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(54) Title: ORGANIC THIN FILM TRANSISTORS WITH MODIFIED SURFACE OF GATE-DIELECTRIC

(57) Abstract: Provided is an organic thin film transistor comprising a self-assembled monolayer interposed between a gate dielectric and an organic semiconductor layer. The monolayer is a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer. The semiconductor layer comprises a material selected from an acene, substituted with at least one electron-donating group, halogen atom, or a combination thereof, or a benzo-annellated acene or polybenzo-annellated acene, which optionally is substituted with at least one electron-donating group, halogen atom, or a combination thereof. Methods of making a thin film transistor and an integrated circuit comprising thin film transistors are also provided.

ORGANIC THIN FILM TRANSISTOR WITH MODIFIED SURFACE OF GATE-DIELECTRIC

Technical Field

This invention relates to organic thin film transistors having improved performance. More particularly, the invention relates to organic thin film transistors having a substituted acene semiconductor and a self-assembled monolayer between the semiconductor and gate dielectric.

Background

Organic semiconductors are of great interest for a variety of applications such as low-cost electronics. Organics can be synthesized to incorporate the necessary electronic properties for a wide variety of devices, and also can be constructed to allow low-cost, roll processing that is not currently possible for crystalline silicon microelectronics.

One area of concern in organic electronic devices is the quality of the interface formed between the organic semiconductor and another device layer. Previous efforts to control the semiconductor/dielectric interface have included the use of hexamethyldisilazane (HMDS) and silane coupling agents on silicon oxide surfaces. Complex deposition processes involving long times in a vacuum have been used to coat octadecyltrichlorosilane (OTS) onto thermally-grown silicon dioxide gate dielectric materials to affect transistor performance. The materials useful in this process have several disadvantages, including sensitivity to water in the atmosphere and on the surface of a dielectric layer, instability due to crosslinking within the material in competition with the bonding reaction to the dielectric layer, and difficulties in achieving reproducible film properties. EP 1041652 A2 describes the use of several surface treatments to enhance the crystalline domain size of solution cast oligothiophenes on SiO_x for thin film transistors (TFTs), although measured mobility values were generally lower than the untreated controls.

Summary

Briefly, the present invention provides an organic thin film transistor (OTFT) comprising a self-assembled monolayer interposed between a gate dielectric and an organic semiconductor layer, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, the precursor comprising a composition having the formula:

$$X\text{-}Y\text{-}Z_n,$$

wherein X is H or CH_3;

Y is a linear or branched C_5-C_{50} aliphatic or cyclic aliphatic connecting group, or a linear or branched C_8-C_{50} group comprising an aromatic group and a C_3-C_{44} aliphatic or cyclic aliphatic connecting group;

Z is selected from $-PO_3H_2$, $-OPO_3H_2$, benzotriazolyl ($-C_6H_4N_3$), benzotriazolylcarbonyloxy ($-OC(=O)C_6H_4N_3$), benzotriazolyloxy ($-O-C_6H_4N_3$), benzotriazolylamino ($-NH-C_6H_4N_3$), -CONHOH, -COOH, -OH, -SH, -COSH, -COSeH, $-C_5H_4N$, -SeH, $-SO_3H$, -NC, $-SiCl(CH_3)_2$, $-SiCl_2CH_3$, amino, and phosphinyl;
and n is 1, 2, or 3 provided that n = 1 when Z is $-SiCl(CH_3)_2$ or $-SiCl_2CH_3$; and wherein the organic semiconductor layer comprises a material selected from an acene, substituted with at least one electron-donating group, halogen atom, or a combination thereof, or a benzo-annellated acene or polybenzo-annellated acene, which optionally is substituted with at least one electron-donating group, halogen atom, or a combination thereof.

The present invention also provides an organic thin film transistor comprising a self-assembled monolayer interposed between a gate dielectric and an organic semiconductor layer, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, the precursor comprising a composition having the formula:

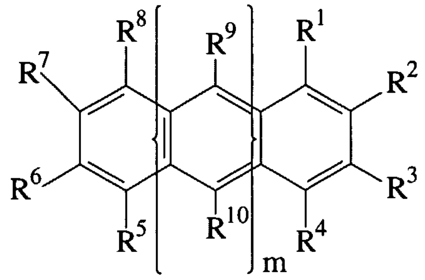
$$X\text{-}Y\text{-}Z_n,$$

wherein X is H or CH_3;

Y is a linear or branched C_5-C_{50} aliphatic or cyclic aliphatic connecting group, or a linear or branched C_8-C_{50} group comprising an aromatic group and a C_3-C_{44} aliphatic or cyclic aliphatic connecting group;

Z is selected from $-PO_3H_2$, $-OPO_3H_2$, benzotriazolyl ($-C_6H_4N_3$), benzotriazolylcarbonyloxy ($-OC(=O)C_6H_4N_3$), benzotriazolyloxy ($-O-C_6H_4N_3$), benzotriazolylamino ($-NH-C_6H_4N_3$), -CONHOH, -COOH, -OH, -SH, -COSH, -COSeH, $-C_5H_4N$, -SeH, $-SO_3H$, -NC, $-SiCl(CH_3)_2$, $-SiCl_2CH_3$, amino, and phosphinyl;

and n is 1, 2, or 3 provided that n = 1 when Z is $-SiCl(CH_3)_2$ or $-SiCl_2CH_3$; and wherein the organic semiconductor layer comprises a semiconductor of the formula:



wherein each R group is independently selected from electron-donating groups, halogen atoms, hydrogen atoms, and combinations thereof, provided that not all R groups are hydrogen; m is 1, 2, 3, or 4; each R^9 and R^{10} is independently H or any R group; and any combination of two adjacent R groups may together form a five or six carbon cyclic aliphatic or aromatic group; provided that neither R^2 with R^3 nor R^6 with R^7 form part of a six-member aromatic ring; and provided that when m is 1 neither R^9 nor R^{10} form part of a six-member aromatic ring.

As used herein, "electron-donating group" means C_1-C_{24} alkyl, alkoxy, thioalkoxy, or combinations thereof, which may be substituted or unsubstituted and "substituted" means, for a chemical species, substituted by a group that does not interfere with the desired product or process, *e.g.*, substituents can be alkyl, alkoxy, aryl, phenyl, halo (F, Cl, Br, I), etc.

Various thin film transistor construction options are possible. For example, the source and drain electrodes may be adjacent to the gate dielectric with the organic semiconductor layer over the source and drain electrodes, or the organic semiconductor layer may be interposed between the source and drain electrodes and the gate dielectric.

In another aspect, the present invention provides a method of making a thin film transistor comprising the steps of providing a substrate, providing a gate electrode material on the substrate, providing a gate dielectric on the gate electrode material, providing a self-assembled monolayer (SAM) adjacent to the gate dielectric, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, applying an organic semiconductor layer on the monolayer, and providing a source electrode and a drain electrode contiguous to the organic semiconductor layer. The precursor is as described above with the organic thin film transistor article. The organic semiconductor layer also is as described above with the organic thin film transistor article. An integrated circuit comprising organic thin film transistor articles is also provided.

It is an advantage of the present invention to provide organic thin film transistors with one or more improvements over known devices that lack the features of the present invention. With the invention, improvements in properties such as threshold voltage, subthreshold slope, on/off ratio, and charge-carrier mobility can be achieved. The improvements in device performance provided by the present invention enable the production of more complicated circuits having faster switching speeds and simpler processing conditions. This invention also enables the production of larger circuit elements having comparable performance to devices with very small features. Devices with larger feature sizes can be less expensive as they do not require expensive precision patterning processes.

Other features and advantages of the invention will be apparent from the following detailed description of the invention and the claims. The above summary of principles of the disclosure is not intended to describe each illustrated embodiment or every implementation of the present disclosure. The following detailed description more particularly exemplifies certain preferred embodiments utilizing the principles disclosed herein.

Detailed Description

Generally, a thin film transistor includes a gate electrode, a gate dielectric on the gate electrode, a source electrode and a drain electrode adjacent to the gate dielectric, and a semiconductor layer adjacent to the gate dielectric and adjacent to the source and drain electrodes. More specifically, an organic thin film transistor (OTFT) has an organic semiconductor layer. Such OTFTs are known in the art as shown, for example, in copending application USSN 09/947,845, Attorney Docket No. 56999US002, filed on September 6, 2001.

