

Solution-Processed Inorganic films for Organic Thin Film Transistors

Reference to Related Application

- 5 Reference is made to our earlier United States provisional patent application number 60/802,122 filed May 22, 2006 for an invention titled " Solution Processed Inorganic films As Gate Dielectric for Organic Thin Film Transistors " the priority of which is hereby claimed, and the contents of which are hereby incorporated by reference as if disclosed herein in their entirety.

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Technical Field

- This invention relates to electronic devices with solution-processed inorganic films and methods of fabricating such devices and particularly, though not exclusively, relates to thin-film transistors ("TFT"s) with solution-processed films of an inorganic material
- 15 and/or mixtures of inorganic materials, and methods of fabricating such thin-film transistors. In particular, but not exclusively so, the invention relates to organic thin-film transistors ("OTFT"s) with at least one dielectric layer and/or surface modifier layer fabricated with a low temperature solution to improve carrier mobility in the transistor structure.

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Background

Research into OTFTs has gained great interest because of their potential applications in low cost and large area flexible electronics. These include driving circuits for future all-

organic OLED-based flat panel displays, plastic RF-ID circuits, gas sensors, and chemical sensors.

The most common gate dielectric in organic OTFTs is a thermally-grown silicon oxide (SiO₂) on crystalline silicon. However, for low-cost, all-plastic, and large-area applications the use of thermally grown SiO₂ is not of particular interest. A solution-processable gate dielectric is the most attractive alternative as it can be easily prepared by spin coating, casting, or printing at low temperature and under ambient conditions.

Various solution-processable gate dielectrics have been used in the past. These include poly-4-vinylphenol (PVP), polymethyl methacrylate (PMMA), poly vinyl alcohol ("PVA"), benzocyclobutene ("BCB"), polyimide ("PI"), and self-assembled monolayers. OTFTs using a polymer dielectric operate at high voltages due to low dielectric constant (*k*) values. Therefore, inorganic oxides such as TiO₂, Ta₂O₅, and Al₂O₃ are used as they have higher *k* values and thus the operating voltages can be reduced. However, inorganic oxides require fabrication techniques such as anodic oxidation, magnetron sputtering, and electron-beam evaporation. This makes the deposition process and consequential device fabrication relatively difficult and expensive. It is therefore desirable to have solution-processable inorganic dielectrics for low operating voltage OTFTs.

Summary

According to an exemplary aspect there is provided a method for fabricating a sol-gel film composition for use in a thin film transistor, the method comprising fabricating the

sol-gel dielectric composition by solution processing at a temperature in the range 60 °C to 225 °C.

The sol-gel film composition may be made from a precursor. The precursor may
5 comprise at least one of: organosilicates, organosilanes, silane coupling agents, silicates derivatives, tetraalkylorthosilicate, and silane derivatives. Alternatively, the precursor may comprise at least one member selected from the group consisting of:
organosilicates, organosilanes, silane coupling agents, silicates derivatives,
tetraalkylorthosilicate, silanes derivatives, metal alkoxides, metal alkoxyalkoxide; and
10 at least one polymer consisting of at least one of: poly(methyl methacrylate), poly(vinyl alcohol), polyethylene oxide-based block copolymers, and polystyrene-poly(4-vinyl pyridine) diblock copolymer.

The sol-gel film may be fabricated from at least one of: undoped spin-on-glass, and
15 doped spin-on-glass. The sol-gel film may be a mixture of one or more of: an organic polymer, an organic monomers, and organically modified sol-gels. The sol-gel film may be doped by at least one of: a metal oxide, and a block copolymer composite with core comprising inorganic materials, metal, or metal-oxide. The block copolymer may comprise polystyrene-poly(4-vinyl pyridine), and may contain metallorganic precursors.
20 The metal precursors may comprise titanium isopropoxide. The metal oxide may be at least one of: metal alkoxyalkoxide, and metal alkoxide.

The sol-gel may further comprise a mixture of hydrophobic molecules. The hydrophobic molecules may comprise at least one of: octadecyltrichlorosilane, hexamethyldisilazane, and derivatives thereof.

- 5 The sol-gel film composition may have a dielectric constant in the range 2 to 50, and may be formed on a substrate. The substrate may be selected from: glass, plastic, quartz, metal foil, undoped silicon and heavily doped silicon.

According to another exemplary aspect there is provided a sol-gel film composition
10 when prepared by the above.

According to a further exemplary aspect there is provided a sol-gel film for use in organic thin film transistors as a dielectric film, the sol-gel film comprising at least one of: a polymer, and a co-polymer; the at least one of the polymer and co-polymer
15 containing clusters of nano-particles of at least one selected from the group consisting of: inorganic materials, metal, and metal-oxide.

The sol-gel film may comprise at least one member selected from of: organosilicates, organosilanes, silane coupling agents, silicates derivatives, silanes derivatives, metal
20 alkoxides, metal alkoxyalkoxide, tetraalkylorthosilicate; and a polymer consisting of at least one member of the group consisting of: poly(methyl methacrylate), poly(vinyl alcohol), polyethylene oxide-based block copolymers, and polystyrene-poly(4-vinyl pyridine) diblock copolymer.

