FIELD EFFECT ELEMENTS

Abstract: A field effect element comprising: a source electrode (6) and a drain electrode (7), a semiconducting layer (2) comprising a semiconducting compound being in contact with the source electrode (6) and the drain electrode (7), - a gate electrode (5), and a dielectric layer (3) comprising one or more compounds selected from hygroscopic organic compounds and/or from nanoparticulate inorganic compounds being arranged between the semiconducting layer (2) and the gate electrode (5), wherein said hygroscopic organic compounds have a water absorption capability of more than 1.2 % by weight, and a hydrophobic insulating layer (4) being arranged between the gate electrode (5) and the dielectric layer (3) preventing diffusion of water into the one or more hygroscopic compounds of the dielectric layer during the time of use of the field effect element, said hydrophobic insulating layer (4) having a water absorption capability of less than 1.2 % by weight, the semiconducting layer (2), the dielectric layer (3) or the hydrophobic insulating layer (4), or a combination thereof, being disposable from a liquid; and a process for producing the same.
Field Effect Elements

Field effect elements, particularly field effect transistors (FET), based on inorganic materials are known for decades. A typical FET comprises several layers which may be adapted to the intended use. It typically contains a dielectric, a semiconductor, a source and a drain electrode electrically connected to the semiconductor and a gate electrode which are disposed on a substrate in a layer structure.

In recent years, most of thin film transistors (TFT) used for display application consisted of amorphous silicon as the semiconductor, silicon oxide, or silicon nitride as the dielectrics, and metal electrodes. However, with the recent development of various conductive organic materials, research into developing an organic thin film transistor (OTFT) using an organic material as the semiconductor has been made actively. Since its first development in the 1980s, the OTFT has widened its application into functional electronic devices and optical devices.

The organic semiconductor in the OTFT has several advantages with respect to its inorganic counterpart. It can be processed in any shape from fiber to film, shows high mechanical flexibility, can be manufactured at a low cost and is of low weight. The main advantage, however, is the possibility to manufacture the whole semiconductor device by depositing the layer structure on a plastic substrate under atmospheric pressure, e.g. by printing, so that low-priced FET can be realized.

In some applications water or polar solvent processible dielectric materials are used. However these materials mostly contain polymers comprising hydrophilic functional groups like hydroxyl, ether, or ester groups. During the use of the FETs these hygroscopic polymers have the tendency to incorporate water in amounts changing the characteristics of the dielectric layer dramatically, particularly in a top gate configuration where the hygroscopic insulator is deposited on top of the semiconducting layer.

WO 03/052841 discloses a layer structure for an OFET comprising a low-k non-polar organic insulating layer, which may be combined with a high-k organic layer. The low-k layer is arranged to be in direct contact with the semiconducting layer.

US-A 2005/0001210 discloses a layer structure comprising a high k organic material being in direct contact with the gate electrode, which is combined with a low-k organic insulating layer.

Despite their obvious advantages, the relatively large hysteresis of OTFTs fabricated with polar gate dielectrics has been a serious obstacle to the realization of functional circuits. For general organic circuits applications such as radio-frequency identification
transponders (RFIDs), it is essential to reduce the hysteresis because the threshold voltage \( V_t \) shift caused by the hysteresis behaviour may result in failure of the circuit.

In WO 01/47043 a diffusion barrier layer containing both hydrophilic and hydrophobic groups is described. The barrier layer protects the semiconducting layer and the insulating layer against unintentional doping by impurities and ionic diffusion during the deposition of the gate electrode. Optionally, the diffusion barrier layer may comprise a non-polar polymer, preferably a semiconducting non-polar conjugated polymer or a polyfluorene derivate. Since they were not exposed to humidity before testing there is no difference shown between the use of a diffusion barrier or non-use of it.

Although polyvinyl alcohol (PVOH) is mentioned as potential insulating material, which is a hydrophilic polymer, it is used in a much thinner insulating layer which reduces the hysteresis effect of water incorporated in the dielectric after the manufacturing process has been finished.

It is therefore an object of the present invention to provide an organic field effect element which shows a low hysteresis particularly if hygroscopic dielectric materials are used to form the dielectric layer.

Unexpectedly it was found that, when using a multi-layered gate insulator including a dielectric layer and a hydrophobic insulating layer arranged between the gate electrode and the dielectric layer, the OTFT thus obtained exhibits low hysteresis during the whole lifetime.

Therefore, according to a first aspect of the present invention a field effect element is provided comprising

- a source electrode and a drain-electrode,
- a semiconducting layer comprising an organic semiconductor compound being in contact with the source electrode and the drain electrode,
- a gate electrode, and
- a dielectric layer comprising one or more compounds selected from hygroscopic organic compounds and from nanoparticulate inorganic compounds being arranged between the semiconducting layer and the gate electrode, wherein said hygroscopic organic compounds have a water absorption capability of more than 1.2 % by weight, and
- a hydrophobic insulating layer being arranged between the gate electrode and the dielectric layer preventing diffusion of water into the one or more hygroscopic compounds of the dielectric layer during the time of use of the field effect element, said hydrophobic insulating layer having a water absorption capability of less than 1.2 % by weight.
The semiconducting layer, the dielectric layer or the hydrophobic insulating layer, or a combination thereof, must be disposable from a liquid.