The organic thin film transistor of the present invention further includes a self-assembled monolayer (SAM) interposed between the gate dielectric and the organic semiconductor layer, and wherein the organic semiconductor comprises a substituted acene.

Substrate

A substrate can be used to support the OTFT, *e.g.*, during manufacturing, testing, storage, use, or any combination thereof. The gate electrode and/or gate dielectric may provide sufficient support for the intended use of the resultant OTFT such that another substrate is not required. For example, doped silicon can function as the gate electrode and support the OTFT. In another example, one substrate may be selected for testing or screening various embodiments while another substrate is selected for commercial embodiments. In another embodiment, a support may be detachably adhered or mechanically affixed to a substrate, such as when the support is desired for a temporary purpose. For example, a flexible polymeric substrate may be adhered to a rigid glass support, which support could be removed. In some embodiments, the substrate does not provide any necessary electrical function for the OTFT. This type of substrate is termed a "non-participating substrate" in this document.

Useful substrate materials can include organic and/or inorganic materials. For example, the substrate may comprise inorganic glasses, ceramic foils, polymeric materials, filled polymeric materials, coated metallic foils, acrylics, epoxies, polyamides, polycarbonates, polyimides, polyketones, poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (sometimes referred to as poly(ether ether ketone) or PEEK), polynorbornenes, polyphenyleneoxides, poly(ethylene naphthalenedicarboxylate) (PEN), poly(ethylene terephthalate) (PET), poly(phenylene sulfide) (PPS), and fiber-reinforced plastics (FRP), and combinations thereof.

A flexible substrate is used in some embodiments of the present invention. This allows for roll processing, which may be continuous, providing economy of scale and economy of manufacturing over flat and/or rigid substrates. The flexible substrate chosen preferably is capable of wrapping around the circumference of a cylinder of less than about 50 cm diameter without distorting or breaking. The substrate chosen more preferably is capable of wrapping around the circumference of a cylinder of less than about 25 cm diameter without distorting or breaking the substrate. In some embodiments, the substrate chosen most preferably is capable of wrapping around the circumference of a cylinder of less than about 10 cm diameter, or even about 5 cm diameter, without distorting or breaking the substrate. The force used to wrap the flexible substrate of the invention around a particular cylinder typically is low, such as by unassisted hand, *i.e.*, without the aid of levers, machines, hydraulics, and the like. The flexible substrate may be rolled upon itself.

Gate Electrode

The gate electrode can be any useful conductive material. For example, the gate electrode may comprise doped silicon, or a metal, such as aluminum, chromium, copper, gold, silver, nickel, palladium, platinum, tantalum, and titanium. Conductive polymers also can be used, for example polyaniline, poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS). In addition, alloys, combinations, and multilayers of these materials may be useful.

In some embodiments of the invention, the same material can provide the gate electrode function and also provide the support function of the substrate. For example, doped silicon can function as the gate electrode and support the OTFT.

Gate Dielectric

The gate dielectric is provided on the gate electrode, for example, through a deposition process. This gate dielectric electrically insulates the gate electrode under the operating conditions of the OTFT device from the balance of the device. Thus, the gate dielectric comprises an electrically insulating material. The gate dielectric should have a dielectric constant above about 2, more preferably above about 5. The dielectric constant of the gate dielectric also can be very high, for example, 80 to 100 or even higher. Useful materials for the gate dielectric may comprise, for example, an organic or inorganic electrically insulating material, or combinations thereof.

The gate dielectric may comprise a polymeric material, such as polyvinylidenefluoride (PVDF), cyanocelluloses, polyimides, epoxies, etc. In some embodiments, an inorganic capping layer comprises the outer layer of an otherwise polymeric gate dielectric.

Some specific examples of inorganic materials useful for the gate dielectric include strontiates, tantalates, titanates, zirconates, aluminum oxides, silicon oxides, tantalum oxides, titanium oxides, silicon nitrides, barium titanate, barium strontium titanate, barium zirconate titanate, zinc selenide, and zinc sulfide. In addition, alloys, combinations, and multilayers of these can be used for the gate dielectric. Of these materials, aluminum oxides, silicon oxides, silicon nitrides, and zinc selenide are preferred.

The gate dielectric can be deposited in the OTFT as a separate layer, or formed on the gate such as by oxidizing, including anodizing, the gate material to form the gate dielectric.

Source and Drain Electrodes

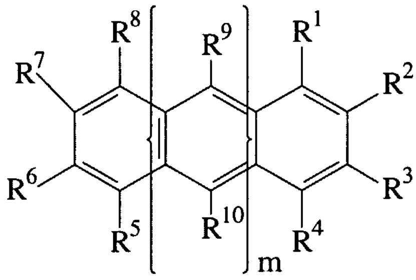
The source electrode and drain electrode are separated from the gate electrode by the gate dielectric, while the organic semiconductor layer can be over or under the source electrode and drain electrode. The source and drain electrodes can be any useful conductive material. Useful materials include those described above for the gate electrode as well as barium and calcium.

The thin film electrodes (*e.g.*, gate electrode, source electrode, and drain electrode) can be provided by any useful means such as physical vapor deposition (*e.g.*, thermal evaporation, sputtering) or ink jet printing. The patterning of these electrodes can be accomplished by known methods such as shadow masking, additive photolithography, subtractive photolithography, printing, microcontact printing, and pattern coating.

Organic Semiconductors

In an embodiment of the present invention, the organic semiconductor layer comprises a material selected from an acene, substituted with at least one electron-donating group, halogen atom, or a combination thereof, or a benzo-annellated acene or polybenzo-annellated acene, which optionally is substituted with at least one electron-donating group, halogen atom, or a combination thereof. The electron-donating group is selected from an alkyl, alkoxy, or thioalkoxy group having from 1 to 24 carbon atoms.

In another embodiment of the present invention, the organic semiconductor layer comprises a semiconductor of the formula:



wherein each R group is independently selected from electron-donating groups, halogen atoms, hydrogen atoms, and combinations thereof, provided that not all R groups are hydrogen; m is 1, 2, 3, or 4; each R^9 and R^{10} is independently H or any R group; and any combination of two adjacent R groups may together form a five or six carbon cyclic aliphatic or aromatic group; provided that neither R^2 with R^3 nor R^6 with R^7 form part of a six-member aromatic ring; and provided that when m is 1 neither R^9 nor R^{10} form part of a six-member aromatic ring.

Alkyl- or polyalkyl-substituted acenes are preferred classes of organic semiconductor materials that are useful in this invention. As used herein, "polyalkyl", and "polyalkoxy", and "polybenzo" mean more than one alkyl, alkoxy, or benzo group.

Non-limiting examples of benzo-annellated and polybenzo-annellated acenes include 1,2-benzanthracene (benz[a]anthracene or tetraphene), 1,2:3,4-dibenzanthracene (dibenz[a,c]anthracene), 1,2:5,6-dibenzanthracene (dibenz[a,h]anthracene), 1,2:7,8-dibenzanthracene (dibenz[a,j]anthracene), 1,2:3,4:5,6-tribenzanthracene (tribenz[a,c,h]anthracene), 1,2:3,4:5,6:7,8-tetrabenzanthracene (tetrabenz[a,c,h,j]anthracene, 1,2-benzotetracene (benzo[a]naphthacene), 1,2:3,4-dibenzotetracene (dibenzo[a,c]naphthacene), 1,2:7,8-dibenzotetracene (dibenzo[a,j]naphthacene), 1,2:9,10-dibenzotetracene (dibenzo[a,l]naphthacene), 1,2:3,4:7,8-tribenzotetracene (tribenzo[a,c,j]naphthacene), 1,2:3,4:7,8:9,10-tetrabenzotetracene (tetrabenzo[a,c,j,l]naphthacene), 1,2-benzopentacene (benzo[a]pentacene), 1,2:3,4-dibenzopentacene (dibenzo[a,c]pentacene), 1,2:8,9-dibenzopentacene (dibenzo[a,l]pentacene), 1,2:10,11-dibenzopentacene (dibenzo[a,n]pentacene), 1,2:3,4:8,9:10,11-tetrabenzopentacene (tetrabenzo[a,c,l,n]pentacene, 1,2-benzohexacene (benzo[a]hexacene), and substituted derivatives thereof. Further examples include benzoacenes with the benzo group attached to two rings of the acene, such as dibenzo[de,qr]tetracene (dibenzo[de,qr]naphthacene or naphtho[2,3-e]pyrene), zethrene (dibenzo[de,mn]naphthacene), dibenzo[de,st]pentacene, and dibenzo[de,uv]pentacene. In the preceding list, the common name is given followed by alternative names or Chemical Abstracts Service (CAS) names in parentheses.