- The sol-gel film may comprise at least one of: undoped spin-on-glass, and doped spin-on-glass. The sol-gel film may be a mixture of one or more of: an organic polymer, an organic monomers, and organically modified sol-gels. The sol-gel film may be doped by at least one of: a metal oxide, and a block copolymer composite with core
- 5 comprising inorganic materials, metal, or metal-oxide. The block copolymer may comprise polystyrene-poly(4-vinyl pyridine), and may contain metallorganic precursors. The metal precursors may comprise titanium isopropoxide. The metal oxide may be at least one of: metal alkoxyalkoxide, and metal alkoxide.
- 10 The sol-gel may further comprise a mixture of hydrophobic molecules. The hydrophobic molecules may comprise at least one of: octadecyltrichlorosilane, hexamethyldisilazane, and derivatives thereof. The sol-gel film composition may have a dielectric constant in the range 2 to 50.
- 15 According to a yet further aspect there is provided an organic thin film transistor comprising a sol-gel film as described above, the sol-gel film being formed as layer before the semiconductor layer and/or on substrate.
- The substrate may be of: glass, plastic, quartz, metal foil, undoped silicon and/or
- 20 heavily doped silicon. The organic thin film transistor may have at least one property selected from: a sub-threshold slope less than 2 volts per decade, and an on/off ratio of at least 10^3 .

The sol-gel film may be a surface modifier to enhance the transport properties in a semiconductor. The semiconductor may be at least one of: organic, inorganic, hybrids, or mixtures thereof. The semiconductor may be pentacene.

- 5 The organic thin film transistor may further comprise a layer of poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] and/or a capping layer of organic, inorganic, hybrids, or mixtures thereof between the sol-gel layer and the semiconductor layer. The capping layer may be at least one of: poly- α -methylstyrene and octyltrichlorosilane
- 10 The organic thin film transistor may comprise one of: a bottom gate with top contact, a bottom gate with bottom contact, top gate with top contact, a top gate with bottom contact, a top gate with top contact enhanced by surface modifier, and a top gate with bottom contact enhanced by surface modifier.
- 15 According to a final exemplary aspect there is provided an organic thin film transistor comprising a sol-gel film as described above wherein the sol-gel film further comprises a semiconductor comprising at least one of: a semiconductor material, a plurality of semiconductor materials, and a mixture of semiconductor materials. The semiconductor may be deposited on the sol-gel film. Alternatively, the semiconductor may not be
- 20 deposited on the sol-gel film. The semiconductor may be at least one of: organic, inorganic, hybrids, or mixtures thereof..

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments of the present invention, the description being with reference to the accompanying illustrative drawings.

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In the drawings:

Figure 1 is a schematic representation of exemplary device structures of TFTs with sol-gel used in dielectric stack and/or surface modifier stack (sol-gel TFTs);

Figure 2 is a schematic representation of exemplary sol-gel use in gate dielectric stack and/or surface modifier stack;

Figure 3 is a series of AFM images of different films;

Figure 4 is a graph of an X-ray diffraction scan;

Figure 5 is capacitance-voltage curve of a metal-insulator-semiconductor capacitor with sol-gel dielectric;

Figure 6 is three graphs showing the output characteristic of a control sample and two exemplary embodiments;

Figure 7 is three graphs showing the transfer characteristics of a control sample and two exemplary embodiments;

Figure 8 is representations of a solution processed PQT, and its performance contrasted with a control sample;

Figure 9 is representations of a solution processed PQT with a sol-gel dielectric, and its performance contrasted with a control sample;

Figure 10 is representations of a solution processed PQT with a sol-gel dielectric and a SiO₂ blocking layer, and its performance contrasted with a control sample; and

Figure 11 is a representation of an exemplary embodiment with a nitride blocking layer on flexible substrates and its performance contrasted with a control sample.

Detailed Description of the Exemplary Embodiments

5 In Figure 1 there is shown a number of structures of sol-gel TFTs with sol-gel film in gate dielectrics stack and/or surface modifier stack:

- (a) is a common bottom gate with top contact;
- (b) is a common bottom gate with bottom contact;
- (c) is a patterned bottom gate with top contact;
- 10 (d) is a patterned bottom gate with bottom contact;
- (e) is a top gate with top contact;
- (f) is a top gate with bottom contact;
- (g) is a top gate with top contact enhanced by surface modifier;
- (h) is a top gate with bottom contact enhanced by surface modifier.

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The dielectric stack and/or surface modifier stack are as described with reference to Figure 2. The dielectric stack and/or surface modifier stack may comprise one or more of sol-gel film and/or non-sol-gel film. The non-sol-gel film may be organic, inorganic, hybrids, or mixtures thereof.