In this way the absorption of water molecules by highly hygroscopic dielectric during its use is avoided and thus the parasitic polarization effects in the dielectric layer caused by water is reduced.

Hygroscopic according to the present invention characterizes a material having a water absorption capability, i.e. a saturated water content at equilibrium, of more than 1.2 % by weight at a temperature of 22 °C and a relative humidity of 47 %. Preferably the water absorption capability is 1.5 % by weight or more, more preferably 2 % by weight or more, even more preferably 2.5 % by weight or more. Most preferably the water absorption capability is 3 % by weight or more. The hygroscopic material may be a single compound or a mixture of compounds.

The dielectric layer may also comprise a nanocomposite dielectric material comprising nanoparticulate inorganic materials, preferably metal oxides. Examples of nanoparticulate materials are Ta2O5, Y2O3, TiO2, CeO2, ZrO2. To be disposable from a liquid, particularly to be printable, these materials have to be bound in a polymer matrix of an insulating polymer as described for example in US 2005/0001210 A1. These polymers forming the matrix may be hygroscopic or non-hygrosopic. The nanoparticulate inorganic materials preferably have a diameter of 1 to 100 nm without being restricted thereto. The dielectric layer may also comprise any inorganic dielectric material as SiO2, Spin on Glass (e.g. organosilane) or Al2O3.

In a preferred embodiment the contact angle of the dielectric layer is 60° or less, more preferably 55° or less, most preferably 50° or less.

Hydrophobic in the meaning of the present invention characterizes a material having a water absorption capability of less than 1.2 % by weight at a temperature of 22 °C and a relative humidity of 47 %. Preferably the water absorption capability is 0.8 % or less, more preferably 0.6 % by weight or less. Most preferably the water absorption capability of the hydrophobic material is 0.4 % by weight or less. The hydrophobic material forming the hydrophobic insulating may be a single compound or a mixture of compounds.

In a preferred embodiment the water barrier layer prevents the hygroscopic dielectric layer being penetrated by water at least a factor 10, preferably a factor 100, most preferably a factor 1000 slower than without the barrier layer.
In a preferred embodiment the contact angle of the barrier layer is 60° or more, more preferably 62° or more, most preferably 64° or more.

In a particularly preferred embodiment of the present invention, realizing a bottom contact/top gate configuration, the organic field effect element comprises:

- a source electrode and a drain-electrode,
- a semiconducting layer comprising an organic semiconductor compound being in contact with the source electrode and the drain electrode,
- a dielectric layer,
- a hydrophobic insulating layer, and
- a gate electrode,

arranged in the aforesaid sequence.

Generally the field effect element can have one or more source electrodes and drain-electrodes, one or more semiconducting layers, one or more dielectric layer, one or more hydrophobic insulating layers, and one or more gate electrodes.

In an alternative embodiment (top contact/top gate configuration) the organic field effect element comprises:

- a semiconducting layer comprising an organic semiconductor compound,
- a source electrode and the drain-electrode, both being in contact with the semiconducting layer,
- a dielectric layer,
- a hydrophobic insulating layer, and
- a gate electrode,

arranged in the aforesaid sequence.

The whole dielectric structure may consist only of the dielectric layer comprising one or more compounds selected from hygroscopic organic compounds and from nanoparticulate inorganic compounds according to the present invention or may comprise further layers comprising insulating materials. Therefore the whole dielectric structure may be a mono, di, tri or multiple layer structure. It is preferred to have a low-k insulating layer being arranged between the semiconducting layer and the dielectric layer.

The present invention is particularly useful, if highly hygroscopic dielectrics are used, since they can easily be manufactured by printing from solutions containing water or highly polar solvents like alcohols. It is therefore most preferred for the dielectric layer to comprise polymers having at least one functional group containing at least one hydro-
gen atom, said functional group being capable of forming hydrogen bonds with water. Such functional groups are normally capable of incorporating high amounts of water.

Particularly useful functional groups comprise elements selected from N, O, S and P.

Particularly useful functional groups may be selected e.g. from amine, amide, hydroxyl, carboxyl, thiol or combinations thereof. These functional groups contain at least one hydrogen atom.

In a further preferred embodiment the semiconducting layer, the dielectric layer and the hydrophobic insulating layer essentially consist of organic compounds. It is particularly preferred to form the whole layer structure on a highly flexible organic polymer substrate like polyethylene terephthalate, polyethylene naphthalate or polyimide or mixture thereof without being restricted thereto.

Since the layer structure of the organic field effect element according to the present invention is preferably deposited by mass printing the dielectric layer preferably has a thickness of more than 50 nm, more preferably from 100 nm to 10,000 nm, most preferably from 200 nm to 8,000 nm.