Such acenes may be substituted, such as with at least one alkyl group. Preferred but non-limiting examples of alkyl groups are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, 2-methylhexyl, 2-ethylhexyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-dodecyl, *n*-octadecyl, and 3,5,5-trimethylhexyl.

Examples of alkyl-substituted acenes useful in the present invention include but are not limited to the following: 1-methylanthracene, 2-methylanthracene, 1,2-dimethylanthracene, 2,3-dimethylanthracene, 2,3,6,7-tetramethylanthracene, 1,2,3,4-tetramethylanthracene, 2-ethylanthracene, 2,6-diethylanthracene, 2-hexylanthracene, 2,6-

dihexylanthracene, 1-methyltetracene, 2-methyltetracene, 2,3-dimethyltetracene, 2,8-dimethyltetracene, 2,3,9,10-tetramethylpentacene, 2-ethyltetracene, 2,8-diethylpentacene, 2,9-diethylpentacene, 2-hexyltetracene, 2-nonyltetracene, 1-methylpentacene, 2-methylpentacene, 2,3-dialkylpentacenes, 2,9-dialkylpentacenes, and 2,10-dialkylpentacenes (*e.g.*, 2,3-dimethylpentacene, 2,9-dimethylpentacene, 2,10-dimethylpentacene), 2-ethylpentacene, 2,10-dialkoxypentacenes, 2,3,9,10-tetraalkylpentacenes, 1,4,8,11-tetraalkoxypentacenes, and 1,2,3,4,8,9,10,11-octaalkylpentacene, wherein the alkyl or alkoxy group in each of the formulas above has from 1 to 24 carbons. Preferred dialkyl acenes include 2,6-dialkylanthracene, 2,8-dialkyltetracene, and 2,9-dialkylpentacene.

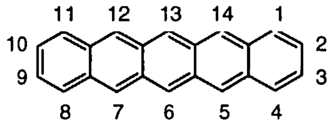
Alkyl-substituted acenes can be prepared by any known method. For example, various methyl-substituted anthracenes are taught in Table XXIV in E. Clar, Polycyclic Hydrocarbons, Volume 1, Academic Press (London and New York) and Springer-Verlag (Berlin, Gottingen and Heidelberg), 1964, pages 298-299. Other alkylanthracenes can be prepared by similar methods as described in Table XXIV of the same reference.

Substituted tetracenes also can be prepared by any known method, including for example, the following sequence of reactions: 1) the condensation of naphthalene-2,3-dicarboxylic anhydride and benzene derivatives, 2) dehydration to form the corresponding tetracene -5,12-quinone, 3) and reduction of the quinone to give the corresponding tetracene derivative. Such methods are taught, *e.g.*, in Waldmann, H. and Mathiowetz, H., *Ber. dtsch. Chem. Ges.* **64**, 1713 (1931), Weizmann, C., Haskelberg, L.and Berlin, T., *J. Chem. Soc.* 398 (1939); Waldemann, H. and Plak, G., *J. prakt. Chem.* (2) **150**, 113, 121 (1938). Other examples of synthesis of alkyl homologues of tetracene include: 2-methyltetracene (Coulson, E. A., *J. Chem. Soc.* 1406 (1934)), 5-methyltetracene (Clar, E. and Wright, J. W., *Nature, Lond.* **63**, 921 (1949)), 2-isopropyltetracene (Cook, J.W., *J. Chem. Soc.* 1412 (1934)), 1,6-dimethyltetracene (Fieser, L. F. and Hershberg, E. B. *J. Amer. Chem. Soc.* **62**, 49 (1940)), 2,8-dimethyltetracene (Fieser, L. F. and Hershberg, E. B. *J. Amer. Chem. Soc.* **62**, 49 (1940) and Coulson, E. A., *J. Chem. Soc.* 1406 (1934)), 2,9-dimethyltetracene (Coulson, E. A., *J. Chem. Soc.* 1406 (1934)), and 5,12-dimethyltetracene (Wolf, J., *J. Chem. Soc.* 75, 2673 (1953)).

Substituted pentacene compounds that are useful as organic semiconductors in the present invention include compounds comprising at least one substituent selected from the group consisting of electron-donating substituents (*e.g.*, alkyl, alkoxy, thioalkoxy), halogen substituents, and combinations thereof. Useful substituted pentacenes include but are not limited to 2,9-dialkylpentacenes and 2,10-dialkylpentacenes, 2,10-dialkoxypentacenes, 2,3,9,10-tetraalkylpentacenes, and 1,4,8,11-tetraalkoxypentacenes, wherein each alkyl or alkoxy group in the preceding formulas has from 1 to 24 carbons. Such substituted pentacenes are taught in copending applications USSN 09/966,954, Attorney Docket No. 57087US002, and USSN 09/966,961, Attorney Docket No. 57088US002, both filed on September 26, 2001.

Further details of benzo-annellated and polybenzo-annellated acenes can be found in the art, for example, in NIST Special Publication 922 "Polycyclic Aromatic Hydrocarbon Structure Index", U.S. Govt. Printing Office, by Sander and Wise (1997).

As used herein, the numbering sequence that is used for pentacene is exemplified with the structure shown below.

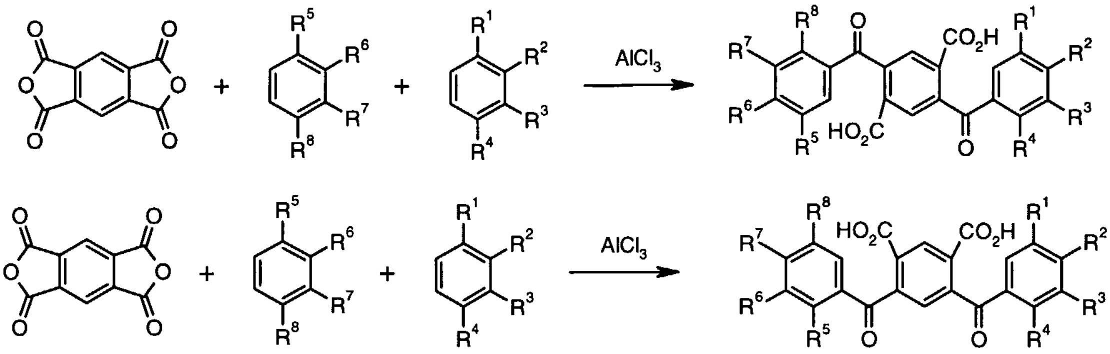


The location of a substituent on such a compound is commonly specified by reference to the number of the carbon atom to which the substituent is bonded. There is one hydrogen atom bonded to each numbered carbon atom if no substituent is indicated.

Substituted pentacene semiconductors useful in the present invention can be prepared by a process comprising the steps of (1) combining at least one substituted benzene (more specifically, at least one mono-, di-, tri-, or tetrasubstituted benzene having at least two adjacent ring carbon atoms that are bonded to hydrogen) and pyromellitic dianhydride (or a derivative thereof), in the presence of a Lewis acid (for example, $AlCl_3$), to form substituted bis(benzoyl)phthalic acids via a Friedel-Crafts reaction; (2) reducing the substituted bis(benzoyl)phthalic acids to give the corresponding substituted bis(benzyl)phthalic acids; (3) cyclizing the substituted bis(benzyl)phthalic acids to give the corresponding substituted pentacenediones; (4) reducing the substituted pentacenediones to give the corresponding substituted pentacenediols; and (5) dehydrating the substituted pentacenediols to form the corresponding substituted pentacenes. As used herein, the term "phthalic acid" refers to terephthalic acid (1,4-benzenedicarboxylic acid), isophthalic acid (1,3-benzenedicarboxylic acid), and combinations thereof.

