7, Table 7). All OTFT measurements described herein were carried out in air using a Keithly 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a local Labview program and GPIB communication. Triaxial and/or coaxial shielding was incorporated into Signatone probe stations to minimize the noise level. A digital capacitance meter (Model 3000, GLK Instruments) and an HP4192A Impedance Analyzer were used for capacitance measurements.

Compatibility with various p-type and n-type semiconductors was also demonstrated. FIGS. 11A and 11B provide output plots for OFETs fabricated with the printed PVP-EGOAc formulation of Entry 7 in Table 5 as the dielectric component and, as the semiconductor component N,N'-bis (n-octyl)-(1,7 and 1,6)-dicyanoperylene-3, 4:9,10-bis(dicarboximide) (PDI-8CN₂) and 5,5'-di-(p-hexylphenyl)-2,2'-bithiophene (DH-PTTP), respectively. PDI-8CN₂ was prepared according to the procedures described in U.S. Patent Application Publication No. US 2005/0176970, the disclosure of which is incorporated by reference herein.

It was also found that very high carrier mobilities (\(\mu\)) and current on-off ratios (\(I_{on}:I_{off}\)) could be achieved by OFETs fabricated with the dielectric films of the present teachings, implying very low charge trapping states and good semiconductor film crystallinity. Table 8 summarizes data (carrier mobilities, current on-off ratios) related to OFET performance for different semiconductors (pentacene, PDI-8CN₂, DFHC04T, and dihexylsexithiophene (DH-6T)) on a variety of dielectric films of the present teachings. DH-6T was prepared according to the procedures described in U.S. Pat. No. 6,585,914, the disclosure of which is incorporated by reference herein. In all cases, the transistors were active and the reported carrier mobilities were among the highest obtained for these semiconductor materials.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP(mg):</th>
<th>C60Ac(mg)</th>
<th>Semiconductor</th>
<th>(\mu) (cm²/Vs)</th>
<th>(I_{on}:I_{off})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100:50 (ITO)</td>
<td>Pentacene</td>
<td>10-90</td>
<td>4-6 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>100:40 (ITO)</td>
<td>Pentacene</td>
<td>5-20</td>
<td>2-3 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100:30 (ITO)</td>
<td>Pentacene</td>
<td>4-15</td>
<td>1-2 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>100:30 (Al)</td>
<td>Pentacene</td>
<td>4-30</td>
<td>1-2 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50:25 (Al)</td>
<td>Pentacene</td>
<td>10-20</td>
<td>4-6 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>100:50 (ITO)</td>
<td>DH-6T</td>
<td>0.006-0.008</td>
<td>1-5 x 10²</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>100:50 (ITO)</td>
<td>PDI-8CN₂</td>
<td>0.08</td>
<td>1-5 x 10²</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>100:40 (ITO)</td>
<td>PDI-8CN₂</td>
<td>0.06</td>
<td>1-5 x 10²</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>100:30 (ITO)</td>
<td>PDI-8CN₂</td>
<td>0.05</td>
<td>1-5 x 10²</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>100:30 (ITO)</td>
<td>DHFC04T</td>
<td>0.05</td>
<td>1-5 x 10³</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 8-continued

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP(mg):</th>
<th>EGOAc(mg)</th>
<th>Semiconductor</th>
<th>(\mu) (cm²/Vs)</th>
<th>(I_{on}:I_{off})</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>100:50 (Al)</td>
<td></td>
<td>Pentacene</td>
<td>5-10</td>
<td>1-2 x 10⁶</td>
</tr>
<tr>
<td>14</td>
<td>100:40 (Al)</td>
<td></td>
<td>Pentacene</td>
<td>5-7</td>
<td>2-3 x 10⁶</td>
</tr>
</tbody>
</table>

WAXRD (wide angle x-ray diffraction) spectra of pentacene as well as PDI-8CN₂ and DH-6T on dielectric films of the present teachings (not shown) exhibit sharp multiple reflections demonstrating a great degree of texture. Printed OFETs can be mechanically flexible.