The hydrophobic insulating layer has generally a thickness of from about 10 nm to about 1000 nm, preferably from about 50 to about 500 nm, most preferably from about 100 nm to about 300 nm. A thicker hydrophobic insulating layer would decrease the overall dielectric layer formed by the dielectric layer and the hydrophobic insulating layer too much, a thinner hydrophobic insulating layer would not form a useful barrier to water during the use of the field effect element which may be months or years.

According to a further aspect of the present invention a process for preparing an organic field effect element is provided, the process comprising:

i) providing a substrate,
ii) providing a source electrode and a drain-electrode,
iii) depositing a semiconducting layer comprising an organic semiconductor compound,
iv) depositing dielectric layer comprising a dielectric material, and
v) depositing a hydrophobic insulating layer, and
vi) depositing a gate electrode on the hydrophobic insulating layer,

wherein steps ii) and iii) may be carried out interchangeably and wherein the deposition in at least one of steps iii), iv) and v) is carried out from a liquid. Preferably the steps are carried out sequentially.
In a preferred embodiment the dielectric layer is deposited from a liquid comprising the semiconductor compound. It may be for example a solution or suspension of the dielectric material a solvent. The dielectric layer is preferably deposited from a solution in an aprotic polar solvent.

Besides one layer the whole layer structure can be deposited by any process known in the art. However, it is preferred to deposit all the layers from a liquid, most preferably by a printing process. The liquid may be any liquid capable of dissolving (one phase) or dispersing (at least two phases) the semiconducting compound, which does not strongly interact with the layer deposited below. Preferably the semiconducting layer may be deposited from a solution comprising the semiconductor compound in a solvent. Alternatively the semiconducting layer is deposited from a dispersion or suspension comprising the semiconductor in a liquid. The dielectric layer and the hydrophobic insulating layer may also be deposited from a suspension or preferably from a solution.

Particularly useful solvents for depositing the dielectric layer are protic solvents like water, alcohols or polar aprotic solvents like ketones, ethers without being restricted thereto. Alternatively, non-polar aprotic solvents may be used. Protic solvents are preferred.

In a particular embodiment the liquid for depositing the dielectric layer comprises 10 % by weight or more, preferably more than 20 %, particularly preferred more than 40% of water.

The field effect element is particularly useful for manufacturing of Radio Frequency Identification (RFID) devices, backplane display circuitry, or any integrated circuitry or drivers for memory arrays without being restricted thereto.

Hereinafter, the present invention will be described in more detail with reference to the figures and examples. However, these figures and examples are provided only for illustrative purposes and are not to be construed as limiting the scope of the present invention.

It is shown in

Fig. 1 a bottom contact/top gate arrangement of layers in an OTFT according to a preferred embodiment of the present invention.

Fig. 2 plots of the drain current as a function of gate voltage of an OTFT with a high-k dielectric and a hydrophobic insulation layer as prepared in Example 1

a) after exposition to air;

b) in a glove box without exposition to air.
Fig. 3 plots of the drain current as a function of gate voltage of an OTFT with only a high-k dielectric layer as prepared in comparative Example A
a) after exposition to air;
b) in a glove box without exposition to air.

Fig. 4 plots of the drain current as a function of gate voltage of an OTFT with only a high-k dielectric and a hydrophobic insulation layer in “reverse order” as prepared in comparative Example B.

Fig. 5 plots of the drain current as a function of gate voltage of an OTFT with a sandwiched low-k/high-k/hydrophobic insulation layer arrangement as prepared in Example 2.

Fig. 1 schematically shows a preferred embodiment of the present invention representing a top gate layer structure of an organic field effect transistor. Alternatively, any other layer structure can be used to realize the present invention, as long as the hydrophobic insulating layer is arranged between the gate electrode and the high-k dielectric layer.

The layer structure comprises a substrate 1 on which source and a drain electrodes 6, 7 are formed. On top of the structure the gate electrode 5 is formed. In a bottom gate structure the positions of gate and source/drain electrodes are exchanged.

Materials for the substrate 1 can be any known materials in the art of field effect transistors. Preferably, the substrate is made of plastic, glass, quartz, or silicon, most preferably of thermoplastic polymers like Polyethylene terephthalate.

Materials for the gate electrode 5 and the source/drain electrodes 6, 7 can be any known materials in the art of the thin film transistors. Preferably, the gate and source/drain electrodes are made of inorganics like gold (Au), silver (Ag), aluminum (Al), nickel (Ni), indium thin oxide (ITO), but are not limited thereto. Alternatively, the gate and source and drain electrodes can be manufactured from any conductive organic material, for example polyethylenedioxythiophene, polyaniline or polypyrrole.

With reference to Fig. 1 a semiconducting layer 2 is formed on the substrate 1 or source 6 and drain 7, respectively.

In the organic field effect element of the present invention, the organic semiconducting layer 2 can be made of any materials known as an organic semiconductor including a conducting polymer. Preferably, the organic semiconducting layer is prepared from pentacene, copper phthalocyanine, polythiophene, polyaniline, polyacetylene, polypyr-
role, polyphenylene vinylene or derivatives thereof, but is not limited thereto. Particularly preferred is polythiophene.