The step of combining at least one substituted benzene with pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic acid dianhydride) or a derivative thereof (for example, dimethyl 2,5-bis(chlorocarbonyl)terephthalate) to form substituted bis(benzoyl)phthalic acids can be represented by the following general scheme:

Reaction Scheme A



wherein each R (that is, each of the groups R^1 through R^8) is independently selected from the group consisting of electron-donating groups, halogen atoms, hydrogen atoms, and combinations thereof. Preferably, each R is independently selected from alkyl groups, alkoxy groups, thioalkoxy groups, halogen atoms, hydrogen atoms, and combinations thereof. More preferably, each R is independently selected from alkyl groups, alkoxy groups, hydrogen atoms, and combinations thereof. Even more preferably, each R is independently an alkyl group or a hydrogen atom. Most preferably, each R is independently methyl, *n*-hexyl, *n*-nonyl, *n*-dodecyl, *n*-octadecyl, *sec*-butyl, 3,5,5-trimethylhexyl, 2-ethylhexyl, or a hydrogen atom. Preferably, R^2 and R^6 (or R^2 and R^7) are moieties other than hydrogen while hydrogen comprises the balance of the R groups. In addition, R^2 and R^6 preferably are moieties other than hydrogen for the substituted bis(benzoyl)terephthalic acid and R^2 and R^7 preferably are moieties other than hydrogen for the substituted bis(benzoyl)isophthalic acid.

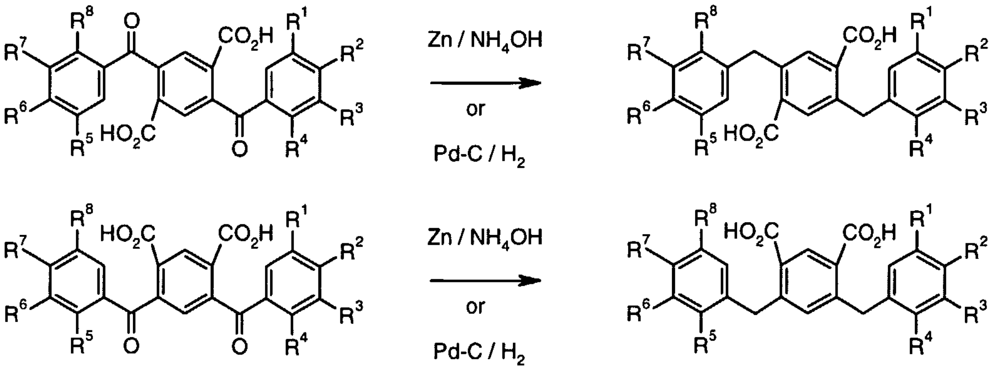
Reactions of this type (electrophilic aromatic substitution reactions) are known and have been described, for example, by Diesbach and Schmidt in Helv. Chim. Acta 7, 648 (1924); by Mills and Mills in J. Chem. Soc. 101, 2200 (1912); by Philippi in Monatshefte fuer Chemie 32, 634 (1911); by Philippi and Seka in Monatshefte fuer Chemie 43, 615 (1922); by Philippi and Auslaender in Monatshefte fuer Chemie 42, 1 (1921); and by Machek in Monatshefte fuer Chemie 56, 130 (1930). Preferably, the reaction is carried out in the presence of an inert solvent and an amine base in order to keep the reaction mixture fluid and to decrease the amount of rearrangement of the substituents on the aromatic ring during the reaction. Examples of useful inert solvents include 1,2-dichloroethane, dichlorobenzene, dichloromethane, carbon disulfide, nitrobenzene, and nitromethane. Examples of useful amine bases include tertiary amines such as triethylamine, diisopropylethylamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO). If desired, the reaction mixture can be agitated and/or heated.

Representative examples of substituted benzenes that can be used to prepare the substituted bis(benzoyl)phthalic acids include mono- and dialkoxybenzenes; mono- and dithioalkoxybenzenes; mono- and dihalobenzenes; and mono-, di-, tri-, and tetraalkylbenzenes (for example, toluene, hexylbenzene, nonylbenzene, dodecylbenzene, *sec*-butylbenzene, p-xylene, 1,2,3,4-tetrahydronaphthalene, 3,5,5-trimethylhexylbenzene, 2-ethylhexylbenzene, and 1,2,3,4-tetramethylbenzene).

Alternatively, the substituted bis(benzoyl)phthalic acids can be prepared by reaction of pyromellitic dianhydride or a derivative thereof with a substituted aromatic organometallic reagent (for example, an aryl magnesium halide or an aryl lithium compound).

The resulting substituted bis(benzoyl)phthalic acids can be reduced to the corresponding substituted bis(benzyl)phthalic acids via reduction methods known in the art. For example, the reduction can be accomplished by using either zinc and aqueous ammonium hydroxide (preferably, with agitation) or catalytic hydrogenation with, for example, palladium or platinum on carbon at, for example, about 2 to 3 atmospheres (preferably, by catalytic hydrogenation; more preferably, by catalytic hydrogenation with palladium on carbon) as shown, for example, below:

Reaction Scheme B



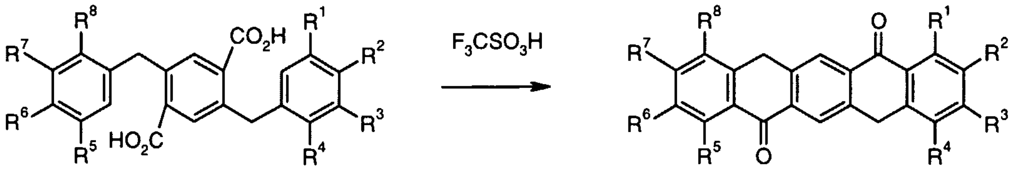
wherein each R (that is, each of the groups R^1 through R^8) is as defined above for Scheme A. If desired, the substituted bis(benzoyl)terephthalic acids can be separated from the substituted bis(benzoyl)isophthalic acids by methods commonly used in the art (for example, by recrystallization, trituration, or chromatography) before the reduction reaction is carried out (or, alternatively, the resulting substituted bis(benzyl)phthalic acid isomers can be separated thereafter).

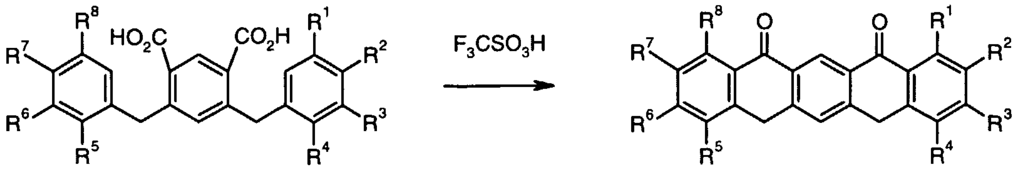
The cyclization step of the process can be accomplished via intramolecular Friedel-Crafts cyclization of the substituted bis(benzyl)phthalic acids to form the corresponding substituted pentacenediones (the substituted 7,14-dihydropentacene-5,12-diones and the substituted pentacene-5,7(12*H*,14*H*)-diones; hereinafter, the "5,12-diones" and the "5,7-diones").

The use of acid catalyzed Friedel-Crafts cyclization to form cyclic ketones is well known in the literature and has been described, for example, by Premasagar et al. in J. Org. Chem., 46(14), 2974 (1981); by Allen et al. in Tetrahedron, 33(16), 2083 (1977); and by Hulin et al. in J. Org. Chem., 49, 207 (1984). These reactions can generally be carried out at about 0°C to 100°C in the presence of a strong acid such as concentrated sulfuric acid, fuming sulfuric acid, polyphosphoric acid or anhydrous hydrofluoric acid. For example, unsubstituted bis(benzoyl)phthalic acid will form the corresponding tetrone when heated to 100°C with concentrated sulfuric acid for several hours.