EXAMPLE 18

Dielectric Properties of Dielectric Films Prepared from Precursor Compositions Containing Polymeric Crosslinkers

Tables 9 and 10 summarize the properties of various dielectric films obtained from different polymer-crosslinkable copolymer precursor formulations having the formula:

\[
\text{PVAn} \quad \text{Si(OAc)}_3 \quad \text{Cxn}
\]

TABLES

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP(mg):</th>
<th>C60Ac(mg)</th>
<th>Semiconductor</th>
<th>(\mu) (cm²/Vs)</th>
<th>(I_{on}:I_{off})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>50:25 (Al)</td>
<td></td>
<td>Pentacene</td>
<td>5-7</td>
<td>1-2 x 10⁶</td>
</tr>
<tr>
<td>16</td>
<td>100:50 (ITO)</td>
<td></td>
<td>Pentacene</td>
<td>10-15</td>
<td>4-6 x 10⁵</td>
</tr>
</tbody>
</table>

5 Carrier mobility has been calculated in saturation.

Printed OFETs can be mechanically flexible.
Table 9

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP (mg)</th>
<th>PVA_{n}C_{x} (mg)</th>
<th>Solvent</th>
<th>Method</th>
<th>Quality</th>
<th>C_{r} (nF/cm²)</th>
<th>BV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>10</td>
<td>Dioxane (2 mL)</td>
<td>SC</td>
<td></td>
<td>63-64</td>
<td>&gt;60</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>20</td>
<td>Dioxane (2 mL)</td>
<td>SC</td>
<td>excellent</td>
<td>54-55</td>
<td>&gt;60</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>40</td>
<td>Dioxane (2 mL)</td>
<td>SC</td>
<td>good</td>
<td>34-35</td>
<td>&gt;60</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>Dioxane (2 mL)</td>
<td>SC</td>
<td>good</td>
<td>32-33</td>
<td>&gt;60</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>40</td>
<td>AcOEt (0.6 mL)</td>
<td>Print</td>
<td></td>
<td>12-13</td>
<td>&gt;60</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>40</td>
<td>AcOEt (0.6 mL)</td>
<td>Print</td>
<td>excellent</td>
<td>17-18</td>
<td>&gt;60</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>40</td>
<td>AcOEt (1.0 mL)</td>
<td>Print</td>
<td>excellent</td>
<td>18-19</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

Table 10 shows that relatively high capacitance films can be fabricated both by spin-coating and printing various photochemically curable polymer-crosslinkable copolymer precursor formulations.

Table 10

<table>
<thead>
<tr>
<th>Entry</th>
<th>PVP (mg)</th>
<th>PVP_{n}C_{x} (mg)</th>
<th>EGOAc (mg)</th>
<th>Solvent</th>
<th>Method (Curing)</th>
<th>Quality</th>
<th>C_{r} (nF/cm²)</th>
<th>BV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>50</td>
<td>AcOEt (0.4 mL)</td>
<td>Print (i)</td>
<td>excellent</td>
<td>14-16</td>
<td>&gt;80</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>0</td>
<td>80</td>
<td>Dioxane (2 mL)</td>
<td>SC (i)</td>
<td>excellent</td>
<td>28-32</td>
<td>&gt;70</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>0</td>
<td>40</td>
<td>Dioxane (2 mL)</td>
<td>SC (i)</td>
<td>good</td>
<td>80-90</td>
<td>&gt;60</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>THF (2 mL)</td>
<td>SC (i)</td>
<td>good</td>
<td>80-90</td>
<td>&gt;60</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0</td>
<td>30</td>
<td>AcOEt (0.4 mL)</td>
<td>Print (i)</td>
<td>excellent</td>
<td>5-7</td>
<td>&gt;80</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0</td>
<td>25</td>
<td>AcOEt (0.4 mL)</td>
<td>Print (i)</td>
<td>good</td>
<td>13-16</td>
<td>&gt;50</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>Dioxane (2 mL)</td>
<td>SC (iv)</td>
<td>excellent</td>
<td>41-42</td>
<td>&gt;50</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>40</td>
<td>20</td>
<td>Dioxane (2 mL)</td>
<td>SC (iv)</td>
<td>excellent</td>
<td>43-45</td>
<td>&gt;50</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>40</td>
<td>10</td>
<td>Dioxane (2 mL)</td>
<td>SC (iv)</td>
<td>good</td>
<td>42-43</td>
<td>&gt;50</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>40</td>
<td>0</td>
<td>Dioxane (2 mL)</td>
<td>SC (iv)</td>
<td>good</td>
<td>37-39</td>
<td>&gt;50</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>AcOEt (0.4 mL)</td>
<td>Print (iv)</td>
<td>excellent</td>
<td>41-43</td>
<td>&gt;50</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>40</td>
<td>10</td>
<td>Dioxane (2 mL)</td>
<td>SC (iii)</td>
<td>good</td>
<td>43-45</td>
<td>&gt;50</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>40</td>
<td>0</td>
<td>Dioxane (2 mL)</td>
<td>SC (iii)</td>
<td>good</td>
<td>42-43</td>
<td>&gt;50</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>100</td>
<td>50</td>
<td>AcOEt (0.4 mL)</td>
<td>Print (iv)</td>
<td>poor</td>
<td>8-20</td>
<td>&gt;60</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>200</td>
<td>100</td>
<td>AcOEt (0.3 mL)</td>
<td>Print (iv)</td>
<td>poor</td>
<td>8-16</td>
<td>&gt;60</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>AcOEt (0.3 mL)</td>
<td>Print (iv)</td>
<td>excellent</td>
<td>12-13</td>
<td>&gt;60</td>
</tr>
<tr>
<td>18</td>
<td>200</td>
<td>50</td>
<td>50</td>
<td>AcOEt (0.3 mL)</td>
<td>Print (iv)</td>
<td>excellent</td>
<td>12-13</td>
<td>&gt;50</td>
</tr>
<tr>
<td>19</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>AcOEt (0.3 mL)</td>
<td>Print (iv)</td>
<td>excellent</td>
<td>12-13</td>
<td>&gt;50</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>AcOEt (0.3 mL)</td>
<td>Print (iv)</td>
<td>excellent</td>
<td>15-16</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