The organic semiconductor may be an n or p type. Preferred organic semiconductors have a FET mobility of greater than $10^{-5}$ Cm$^{-2}$V$^{-1}$s$^{-1}$, preferably greater than $10^{-4}$ Cm$^{-2}$V$^{-1}$s$^{-1}$.

The organic semiconductor may be any conjugated aromatic molecule containing at least three aromatic rings. Preferred organic semiconductors contain 5, 6 or 7 membered aromatic rings, especially preferred organic semiconductors contain 5 or 6 membered aromatic rings.

Each of the aromatic rings may optionally contain one or more hetero atoms selected from Se, Te, P, Si, B, As, N, O or S, preferably from N, O or S.

The rings may be optionally substituted with alkyl, alkoxy, polyalkoxy, thioalkyl, acyl, aryl or substituted aryl groups, a fluorine atom, a cyano group, a nitro group or an optionally substituted secondary or tertiary alkylamine or arylamine \(-\text{N} (R_3)(R_4)\), where $R_3$ and $R_4$ each independently is H, optionally substituted alkyl, optionally substituted aryl, alkoxy or polyalkoxy groups. The alkyl and aryl groups may be optionally fluorinated.

The rings may be optionally fused or may be linked with a conjugated linking group such as -C (T1) \(=\text{C} (\text{T2})\), -\(\text{C} (\text{T})\), -\(\text{N} (\text{R})\), \(-\text{N} (\text{N})\), \(-\text{N} = \text{N}\), \(-\text{N} = \text{C} (\text{R})\). T1 and T2 each independently represent H, Cl, F, -\(\text{C} = \text{N}\) or lower alkyl groups particularly C1-4 alkyl groups; R$'$ represents H, optionally substituted alkyl or optionally substituted aryl. The alkyl and aryl groups may be optionally fluorinated.

Other organic semi-conducting materials that can be used in this invention include compounds, oligomers and derivatives of compounds of the following list: conjugated hydrocarbon polymers such as polyacene, polyphenylene, poly(phenylene vinylene), polyfluorene including oligomers of those conjugated hydrocarbon polymers; condensed aromatic hydrocarbons such as anthracene, tetracene, chrysene, pentacene, pyrene, perylene, coronene; oligomeric para substituted phenylenes such as p-quaterphenyl (p-4P), p-quinquephenyl (p-5P), p-sexiphenyl (p-6P); conjugated heterocyclic polymers such as poly (3-substituted thiophene), poly (3, 4-bissubstituted thiophene), polybenzothiophene, polyisothianaphthene, poly(N-substituted pyrrole), poly (3-substituted pyrrole), poly (3, 4-bissubstituted pyrrole), polyfuran, polypyridine, poly-1, 3, 4-oxadiazoles, polyisothianaphthene, poly(N-substituted aniline), poly (2-substituted aniline), poly (3-substituted aniline), poly (2, 3-bissubstituted aniline), polyazulene, polypyrene; pyrazoline compounds; polyselenophene; polybenzofuran; polyindole; polypyrindazine; benzidine compounds; stilbene compounds; triazines; substituted metallo- or metal-free porphines, phthalocyanines, fluorophthalocyanines, naphthalocya-
nines or fluoronaphthalocyanines; C60 and C70 fullerenes; N, N'-dialkyl, substituted
dialkyl, diaryl or substituted diary-1, 4, 5, 8-naphthalenetetracarboxylic diimide and
fluoro derivatives; N, N'- dialkyl, substituted dialkyl, diaryl or substituted diary 3, 4, 9,
10- perylenetetracarboxylicdiimide; bathophenanthroline; diphenoquinones; 1, 3, 4-
oxadiazoles; 11, 11, 12, 12-tetracyanonaptho-2, 6-quinodimethane; a, a'-bis (dithieno
[3, 2-b2', 3'-d] thiophene); 2, 8-dialkyl, substituted dialkyl, diaryl or substituted diary
anthradithiophene; 2, 2'-bibenzo [1, 2-b : 4, 5-b'] dithiophene. Preferred compounds are
those from the above list and derivatives thereof, which are soluble.

WO 99/32537 and WO 00/78843 describe further oligomers and polymers. The disclo-
sures of these applications are incorporated herein by reference, as these materials
are particularly useful as semiconductors in the present invention.

Related materials, which may also find use in this invention have also been described
US 5,677,096 and US 5,279,916.

The semiconducting channel may also be a composite of two or more of the same ty-
pes of semiconductors. Furthermore, a p type channel material may, for example be
mixed with n-type materials for the effect of doping the layer. Multilayer semiconducting
layers may also be used. For example the semiconductor may be intrinsic near the
insulator interface and a highly doped region can additionally be coated next to the
intrinsic layer.

Again with reference to Fig. 1a a dielectric layer 3 is formed on the semiconducting
layer 2.

The dielectric layer 3 is preferably composed of one or more materials having both
high dielectric constant (k) and excellent insulating properties.