However, both substituted bis(benzoyl)phthalic acids and substituted bis(benzyl)phthalic acids are usually unreactive under these conditions. It appears that in general the intramolecular Friedel-Crafts cyclization of these substituted compounds cannot be readily accomplished with the strong acids that are typically used for this type of reaction. It has been discovered, however, that Friedel-Crafts cyclization of substituted bis(benzyl)phthalic acids to form the corresponding substituted pentacenediones can be accomplished using an acid composition comprising trifluoromethanesulfonic acid as shown, for example, below:

Reaction Scheme C



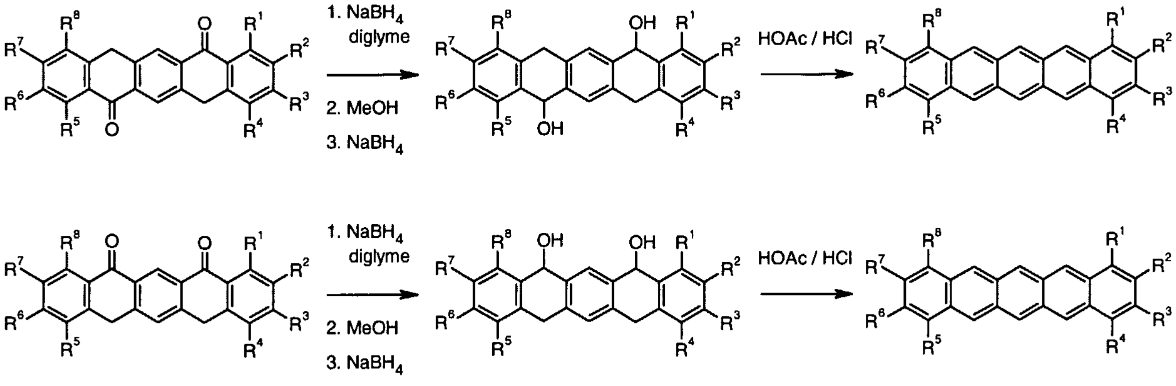


wherein each R (that is, each of the groups R^1 through R^8) is defined as above for Formula II, with the clarification that preferably R^2 and R^6 are moieties other than hydrogen for the substituted 5,12-dione (and that R^2 and R^7 are moieties other than hydrogen for the substituted 5,7-dione).

The cyclization reaction can be carried out at room temperature or, optionally, at elevated temperatures (for example, a temperature in the range of about 20°C to 60°C) and, preferably, with agitation of the reaction mixture. The trifluoromethanesulfonic acid can be used alone or in combination with, for example, trifluoroacetic acid, or a perfluoroalkanesulfonic acid of higher molecular weight than trifluoromethanesulfonic acid, or a neutral solvent that will not react with trifluoromethanesulfonic acid (for example, a hydrocarbon solvent, a chlorinated solvent such as methylene chloride or a fluorinated solvent) or a Lewis acid (for example, antimony pentafluoride).

The resulting substituted pentacenediones can be reduced and dehydrated to give the corresponding substituted pentacenes. Good yields can usually be obtained by, for example, a sodium borohydride reduction procedure, as shown, for example, below:

Reaction Scheme D



wherein each R (that is, each of the groups R^1 through R^8) is defined as above for Reaction Scheme C.

Treatment of the diones with sodium borohydride in solvent, such as alcohol(s) or ether(s) (preferably, diglyme) or a combination thereof, preferably followed by addition of methanol and then treatment with additional sodium borohydride gives the corresponding substituted diols. The diols can then be dehydrated to substituted pentacenes by treatment with an acid (for example, hydrochloric acid), preferably with application of heat (for example, heating to about 50°C to 60°C) and agitation. Suitable acids include, for example, acetic acid, phosphoric acid, hydrochloric acid, sulfuric acid, hydroiodic acid, hydrobromic acid, trifluoroacetic acid, and trifluoromethanesulfonic acid. Optionally, the diols can first be treated with a weak acid, such as acetic acid, followed by treatment with a stronger acid, such as hydrochloric acid.

Benzoacenes can be prepared by any known method, for example, as described in E. Clar, Polycyclic Hydrocarbons, Vol. 1, Academic Press (London and New York) and Springer-Verlag (Berlin, Gottingen and Heidelberg), 1964, which depicts 1,2-benzopentacene and 1,2:3,4-dibenzopentacene at pages 436-446.

If desired, the resulting substituted acenes can be purified one or more times by standard methods such as recrystallization, sublimation, trituration, continuous extraction, chromatography, or a combination thereof. Purification can be accomplished by sublimation, for example, using a 3-zone furnace (*e.g.*, a Thermolyne 79500 tube furnace, available from Barnstead Thermolyne, Dubuque, Iowa) at reduced pressure under a constant flow of nitrogen gas.

The organic semiconductor layer can be provided in the OTFT of the invention by any useful means, such as for example, vapor deposition, spin coating, and printing techniques including transfer printing.

Self-Assembled Monolayer

The self-assembled monolayer (SAM) is interposed between the gate dielectric and the organic semiconductor layer. The monolayer is a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer.

Self-assembled monolayer precursors provide molecules that form a self-assembled layer, typically a monolayer, on the target surface. Self-assembled thin layers are often prepared by coating a substrate of interest in a dilute solution of the self-assembling precursor or by exposure to a vapor phase containing the precursor, and allowing layer formation to proceed. The precursor molecules form a molecular layer on the substrate with the reactive groups attached to the dielectric surface. Once formed, the layer does not redissolve in the solvent from which it was deposited.

Generally, materials that form crosslinks independently of monolayer formation that may be in competition with the adsorption or bonding reaction to the gate dielectric, such as trifunctional silanes, are not desired for the monolayer precursor of the present invention. However, materials that have functional groups effective to bond to the gate dielectric and have other groups that may form crosslinks after formation of the SAM can be used.

The monolayer precursor comprises a composition having the formula:

$$X\text{-}Y\text{-}Z_n,$$

wherein X is H or CH_3;

Y is a linear or branched C_5-C_{50} aliphatic or cyclic aliphatic connecting group, or a linear or branched C_8-C_{50} group comprising an aromatic group and a C_3-C_{44} aliphatic or cyclic aliphatic connecting group;

Z is selected from $-PO_3H_2$, $-OPO_3H_2$, benzotriazolyl ($-C_6H_4N_3$), benzotriazolylcarbonyloxy ($-OC(=O)C_6H_4N_3$), benzotriazolyloxy ($-O-C_6H_4N_3$), benzotriazolylamino ($-NH-C_6H_4N_3$), -CONHOH, -COOH, -OH, -SH, -COSH, -COSeH, $-C_5H_4N$, -SeH, $-SO_3H$, isonitrile (-NC), chlorodimethylsilyl ($-SiCl(CH_3)_2$), dichloromethylsilyl ($-SiCl_2CH_3$), amino, and phosphinyl;

and n is 1, 2, or 3 provided that $n = 1$ when Z is $-SiCl(CH_3)_2$ or $-SiCl_2CH_3$.

Herein, the reaction between any gate dielectric and a functional group within the self-assembled monolayer precursor is preferably a bonding interaction (*e.g.*, covalent or ionic). Herein, a self-assembled monolayer refers to a mono-molecular layer on the order of about 5 Angstroms (Å) to about 30 Å thick.

In preferred embodiments, Y can be a saturated aliphatic group, an unsaturated aliphatic group, a saturated cyclic aliphatic group, and an unsaturated cyclic aliphatic group, or a combination thereof, each of which may be linear or branched.

The monolayer precursor may comprise a linear or branched phosphonoalkane having from 5 to 50 carbon atoms, more preferably 6 to 24. The monolayer precursor may comprise a composition of the formula:

$$CH_3\text{-}(CH_2)_m\text{-}PO_3H_2,$$

wherein m is an integer from 4 to 21.

Particular examples for the monolayer precursor include 1-phosphonooctane, 1-phosphonohexane, 1-phosphonohexadecane, and 1-phosphono-3,7,11,15-tetramethylhexadecane.

One member of a class of branched hydrocarbon monolayer precursors useful in the practice of the present invention is 1-phosphono-3,7,11,15-tetramethylhexadecane. Other members of this class include 1-phosphono-2-ethylhexane, 1-phosphono-2,4,4-trimethylpentane, and 1-phosphono-3,5,5-trimethylhexane. The 1-phosphono-3,7,11,15-tetramethylhexadecane can be prepared from a commercially available allylic alcohol precursor by reduction of the alkene double bond, conversion of the alcohol to the corresponding bromide, and then conversion of the bromide to the corresponding phosphonic acid. More specifically, 1-phosphono-3,7,11,15-tetramethylhexadecane can be obtained by reducing 3,7,11,15-tetramethyl-2-hexadecen-1-ol to 3,7,11,15-tetramethyl-1-hexadecanol, converting the 3,7,11,15-tetramethyl-1-hexadecanol to 1-bromo-3,7,11,15-tetramethylhexadecane, and then converting the 1-bromo-3,7,11,15-tetramethylhexadecane to 1-phosphono-3,7,11,15-tetramethylhexadecane. These synthetic transformations are accomplished using materials and methods familiar to those skilled in the art. Starting materials other than 3,7,11,15-tetramethyl-2-hexadecen-1-ol and individual reaction sequences other than that described above may also be used to synthesize 1-phosphono-3,7,11,15-tetramethylhexadecane, as well as other members of this class of branched hydrocarbon monolayer precursors, and the specifically exemplified monolayer precursor and method of preparation should not be construed as unduly limiting.