As shown in Table 10, crosslinked polymeric dielectric films of excellent quality were fabricated by spin-coating or printing various precursor formulations including a conventional polymer such as PVP, a thermally curable crosslinker such as EGOAc, and optionally a photochemically curable polymeric crosslinker such as PVP_{n}C_{x}. Referring back to FIG. 1, different crosslinking strategies (ii-iv) were employed (using the same numbering schemes).

Using these thermally and/or photochemically curable dielectric materials, high-performance OFETs were fabricated on patterned dielectrics. FIG. 12 shows the transfer plots for pentacene transistors exhibiting carrier mobilities close to 30 cm²/Vs and current on-off ratios greater than 10⁵, demonstrating the great potential of the compositions and processes of the present teachings.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The foregoing embodiments are therefore to be considered in all respects illustrative rather than limiting on the present teachings described herein. Scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are intended to be embraced therein.

What is claimed is:

1. An electronic device comprising a semiconductor component and a dielectric material, wherein the dielectric material comprises a crosslinked polymeric material comprising a thermally cured product of a precursor composition, the precursor composition comprising: (1) a polymeric component and a thermally curable crosslinker, (2) a thermally curable polymeric crosslinker, or both (1) and (2), wherein: the thermally curable crosslinker of (1) has the formula:

\[(X)_{3-m}(Y)_{m}Si\ldots Z\ldots Si(Y)_{m}(X)_{3-m}\text{, and}

the thermally curable polymeric crosslinker of (2) comprises a pendant group comprising a crosslinking moiety having the formula:

\[-QSi(Y)_{3-m}(X)_{3-m}\text{,}

wherein:

Q, at each occurrence, independently is selected from the group consisting of -L-, \(-O-, \ -O-L, \ -L-O-, \ -NR^4-, \ -NR^4-L-, \ -L-NR^4-, \ and a covalent bond;

X, at each occurrence, independently is selected from the group consisting of a halogen, \(-NR^4-, \ -NR^4-L-, \ -L-NR^4-, \ and a covalent bond;

Y, at each occurrence, independently is selected from the group consisting of H, a C₁₋₆ alkyl group, and a C₁₋₆ haloalkyl group;

Z is Q-W-Q, provided that Q and W do not combine to form a moiety selected from the group consisting of \(-O-, \ -NR^4-, \ -NR^4-L-, \ -L-NR^4-, \ and a covalent bond; and

thermally cured product of a precursor composition, the precursor composition comprising: (1) a polymeric component and a thermally curable crosslinker, (2) a thermally curable polymeric crosslinker, or both (1) and (2), wherein: the thermally curable crosslinker of (1) has the formula:

\[(X)_{3-m}(Y)_{m}Si\ldots Z\ldots Si(Y)_{m}(X)_{3-m}\text{, and}

the thermally curable polymeric crosslinker of (2) comprises a pendant group comprising a crosslinking moiety having the formula:

\[-QSi(Y)_{3-m}(X)_{3-m}\text{,}

wherein:

Q, at each occurrence, independently is selected from the group consisting of -L-, \(-O-, \ -O-L, \ -L-O-, \ -NR^4-, \ -NR^4-L-, \ -L-NR^4-, \ and a covalent bond;

X, at each occurrence, independently is selected from the group consisting of a halogen, \(-NR^4-, \ -OR^3-, \ and \ -OC(OR^3);\n
Y, at each occurrence, independently is selected from the group consisting of H, a C₁₋₆ alkyl group, and a C₁₋₆ haloalkyl group;

Z is Q-W-Q, provided that Q and W do not combine to form a moiety selected from the group consisting of \(-O-, \ -NR^4-, \ -NR^4-L-, \ -L-NR^4-, \ and a covalent bond; and
The electronic device of claim 1, wherein the precursor composition comprises the thermally curable polymeric crosslinker of (2) having the formula:

wherein:

- R¹ is selected from the group consisting of H, a halogen, or a C₁₋₆ alkyl group;
- R² is selected from the group consisting of H, a C₁₋₆ haloalkyl group, a C₆₋₁₄ aryl group, a 5-14 membered heteroaryl group, and a C₁₋₆ alkyl-5-14 membered heteroaryl group;
- R³ and R⁴ are independently selected from the group consisting of H, a C₁₋₆ alkyl group, a C₆₋₁₄ aryl group, a 5-14 membered heteroaryl group, and a C₁₋₆ alkyl-5-14 membered heteroaryl group;
- W is selected from the group consisting of SiXXO, SiXYO, and SiYYO, L, at each occurrence, independently is a divalent C₁₋₆, haloalkyl group, each of which optionally is substituted with 1-4 R⁴ groups;
- X, at each occurrence, independently is H, a C₁₋₆ alkyl group, a C₆₋₁₄ aryl group, a 5-14 membered heteroaryl group, and a C₁₋₆ alkyl-5-14 membered heteroaryl group;
- Y, at each occurrence, independently is 0, 1, or 2;
- Q, X, and Y are as defined in claim 1.

x and y independently are a real number, wherein 0<x<1, 0<y<1, and x+y=1.

8. The electronic device of claim 1, wherein the precursor composition comprises the thermally curable polymeric crosslinker of (2) having the formula:
10. The electronic device of claim 1, wherein the precursor composition further comprises (3) a photochemically curable crosslinker, (4) a photochemically curable polymeric crosslinker, or both (3) and (4).

11. The electronic device of claim 1, wherein the precursor composition further comprises a photochemically curable polymeric crosslinker having the formula:

\[
\begin{array}{c}
\text{OH} \\
\text{O} \\
\text{O} \\
\end{array}
\]

wherein \( x \) and \( y \) independently are a real number, wherein \( 0 < x < 1, 0 < y < 1, \) and \( x + y = 1. \)

12. The electronic device of claim 11, wherein the precursor composition comprises

\[
\text{[CH}_3\text{C(O)O)}_\text{S}^{\text{O}}\text{O}^{\text{O}}\text{S(O)}_{\text{CH}_3}.\]

5 as the thermally curable crosslinker of (1).

13. The electronic device of claim 1, wherein the dielectric material further comprises a plurality of metal oxide particles, the metal oxide particles comprising a metal component selected from the group consisting of a Group I metal, a Group II metal, a Group III metal, a Group IV metal, a transition metal, and combinations thereof.

14. The electronic device of claim 1, wherein the dielectric material has a thickness of less than about 50 nm.

15. The electronic device of claim 1, wherein the electronic device is a thin film transistor, a field-effect device, an organic light-emitting diode, an organic photovoltaic device, a photodetector, a capacitor, or a sensor.

16. The electronic device of claim 1 configured as a thin film transistor.

17. The electronic device of claim 1 comprising an n-type organic semiconductor material.

18. The electronic device of claim 1 comprising a p-type organic semiconductor material.

19. The electronic device of claim 1 comprising an inorganic semiconductor material.

20. The electronic device of claim 1 comprising a substrate selected from the group consisting of doped silicon, indium tin oxide (ITO), ITO-coated glass, ITO-coated mylar, aluminum, and doped polythiophene.

* * * * *