In a preferred embodiment the dielectric layer has a k-value above 3, preferably above
4, more preferably above 5, more preferably above 10, most preferably above 20, for
example between 20 to 200 to maximise the gate capacitance. Preferably, the diele-
tric layer is made of organic polymers having a k-value sufficiently high, or alternatively,
additives may be added to increase the k-value.

Insulating organic polymers particularly useful for preparing the dielectric layer include
highly hygroscopic insulating polymers. Examples of the useful dielectric materials in-
clude, but are not limited to, polyester, polycarbonate, polyvinylalcohol, polyvinylphe-
nol, polyvinylbutyral, polyacetal, polycarbonate, polyamide, polyamidimide, polyetherimide,
polyphenylenether, polyphenylenesulfide, polyethersulfone, polyetherketone,
polyphthalalamide, polyethernitrile, polyethersulfone, polybenzimidazole, polycarbodiim-
ide, polysiloxane, polymethylmethacrylate, polymethacrylamide, nitrile rubbers, acryl rubbers, polyethylenetetrafluoride, epoxy resins, phenol resins, melamine resins, urea resins, polybutene, polypentene, poly(ethylene-co-propylene), poly(ethylene-co-butenediene), polybutadiene, polysisoprene, poly(ethylene-co-propylenediene), butyl rubbers, polymethylpentene, polystyrene, poly(styrene-co-butadiene), hydrogenated poly(styrene-co-butadiene), hydrogenated polysisoprene, hydrogenated polybutadiene, cyanoethylated polysaccharides such as cyanoethylpullulan, polyvinylidenefluoride, polyurethane polymers and poly (vinyl chloride/vinylacetate) polymers, and mixtures thereof.

In a preferred embodiment of the present invention the insulating layer is essentially formed by one or more organic polymers having a dielectric constant of 5 or higher, like polyester, polycarbonate, polyvinylalcohol, polyvinylbutyral, polyacetal, polyarylate, polyvinylphenol, cyanoethylated polysaccharides such as cyanoethylpullulan, polyvinylidenefluoride, polyurethane polymers and poly (vinyl chloride/vinylacetate) polymers, and mixtures thereof without being restricted thereto. Most preferred are Polyvinylalkohols, polyvinylpyrrolidone or 2-(2-ethoxyethoxy ethylester acetate.

The dielectric layer 3 may generally be of any thickness, for example 50 nm to 20 µm.

The present invention is particularly useful if thicknesses of more than about 500 nm are used since the hysteresis effects due to water incorporation into the hygroscopic dielectric layer are much higher than for thinner layers. Preferably the thickness of the dielectric layer is from about 100 nm to about 10 µm, more preferably from about 500 nm to about 10 µm, more preferably from about 600 nm to about 9 µm, more preferably from about 700 nm to about 8 µm, more preferably from about 800 nm to about 7.5 µm, more preferably from about 900 nm to about 7 µm, most preferably from about 1 µm to about 6 µm.

The dielectric layer is preferably deposited by a wet process, most preferably from a solution by printing.

Again with reference to Fig. 1a a hydrophobic insulating layer 4 is formed on the dielectric layer 3. According to the present invention the hydrophobic insulating layer is arranged between the gate electrode and the dielectric layer 3.

The hydrophobic insulating layer 4 essentially consists of one or more hydrophobic insulating materials. Preferably, the hydrophobic insulating layer 4 consists essentially of an organic material, e. g. a polymer. Examples of polymers useful to form the hydrophobic insulating layer are non-polar polymers like polystyrene.
The hydrophobic material may be porous if its barrier function to water is not negatively influenced. However, it is preferred to have non-porous materials since the thickness of the layers may be reduced.

The thickness of the hydrophobic insulating layer is normally from about 5 nm to about 5 µm, preferably from about 10 nm to about 1000 nm, most preferably from about 50 nm to about 500 nm. The total effective dielectric constant \( k \) of the whole insulator can be adjusted by controlling the thickness of the dielectric layer 3 and the hydrophobic insulating layer 4. Preferably the thickness of the dielectric layer is greater than the thickness of the hydrophobic insulating layer to ensure an overall high-\( k \) value. The thickness of the dielectric layer is more preferably 5 times or more, most preferably 10 times or more of the thickness of the hydrophobic insulating layer.

Typical polymers having low water capability useful for the hydrophobic insulating layer are (without limiting to these examples): Fluorinated para-xylene, Fluoropolyarylether, Fluorinated polyimide, Polystyrene, Poly (α-methyl styrene), Poly (α-vinynaphtalene), Poly (vinyltoluene), Polyethylene, cis-polybutadiene, Polypropylene, Polysoprene, Poly (4-methyl-1-pentene), Poly (tetrafluoroethylene), Poly (chorotrifluoroethylene), Poly (2-methyl-1,3-butadiene), Poly (p-xylene), Poly (α-α'-α' tetrafluoro-p-xylene), Poly \( [1,1-(2-methyl propane) bis (4-phenyl) 2.3 carbonate] \), Poly (cyclohexyl methacrylate), Poly (chlorostyrene), Poly (2, 6-dimethyl-1,4-phenylene ether), Polysobutylene, Poly (vinyl cyclohexane), Poly(arylene ether), Polyphenylene. The above list is non-exhaustive and other polymers could be used, including, for example, poly(4-methylstyrene), poly (1,3-butadiene) or polyphenylene. Copolymers containing the repeat units of the above polymers are also suitable. Copolymers offer the possibility of improving solubility, and continuity of the hydrophobic insulating layer.