The self-assembled monolayer precursor is provided on the gate dielectric by any known method. For example, the precursor can be provided through a process such as spray coating, spinning, dip coating, gravure coating, microcontact printing, ink jet printing, stamping, transfer printing, and vapor deposition. The self-assembled monolayer precursor is allowed to interact with the gate dielectric surface. The interaction or reaction may be instantaneous or may require time, in which case increasing the temperature can reduce the necessary time. When a solution of the self-assembled monolayer precursor is provided on the gate dielectric layer, the solvent is removed by a method compatible with the materials involved, for example by heating. Any excess monolayer precursor is typically rinsed away before deposition of the organic semiconductor. In a preferred embodiment, the SAM is provided by the steps consisting essentially of coating the precursor, heating, and rinsing without further processing.

In one embodiment, the source and drain electrodes are provided adjacent to the gate dielectric before providing the monolayer precursor. Then, the monolayer precursor is provided. After the self-assembled monolayer is complete, the organic semiconductor layer is provided over the source and drain electrodes and over the self-assembled monolayer adjacent to the gate dielectric.

The organic thin film transistor (OTFT) of the present invention has one or more advantages over known organic thin film transistors. These advantages are apparent, for example, in charge-carrier mobility. The present invention provides OTFTs having a charge-carrier mobility better than a comparison OTFT not made according to the present invention and thus lacking the inventive self-assembled monolayer, but otherwise similar in every construction feature. The OTFT of the invention preferably has a charge-carrier mobility of at least about 25% better, more preferably at least about 50% better, and in some embodiments at least about 100% better, than the charge-carrier mobility of a comparison OTFT similar in every respect but lacking the SAM of the present invention. Such improvements in charge-carrier mobility are provided while maintaining other OTFT properties within desirable ranges. For example, the above-described improvements are obtained while providing a threshold voltage between about 25 and -25 V, a subthreshold slope below about 10 V/decade (absolute value), and an on/off ratio of at least about 10^4.

More specifically, in an embodiment comprising a substituted pentacene as the organic semiconductor, the invention provides an OTFT with a charge-carrier mobility at least about 0.2 cm^2/Vs, more preferably at least 0.5 cm^2/Vs, and even more preferably at least about 1.0 cm^2/Vs. In some embodiments of the present invention, the charge-carrier mobility is above 2.0 cm^2/Vs.

One embodiment of the present invention provides a p-type semiconductor OTFT having a threshold voltage of between about –25 and 25 V, preferably a threshold voltage of between about 0 and -10 V, more preferably between about 0 and –5 V.

The invention provides an OTFT with a subthreshold slope below about 10 V/decade (absolute value), preferably a subthreshold slope below about 5 V/decade (absolute value), more preferably below about 2 V/decade (absolute value). The invention provides an OTFT with an on/off ratio of at least about 10^4, preferably at least about 10^5, more preferably at least about $5x10^5$, and even more preferably at least about 10^6.

Various combinations of these properties are possible. For example, in one embodiment of the invention, the p-type semiconductor OTFT has a charge-carrier mobility of at least about 1 cm^2/Vs, a negative threshold voltage, a subthreshold slope below about 5 V/decade, and an on/off ratio at least about 10^5.

Methods of Making an OTFT

The present invention also provides a method of making a thin film transistor comprising the steps of: (a) providing a substrate; (b) providing a gate electrode material on the substrate; (c) providing a gate dielectric on the gate electrode material; (d) providing a self-assembled monolayer (SAM) adjacent to the gate dielectric, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, the precursor comprising a composition having the formula $X\text{-}Y\text{-}Z_n$, as described above; (e) applying an organic semiconductor layer as described above on the monolayer; and (f) providing a source electrode and a drain electrode contiguous to the organic semiconductor layer.

The organic semiconductor layer can be provided over or under the source and drain electrodes, as described above in reference to the thin film transistor article. The present invention also provides an integrated circuit comprising a plurality of OTFTs made by the process described above.

The present invention further provides a method of making an integrated circuit comprising providing a plurality of OTFTs as described above. Thus, the present invention is embodied in an article that comprises one or more of the OTFTs described. Such articles include, for example, radio-frequency identification tags, backplanes for active matrix displays, smart cards, memory devices, and the like. In devices containing the OTFTs of the present invention, such OTFTs are operatively connected by means known in the art.

The entire process of making the thin film transistor or integrated circuit of the present invention can be carried out below a maximum substrate temperature of about 450°C, preferably below about 250°C, more preferably below about 150°C, and even more preferably below about 70°C, or even at temperatures around room temperature (about 25°C). The temperature selection generally depends on the substrate and processing parameters known in the art, once one is armed with the knowledge of the present invention contained herein. These temperatures are well below traditional integrated circuit and semiconductor processing temperatures, which enables the use of any of a variety of relatively inexpensive substrates, such as flexible polymeric substrates. Thus, the invention enables production of relatively inexpensive integrated circuits containing organic thin film transistors with significantly improved performance.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Examples

Test Methods

A. Film Thickness

Single wavelength ellipsometry was employed to obtain estimates of surface treatment organic film thickness. Substrate values of Psi and Delta (ψ_s and Δ_s) were obtained from the cleaned substrates at an angle of incidence of 70° and a wavelength of 632.8 nm using a Gaertner Dual Mode Automatic Ellipsometer, model L116A (Gaertner Co., Skokie, IL). The film was applied to the substrates, and film values were measured (ψ_f and Δ_f).

Ellipsometry modeling software, WVASE32 (from J. A. Woollam, Inc., Lincoln, NE) was used to construct an optical model consisting of 1500 Å Al_2O_3 on 10 Å SiO_2 on Si. Typical optical constants (included with the software) were employed for the SiO_2 and Si layers. The floating variables in the fit were the thickness (d) and refractive index (n) of the Al_2O_3. Seed values of 1500 Å and n = 1.77 were used. Typical final fit values were between 1400Å and 1700Å with n between 1.56 and 1.60.

Once ψ_s and Δ_s were fit, the floating variables (d_{Al2O3} and n_{Al2O3}) were then fixed. An organic layer was added to the optical model, between the air and dielectric layers. This layer had a variable thickness, but its refractive index was fixed at 1.46. The organic layer thickness was then varied to achieve the best fit to ψ_f and Δ_f. This organic layer thickness was reported as the thickness of the self-assembled monolayer.

For more information see Laibinis, *et al.*, "Comparison of the structures and wetting properties of self-assembled monolayers of normal-alkanethiols on the coinage metal surfaces, Cu, Ag, Au", *J. Am. Chem. Soc.*, Vol. 113, pages 7152-67, 1991.

B. Thin Film Transistor Performance

Transistor performance was tested at room temperature in air using techniques known in the art, for example as shown in S.M. Sze, *Physics of Semiconductor Devices*, page 442, John Wiley & Sons, New York, 1981. A Semiconductor Parameter Analyzer (model 4145A from Hewlett-Packard, San Jose, CA) was used for the results below.

The square root of the drain current (I_d) was plotted as a function of gate-source bias (V_g), from +10V to –40V for a constant source-drain bias (V_d) of –40V, and the saturation field effect mobility was calculated from the straight line portion of the curve using the specific capacitance of the gate dielectric, the channel width and the channel length. The x-axis extrapolation of this straight-line fit was taken as the threshold voltage (V_t). In addition, plotting I_d as a function of V_g yielded a curve where a straight line fit was drawn along a portion of the curve containing V_t. The inverse of the slope of this line was the subthreshold slope (S). The on-off ratio was taken as the difference between the minimum and maximum current values of the I_d-V_g curve.

Materials

Monolayer Precursor

The self-assembled monolayer precursor, 1-phosphonohexadecane (CH_3-$(CH_2)_{15}$-PO_3H_2), was commercially available from Oryza Laboratories, Chelmsford, MA,

The phosphonic acid as received contained residual ethyl esters, so the material was purified by hydrolysis of residual ester in aqueous hydrochloric acid at 100°C followed by recrystallization of the phosphonic acid from heptane using procedures known to those skilled in the art.