It should be appreciated that certain materials are insoluble in commonly used solvents. If this is the case copolymers can be used. Some examples of copolymers are Poly (ethylene/tetrafluoroethylene), Poly (ethylene/chlorotrifluoroethylene), Fluorinated ethylene/propylene copolymer, Polystyrene-co- α-methyl styrene, Ethylene/ethyl acrylate copolymer, Poly (stylene/10 % butadiene), Poly (stylene/15 % butadiene), Poly (stylene/2, 4 dimethylstyrane), Cytop 2.0 Teflon AF (Du Pont), Polypropylene-co-1-butene. Both random or block copolymers can be used. It is also possible to add some more polar monomer components as long as the overall composition remains sufficiently impermeable to water.

Preferred hydrophobic materials are polypropylene, preferably amorphous polypropylene, or fluoropolymers, for example copolymers of tetrafluoroethylene and dioxoles such as 2, 2 bistrifluoromethyl- 4, 5-difluoro-1, 3-dioxole. Other preferred materials are low permittivity fluoropolymers, fluoroepoxy polymers, fluorsilane, fluoroacrylic polymers, and poly (dimethyl) siloxane and its copolymers. Particularly useful is
poly(styrene-butadiene-styrene) block copolymer. The polymer may optionally be cross-linked after its deposition by heat or radiation.

In another embodiment, intermediate layers can be deposited between the hydrophobic and a high-k dielectric layer of a multilayer insulator stack. Such intermediate layers can improve adhesion or wetting between deposition steps. The intermediate layer, for example can be another low permittivity material with different surface properties. Surface treatments, for example plasma treatment, may also be used to improve layer compatibility.

In a preferred embodiment according to Fig. 1 a layer of low-k insulating material may be arranged between the semiconducting layer 2 and the dielectric layer 3. The charge mobility of the structure can be increased in this way.

The low-k insulating material may be the same as used for the hydrophobic insulating layer or different.

The hydrophobic insulating layer as well as the dielectric layer and semiconducting layer are preferably deposited by a wet process, most preferably from a solution of the one or more hydrophobic insulating, dielectric or semiconducting compounds, respectively, in a solvent. Useful wet processes are dip coating, spin coating, printing, spray coating, or roll coating techniques, but the present invention is not limited thereto. Deposition by printing is preferred. If both the semiconducting layer and the dielectric layer(s) are deposited from solution large areas can be coated.

In one preferred embodiment an FET structure of Fig. 1c is prepared by spin coating the semiconductor onto the substrate with pre-patterned drain and source electrodes. Next, an insulator in the form of a low permittivity polymer of relative permittivity below 3 is spin coated onto the semiconductor followed by the deposition of the gate electrode by vacuum evaporation or liquid deposition of a conductive solution or dispersion. It will be appreciated that the order of process steps may be altered to achieve different structures. It will be appreciated that the OFET could also have a vertical structure. All percent values refer to the weight with respect to the total weight of the respective mixture. All cited documents are incorporated herein by reference.

Examples:

The parameters were determined using the following methods:

The thickness of the layers was determined by profilometry.
The dielectric constant for the dielectric layer was determined by measuring the capacitance between the gate electrode and the source and drain electrodes at 20 Hz.

The water content of the dielectric layer material and the barrier layer material was measured by Karl Fischer titration according to the following procedure:

The samples were heated under vacuum for about 18 h to 160 °C. Then they were conditioned at 22 °C and 47 % humidity (relative) for 24 hours.

The water was removed from the samples in a reactor at 250 °C and sampled. The amount of collected water was determined by Karl-Fischer titration.

Typical water contents of dielectric and barrier layer materials are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene glycol (Plurisol E 4000, BASF)</td>
<td>0.8</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVOH)</td>
<td>5.3</td>
</tr>
<tr>
<td>Polyvinylphenol</td>
<td>3.7</td>
</tr>
<tr>
<td>Polyvinylpyrrolidone</td>
<td>13.2</td>
</tr>
</tbody>
</table>
| Isotactic PS                                              | < 1.1
| Atactic PS                                               | < 0.8
| Hydrogenated poly(styrene-butadiene-styrene) block       | < 0.6
| copolymer                                                |
| Luxprint (nanocomposit dielectrics)                       | < 0.3                |

Example 1:

An organic field effect transistor having a top gate, bottom source/drain structure comprising a hydrophobic insulating layer according to Fig. 1 Structure a) was prepared by the following steps:

1.1 The source electrode 6 and the drain electrode 7 were made of a polyethylenedioxythiophene/polystyrene sulfonate (PEDOT/PSS) patterned polyethylene-terephtalate (PET) film substrate 1. The film was patterned by means of laser ablation. The channel width and length of the thin film transistors (TFTs) were 39 500 and 142 μm, respectively. The PEDOT/PSS film thickness was 70 nm.

1.2 The next step of fabrication of the devices was the deposition of the active semiconducting layer 2. 1-methyl hexyl thiophene oligomer (BASF) was deposited by spin coating at 3000 rpm from a solution of 4 g in 100 ml tetrahydrofuran. After
the deposition the film was heated to 150°C for 10 min, afterwards the temperature was decreased to 135°C and held for one hour.

1.3 The dielectric layer 3 was prepared by spin coating a solution of polyvinyl alcohol (PVOH) 15% by weight solution in a water:butylglycol (95:5) and dried at 80°C for 30 min. The thickness of the dielectric layer 3 was 3600 nm.

1.4 The hydrophobic insulating layer 4 was deposited by spincoating of a 5% by weight solution of hydrogenated poly(styrene-butadiene-styrene) block copolymer (ZK 2604/046H, BASF) in heptane and dried for 5 min at 80°C. The thickness of the hydrophobic insulating layer 4 was 200 nm.

1.5 Access to the drain and source electrodes was created mechanically. A silver gate electrode 5 was dispensed above the conducting channel of the transistor using commercially available silver ink dispersion (Ag dispersion in toluene). Before the measurements the devices were dried for 10 min at 80°C.

The process conditions of each step 1.1 to 1.5 may be used independently of the other steps.

Fig. 2 shows the transfer electrical characteristics of a the OTFT with a hydrophobic dielectric layer 4 between the gate electrode 5 and the dielectric layer 3. The dielectric constant of the whole multilayered insulator (3+4) was k=5.6. A charge carrier mobility of about 4.9x10⁻⁴ V/s/cm², an on-off ratio of 20 and the threshold voltage with respect to the direction of the voltage sweep -6 and -5 V, respectively, were determined. The hysteresis observed at drain-source voltages of -10 V was about 1 V. The capacitance value was typically around 1 nF/cm². There is essentially no difference between the OTFT exposed to air (Fig. 2a) and the OTFT treated in a glove box without exposing it to air (Fig. 2b).

Comparative Example A:

An organic field effect transistor having a top gate, bottom source/drain structure having no hydrophobic insulating layer was prepared.

Example 1 was reproduced with the only exception that step 1.4 was skipped.

Fig. 3a shows the transfer electrical characteristics of the OTFT without a hydrophobic insulating layer after exposition to air. The dielectric constant of the dielectrics was k=5.8. A charge carrier mobility of about 1.7x10⁻² V/s/cm², an on-off ratio of 700 and the threshold voltage with respect to the direction of the voltage sweep -22 and -42 V,
respectively, were obtained. The hysteresis observed at drain-source voltages of -10 V was about 60 V. The capacitance value was typically around 1 nF/cm².

Fig. 3b shows the transfer electrical characteristics of the OTFT without exposure to air. In this case, the hysteresis is as good as the structure with hydrophobic layer indicating that the hysteresis is not caused by the manufacturing process but by the exposure to humidity later on.

Comparative Example B

An organic field effect transistor having a top gate, bottom source/drain structure and comprising a dielectric layer arranged between the hydrophobic insulating layer and the gate electrode (reverse order) was prepared.

Example 1 was reproduced with the only exception that a 4% by weight solution of polytriarylamine (PTPA3, BASF) in tetrahydrofuran was used in step 1.2 and the steps 1.3 and 1.4 were carried out in reverse order, i.e. the dielectric layer was deposited after the hydrophobic insulating layer.

Fig. 4 shows the transfer electrical characteristics of the OTFT with a hydrophobic dielectric layer in "reverse order". The dielectric constant of the whole multilayered insulator (3+4) was k=5.6. A charge carrier mobility of about 2.6x10⁻³ V s/cm², an on-off ratio of 4.16 and the threshold voltage with respect to the direction of the voltage sweep -20 and 10 V, respectively, were determined. The hysteresis observed at drain-source voltages of -10 V was about 30 V. The capacitance value was typically around 1 nF/cm².

Example 2

An organic field effect transistor having a top gate, bottom source/drain structure and comprising two hydrophobic insulating layers, arranged to sandwich a high-k dielectric layer, was prepared.

Example 1 was reproduced with the only exception that a 4% by weight solution of polytriarylamine (PTPA3, BASF) in tetrahydrofuran was used in step 1.2 and that step 1.3 was carried out again after step 1.4, i.e. a sandwiched hygroscopic/hydrophobic dielectric/hydrophobic insulating structure was prepared.