Organic Semiconductor

2,9-Dimethylpentacene was prepared as described in U.S.S.N. 09/966,961 filed on September 27, 2001 and further purified in a gradient furnace at a maximum temperature of 300°C and a pressure of about 0.67 MPa under a flowing gas (nitrogen with 4 volume % hydrogen, 30-35 cm^3/sec). The sublimed material was collected and used without further purification.

Substrate

Single crystal <100> orientation silicon wafers were obtained from Silicon Valley Microelectronics, San Jose, California with a 1500Å layer of alumina deposited on each wafer front via chemical vapor deposition methods and a 5000Å layer of aluminum metal vapor deposited onto the backside of each wafer. The doped wafer capped with aluminum served as the gate electrode and the aluminum oxide functioned as the gate dielectric when organic thin film transistors were prepared with this substrate material.

Example 1 and Comparative Example C1

A silicon wafer substrate described above was cleaned using a 5-minute exposure in a UV/ozone chamber (home-built, short-wavelength UV). The monolayer precursor (1-phosphonohexadecane) was then applied to the alumina surface of the substrate by spin coating a 0.1 weight percent solution of the precursor in absolute ethanol at 300 rpm for 5 seconds followed by 2000 rpm for 15 seconds. The coated substrate was then heated at 150°C for 3 min on a vacuum hotplate, rinsed in fresh ethanol, and dried in a stream of nitrogen. The result was a self-assembled monolayer with a thickness of 19Å (determined as described above) on the alumina layer of the substrate. A control substrate without the monolayer was prepared by treating a silicon wafer substrate described above with consecutive rinses of acetone, methanol, 2-propanol, and water, drying in a stream of nitrogen, baking on a hot plate at 100°C for 3 minutes, and exposure to UV/ozone for 15 minutes in a chamber (home-built, short-wavelength UV).

The purified 2,9-dimethylpentacene was deposited by thermal evaporation under vacuum (approximately 1.33 x 10^{-4} Pa with a source temperature of about 285-300°C) onto the above self-assembled monolayer prepared surface and onto the alumina surface of the control substrate at a rate of 0.5Å per second to reach a thickness of 600Å as measured by a quartz crystal microbalance. Gold source and drain electrodes were then deposited through a shadow mask onto the resulting 2,9-dimethylpentacene layers by thermal evaporation in vacuum. Several hundred organic thin film transistors (OTFTs) without (Comparative Example C1) and with the self-assembled monolayer were prepared in this manner with channel lengths of 30-70 μm and widths of 1000 μm.

A representative sampling of 6 OTFTs with the self-assembled monolayer and 4 OTFTs without the monolayer were tested as described above for device performance. The averaged results appear below in Table 1.

Table 1. OTFT Performance

Example	Mobility (cm^2/Vs)	Threshold Voltage (V)	Subthreshold Slope (V/decade)	On/Off Current Ratio
1	2.48	-3.80	1.92	$1.97x10^6$
C1	1.11	-3.55	1.23	$1.31x10^6$

The results in Table 1 show that the presence of the self-assembled monolayer at the surface upon which the 2,9-dimethylpentacene layer was formed significantly increased the charge carrier mobility of the resulting OTFTs compared with OTFTs without the monolayer (Comparative Example C1).

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

We claim:

1. An organic thin film transistor (OTFT) comprising a self-assembled monolayer interposed between a gate dielectric and an organic semiconductor layer, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, the precursor comprising a composition having the formula:

$$X\text{-}Y\text{-}Z_n,$$

wherein X is H or CH_3; Y is a linear or branched C_5-C_{50} aliphatic or cyclic aliphatic connecting group, or a linear or branched C_8-C_{50} group comprising an aromatic group and a C_3-C_{44} aliphatic or cyclic aliphatic connecting group; Z is selected from $-PO_3H_2$, $-OPO_3H_2$, benzotriazolyl ($-C_6H_4N_3$), benzotriazolylcarbonyloxy ($-OC(=O)C_6H_4N_3$), benzotriazolyloxy ($-O-C_6H_4N_3$), benzotriazolylamino ($-NH-C_6H_4N_3$), -CONHOH, -COOH, -OH, -SH, -COSH, -COSeH, $-C_5H_4N$, -SeH, $-SO_3H$, -NC, $-SiCl(CH_3)_2$, $-SiCl_2CH_3$, amino, and phosphinyl; and n is 1, 2, or 3 provided that n = 1 when Z is $-SiCl(CH_3)_2$ or $-SiCl_2CH_3$; and wherein the organic semiconductor layer comprises a material selected from:

an acene, substituted with at least one electron-donating group, halogen atom, or a combination thereof, or

a benzo-annellated acene or polybenzo-annellated acene, which optionally is substituted with at least one electron-donating group, halogen atom, or a combination thereof.

2. The OTFT of claim 1 wherein the at least one electron-donating group is selected from an alkyl, alkoxy, or thioalkoxy, and having from 1 to 24 carbon atoms.

3. The OTFT of claim 1 having a threshold voltage between about –25 and 25 volts, a subthreshold slope below about 10 volts per decade (absolute value), an on/off ratio of at least about 10^4, and a charge-carrier mobility improvement over a comparison OTFT of the same construction but lacking the self-assembled monolayer selected from at least about 25%, at least about 50%, and at least about 100%.

4. The OTFT of claim 1 wherein the semiconductor layer comprises a material selected from C_1-C_{24} alkyl-, polyalkyl-, alkoxy-, or polyalkoxy-substituted acenes.

5. The OTFT of claim 1 wherein the semiconductor layer comprises a material selected from C_1-C_{24} alkyl-, polyalkyl-, alkoxy-, or polyalkoxy-substituted anthracene.

6. The OTFT of claim 1 wherein the semiconductor layer comprises a material selected from C_1-C_{24} alkyl-, polyalkyl-, alkoxy-, or polyalkoxy-substituted tetracene.

7. The OTFT of claim 1 wherein the semiconductor layer comprises a material selected from C_1-C_{24} alkyl-, polyalkyl-, alkoxy-, or polyalkoxy-substituted pentacene.

8. The OTFT of claim 1 wherein at least one R group is selected from methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, 2-methylhexyl, 2-ethylhexyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-dodecyl, *n*-octadecyl, or 3,5,5-trimethylhexyl.

9. The OTFT of claim 1 wherein the semiconductor comprises a material selected from 1-methylanthracene, 2-methylanthracene, 1,2-dimethylanthracene, 2,3-dimethylanthracene, 2,3,6,7-tetramethylanthracene, 1,2,3,4-tetramethylanthracene, 2-ethylanthracene, 2,6-diethylanthracene, 2-hexylanthracene, 2,6-dihexylanthracene, 1-methyltetracene, 2-methyltetracene, 2,3-dimethyltetracene, 2,8-dimethyltetracene, 2,3,9,10-tetramethylpentacene, 2-ethyltetracene, 2,8-diethylpentacene, 2,9-diethylpentacene, 2-hexyltetracene, 2-nonyltetracene, 1-methylpentacene, 2-methylpentacene, a 2,6-dialkylanthracene, a 2,8-dialkyltetracene, a 2,3-dialkylpentacene, a 2,9-dialkylpentacene, a 2,10-dialkylpentacene, 2-ethylpentacene, 2,10-dialkoxypentacenes, 2,3,9,10-tetraalkylpentacenes, 1,4,8,11-tetraalkoxypentacenes, or 1,2,3,4,8,9,10,11-octaalkylpentacenes, dibenzo[de,qr]tetracene, zethrene, dibenzo[de,st]pentacene, and dibenzo[de,uv]pentacene; wherein said alkyl or alkoxy group in each formula has from 1 to 24 carbons.

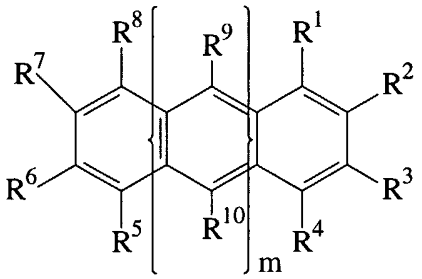
10. The OTFT of claim 1 wherein the semiconductor comprises a material selected from 2,3-dimethylpentacene, 2,9-dimethylpentacene, 2,10-dimethylpentacene, 2,10-

dimethoxypentacene, 2,3,9,10-tetramethylpentacene, 1,4,8,11-tetramethoxypentacene, or 1,2,3,4,8,9,10,11-octamethylpentacene.