Fig. 5 shows the transfer electrical characteristics of the OTFT with this sandwiched layer structure. The dielectric constant of the whole multilayered insulator (3+4) was k=5.6. A charge carrier mobility of about 2.2x10⁻³ V s/cm², an on-off ratio of 695 and the threshold voltage with respect to the direction of the voltage sweep -17 and 4 V, re-
spectively, were determined. The hysteresis observed at drain-source voltages of -10 V was about 20 V. The capacitance value was typically around 1 nF/cm$^2$. 
Claims

1. A field effect element comprising:
   - a source electrode (6) and a drain-electrode (7),
   - a semiconducting layer (2) comprising a semiconducting compound being in contact with the source electrode (6) and the drain electrode (7),
   - a gate electrode (5), and
   - a dielectric layer (3) comprising one or more compounds selected from hygroscopic organic compounds and from nanoparticulate inorganic compounds being arranged between the semiconducting layer (2) and the gate electrode (5), wherein said hygroscopic organic compounds have a water absorption capability of more than 1.2 % by weight, and
   - a hydrophobic insulating layer (4) being arranged between the gate electrode (5) and the dielectric layer (3) preventing diffusion of water into the one or more hygroscopic compounds of the dielectric layer during the time of use of the field effect element, said hydrophobic insulating layer (4) having a water absorption capability of less than 1.2 % by weight, the semiconducting layer (2), the dielectric layer (3) or the hydrophobic insulating layer (4), or a combination thereof, being disposable from a liquid.

2. The organic field effect element according to claim 1, comprising
   - the source electrode (6) and the drain-electrode (7),
   - the semiconducting layer (2) comprising an organic semiconducting compound being in contact with the source electrode (6) and the drain electrode (7),
   - the dielectric layer (3),
   - the hydrophobic insulating layer (4a), and
   - the gate electrode (5),
   arranged in the aforesaid sequence.

3. The organic field effect element according to claim 1, comprising
   - the semiconducting layer (2) comprising an organic semiconducting compound,
   - the source electrode (6) and the drain-electrode (7), both being in contact with the semiconducting layer (2),
   - the dielectric layer (3),
   - the hydrophobic insulating layer (4a), and
   - the gate electrode (5),
   arranged in the aforesaid sequence.
4. The organic field effect element according to any of the preceding claims, wherein said hygroscopic compounds have a water absorption capability of more than 2% by weight, particularly more than 3% by weight.

5. The organic field effect element according to any of the preceding claims, wherein said hydrophobic insulating layer has a water absorption capability of 0.8% by weight or less, particularly 0.6% by weight or less.

6. The organic field effect element according to any of the preceding claims, wherein at least one low-k insulating layer (5) is arranged between the semiconducting layer (2) and the dielectric layer (3).

7. The organic field effect element according to any of the preceding claims, wherein the material of said hydrophobic insulating layer (4) being made of a material having a contact angle of more than 60°, particularly 62°.

8. The organic field effect element according to any of the preceding claims, wherein the dielectric layer has a k-value above 4, preferably above 8.

9. The organic field effect element according to any of the preceding claims, wherein the dielectric layer comprises polymers comprising at least one functional group containing at least one hydrogen atom, said functional group being capable of forming hydrogen bonds with water.

10. The organic field effect element according to claim 9, wherein the functional groups are selected from amine, amide, hydroxyl, carboxyl, thiol comprising at least one hydrogen atom, or mixtures thereof.

11. The organic field effect element according to any of the preceding claims, wherein the hydrophobic insulating layer comprises compounds selected from the group consisting of atactic or isotactic styrene, styrene butadiene copolymers, or mixtures thereof.

12. The organic field effect element according to any of the preceding claims, wherein the semiconducting layer (2), the dielectric layer (3) and the hydrophobic insulating layer (4) essentially consist of organic compounds.

13. The organic field effect element according to any of the preceding claims, wherein the dielectric layer (3) has a thickness of more than 50 nm, particularly more than 200 nm.
14. The organic field effect element according to any of the preceding claims, wherein the hydrophobic insulating layer (4) has a thickness of from 50 nm to 500 nm, particularly from 100 nm to 300 nm.

15. A process for preparing a field effect element comprising:
   i) providing a substrate,
   ii) providing a source electrode (6) and a drain-electrode (7),
   iii) depositing a semiconducting layer (2) comprising a semiconductor compound,
   iv) depositing dielectric layer (3) comprising a dielectric material, and
   v) depositing a hydrophobic insulating layer (4), and
   vi) depositing a gate electrode (5) on the hydrophobic insulating layer (4), wherein steps ii) and iii) may be carried out interchangeably and wherein the deposition in at least one of steps iii), v) and vi) is carried out from a liquid.

16. The process according to claim 15, wherein the dielectric layer (3) is deposited from a liquid comprising the dielectric material.

17. The process according to any one of claims 15 or 16, wherein the semiconducting layer and/or the hydrophobic insulating layer are deposited from a liquid.

18. The process according to claim 17, wherein the liquid comprises 10 % by weight or more of water.

19. A process according to any one of claims 15 to 18, wherein the steps i) to vi) are carried out sequentially.

20. Use of the organic field effect element according to any one of claims 1 to 14 for manufacturing of Radio Frequency Identification (RFID) devices, backplane display circuitry, integrated circuitry or drivers for memory arrays.