11. An organic thin film transistor (OTFT) comprising a self-assembled monolayer interposed between a gate dielectric and an organic semiconductor layer, the monolayer being a product of a reaction between the gate dielectric and a precursor to the self-assembled monolayer, the precursor comprising a composition having the formula:

$$X\text{-}Y\text{-}Z_n,$$

wherein X is H or CH_3; Y is a linear or branched C_5-C_{50} aliphatic or cyclic aliphatic connecting group, or a linear or branched C_8-C_{50} group comprising an aromatic group and a C_3-C_{44} aliphatic or cyclic aliphatic connecting group; Z is selected from $-PO_3H_2$, $-OPO_3H_2$, benzotriazolyl ($-C_6H_4N_3$), benzotriazolylcarbonyloxy ($-OC(=O)C_6H_4N_3$), benzotriazolyloxy ($-O-C_6H_4N_3$), benzotriazolylamino ($-NH-C_6H_4N_3$), -CONHOH, -COOH, -OH, -SH, -COSH, -COSeH, $-C_5H_4N$, -SeH, $-SO_3H$, -NC, $-SiCl(CH_3)_2$, $-SiCl_2CH_3$, amino, and phosphinyl; and n is 1, 2, or 3 provided that n = 1 when Z is $-SiCl(CH_3)_2$ or $-SiCl_2CH_3$; and wherein the organic semiconductor layer comprises a semiconductor of the formula:



wherein each R group is independently selected from electron-donating groups, halogen atoms, hydrogen atoms, and combinations thereof, provided that not all R groups are hydrogen; m is 1, 2, 3, or 4; each R^9 and R^{10} is independently H or any R group; and any combination of two adjacent R groups may together form a five or six carbon cyclic aliphatic or aromatic group;

provided that neither R^2 with R^3 nor R^6 with R^7 form part of a six-member aromatic ring; and

provided that when m is 1 neither R^9 nor R^{10} form part of a six-member aromatic ring.

12. The OTFT of claim 11 wherein Y is selected from a saturated aliphatic group, an unsaturated aliphatic group, a saturated cyclic aliphatic group, and an unsaturated cyclic aliphatic group, or a combination thereof, each of which may be linear or branched.

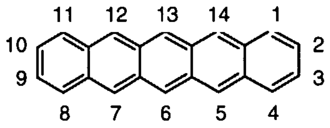
13. The OTFT of claim 11 wherein the monolayer precursor comprises a composition selected from 1-phosphonohexane, 1-phosphonooctane, 1-phosphonohexadecane, and 1-phosphono-3,7,11,15-tetramethylhexadecane.

14. The OTFT of claim 11 wherein the monolayer precursor comprises a composition selected from $CH_3\text{-}(CH_2)_m\text{-}PO_3H_2$, wherein m is an integer from 4 to 21.

15. The OTFT of claim 11 wherein the monolayer precursor comprises a linear or branched phosphonoalkane having from 5 to 50 carbon atoms.

16. The OTFT of claim 15 wherein the organic semiconductor layer comprises a pentacene substituted with at least one alkyl or alkoxy group having from 1 to 24 carbons.

17. The OTFT of claim 16 wherein the pentacene has the structure:



and is substituted at one or more of the 1, 2, 3, 4, 8, 9, 10, and 11 positions.

18. The OTFT of claim 17 wherein the semiconductor is selected from a 2,3-, 2,9-, or 2,10- dialkyl- or dialkoxy-substituted pentacene wherein each alkyl or alkoxy group independently has from 1 to 24 carbons, or a 2,3,9,10- or 1,4,8,11- tetraalkyl- or tetraalkoxy-substituted pentacene wherein each alkyl or alkoxy group independently has from 1 to 24 carbons.

19. The OTFT of claim 15 wherein the organic semiconductor is selected from 2,3-, 2,9- or 2,10-dimethylpentacene.

20. An integrated circuit comprising a multiplicity of thin film transistors according to claim 1.

21. An integrated circuit comprising a multiplicity of the thin film transistors of claim 1 on a non-participating substrate, which optionally is flexible.

22. A method of making an organic thin film transistor comprising:

a) providing a substrate;

b) providing a gate electrode material on the substrate;

c) providing a gate dielectric on the gate electrode material;

d) providing a self-assembled monolayer according to claim 1 adjacent to the gate dielectric and

e) applying an organic semiconductor layer according to claim 1 on the monolayer; and

f) providing a source electrode and a drain electrode contiguous to the organic semiconductor layer.

23. The method of claim 22 wherein the steps are performed in the order (a) through (f).

24. The method of claim 22 wherein an excess of the precursor is provided in step (d), followed by allowing sufficient time for interaction, and removing excess precursor.

25. The method of claim 22 wherein the substrate is flexible.

26. The method of claim 22 carried out in its entirety below a peak substrate temperature selected from below about 250°C, below about 150°C, and below about 70°C.

27. The method of claim 22 carried out on a web.

28. An integrated circuit comprising a plurality of thin film transistors made by the method of claim 22.

INTERNATIONAL SEARCH REPORT

Inter[illegible]nal Application No
PCT/US 03/03905

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/40 H01L51/30 H01L51/20

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*)
IPC 7 H01L B05D

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 practical, search terms used)

EPO-Internal, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 01502 A (THIN FILM ELECTRONICS ASA ;WANG JIANNA (US); JACKSON THOMAS (US)) 4 January 2001 (2001-01-04) page 9, line 22 - line 25; figure 6 ---	1,20-22, 25,28

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document 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 23 June 2003	Date of mailing of the international search report 01/07/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Pusch, C

INTERNATIONAL SEARCH REPORT

Inte[illegible]onal Application No
PCT/US 03/03905

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHUNG-KUN SONG: "Effects of hydrophobic treatment on the performance of pentacene TFT" INTERNATIONAL DISCUSSION AND CONFERENCE ON NANO INTERFACE CONTROLLED ELECTRONIC DEVICES, KYONGJU, SOUTH KOREA, 16-20 JULY 2001, vol. 12C, no. 2, pages 136-138, XP009012128 KIEE International Transactions on Electrophysics and Applications, April 2002, Korean Inst. Electr. Eng, South Korea ISSN: 1598-2610 the whole document	1,2, 4-19,22
Y	US 4 539 061 A (SAGIV JACOB) 3 September 1985 (1985-09-03) column 4, line 11 - line 39	1,2, 12-15,22
Y	DE 198 15 220 A (UNIV DRESDEN TECH) 30 September 1999 (1999-09-30) column 2, line 15 - line 49	1,2, 12-15,22
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 03, 30 March 2000 (2000-03-30) & JP 11 354277 A (NEC CORP), 24 December 1999 (1999-12-24) abstract	1,2, 4-11, 16-19,22
Y	US 4 363 859 A (SASAKI MASAOMI ET AL) 14 December 1982 (1982-12-14) column 1, line 51 - line 69	1,2, 4-11, 16-19,22
Y	US 6 232 157 B1 (RAJU VENKATARAM REDDY ET AL) 15 May 2001 (2001-05-15) column 5, line 61 - line 62	1,2, 4-11, 16-19,22
Y	EP 0 344 111 A (CIBA GEIGY AG) 29 November 1989 (1989-11-29) page 2, line 5-8	1,11,22

2

Continuation of Box I.2

Claims Nos.: 3

Present claim 3 relates to a product defined by reference to a desirable characteristic or property, namely

- a specific threshold voltage,
- a specigfic subthtreshold slope,
- a specific on/off ratio, and
- a specific charge carrier mobility

without describing the parameters necessary for obtaining these properties (device geometry, organic semiconductor, film thicknesses etc.). In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, no search has been carried out for claim 3.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/03905

Box I Observations where certain claims were found unsearchable (Continuation of item 1 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.: 3
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:
see FURTHER INFORMATION sheet PCT/ISA/210

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 II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

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

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 an additional fee, this Authority did not invite payment of any additional fee.

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.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter[illegible]onal Application No
PCT/US 03/03905

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