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The sol-gel solution and/or film may be formed from precursors comprising a polymer and/or co-polymer and containing clusters of nano-particles of inorganic materials, metals or metal-oxide. The precursors may be one or more of: organosilicates, organosilanes, silane coupling agents, silicates derivatives, silanes derivatives, metal

alkoxides, and alkoxyalkoxide The polymer may be one or more of: poly(methyl methacrylate), poly(vinyl alcohol), polyethylene oxide-based block copolymers, and polystyrene-poly(4-vinyl pyridine) ("PS-P4VP") diblock copolymer. The co-polymer may be polystyrene-poly(4-vinyl pyridine) containing metallorganic precursors such as,
5 for example, titanium isopropoxide($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$).

The sol-gel solution and/or film may be fabricated from undoped spin-on-glass and/or doped spin-on-glass. Doping may be by use of a metal oxide and/or block copolymer composite with a core of inorganic materials, metal, or metal-oxide. The core may be
10 one or more of: metal alkoxyalkoxide, and metal alkoxide. The sol-gel solution and/or film may be a mixture of one or more of: an organic polymer, organic monomers, and organically modified sol-gels. The sol-gel solution and/or film may include a mixture of hydrophobic molecules such as, for example, octadecyltrichlorosilane, hexamethyldisilazane, and derivatives thereof.

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The sol-gel film may have a dielectric constant in the range from 2 to about 50 and may be used as surface modifier to enhance the transport properties in the semiconductor.

The organic thin film transistor may have:

- a) a sub-threshold slope below about or less than 2 volts per decade; and/or
- 20 b) an on/off ratio of at least about 10^3 ; and/or
- c) a charge-carrier mobility at least about 100% greater than a comparison OTFT that lacks the sol-gel layer.

Sol-gel processing to fabricate dielectrics for OTFTs may be performed by combining a precursor such as, for example, tetraethylorthosilicate ("TEOS") at 99.9 % purity, ethanol, deionizer water, and concentrated HCl then stirring at room temperature for 90 minutes in the following molar ratios: 1:10:3.5:0.003. Base catalyst such as, for
5 example, 0.1 M NH_4OH may be added. The solution may be aged at temperature ranges 0 to 100 C and/or combinations thereof. The aging time may range from 10 minutes to 14 days. Films may be made from filtered solution by solution processing methods. One of the methods can be spin coating (ranges from 500 rpm to 6000 rpm). It may be deposited onto substrates. The substrate may be of a material such as, for example,
10 glass, plastic, quartz, metal foil, undoped silicon and heavily doped silicon with and without other materials on the substrate. Such as, for example, sol-gel film is deposited onto a bare n-Si wafer substrate or Si wafers (as a gate electrode), with thermally grown SiO_2 (as a gate leakage blocking layer). The substrates are carefully cleaned and/or treated prior to spin coating. The sol-gel films may be dried at ambient condition and/or
15 under different conditions. The different conditions may have O_2 molecules and/or other molecules as the environment gas. Solution processing is preferably at a relatively low temperature more preferably in the range about 60 °C to about 225 °C.

A thermally grown 30 nm thick SiO_2 onto n-type Si- wafer can be used as a reference
20 sample for OTFT fabrication. The sol-gel and control sample may be heated at 100 °C in vacuum to further treat the sol-gel.

The semiconductor may be organic, inorganic, hybrids, or mixtures thereof. The semiconductor materials may be mixed in the sol-gel solution and/or film.

To fabricate the OTFT pentacene was purified prior to use. A 50 nm thick pentacene film was deposited at 0.5 Å/s rate on both the sol-gel and the control sample in an evaporator at a base pressure of 10^{-7} mbar and maintaining the substrate temperature at 100 °C. Gold source and drain electrodes were deposited on the surface of the pentacene film by shadow mask evaporation to obtain a top-contact structure as shown in Figure 1a (but without the passivation layer). Gate width may vary from 500 to 4000 μm, while gate length may vary from 100 to 200 μm.

- 10 The OTFTs were characterized using a Keithley SCS-4200 characterization system under vacuum conditions ($\sim 10^{-4}$ to 10^{-5} Torr) using a Desert Cryogenic probe station.

The mobility values in the saturation regime ($V_D > V_G$) were extracted from:

$$I_D = C_i \times \mu (W / 2L) (V_G - V_T)^2$$

- where I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, V_D is the drain voltage, V_G is the gate voltage, V_T is the threshold voltage, μ is the field-effect mobility, and W and L are the channel width and length dimensions, respectively. The V_T of the device was determined from the relationship between the square root of the source-drain current I_D at the saturated regime and the V_G of the device by extrapolating the measured data to $I_D=0$.

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The sol-gel and pentacene films were analyzed by atomic force microscopy to investigate the film quality and surface roughness. Figure 3 has images that illustrate the result of the analysis. Figure 3a is a 45 nm thick thermally-grown SiO₂ on silicon substrate and Figure 3b is a 399 nm thick spin coated sol-gel film on silicon substrate.

The sol-gel films were typically 399 nm thick, uniform, and displayed a smooth surface with root-mean-square roughness of ~ 1.9 Å whereas the thermally grown films displayed a much rougher surface of ~ 3.1 Å rms.

5 Figure 2c shows a 50 nm thick pentacene film on thermally grown SiO₂ whereas Figure 2d is a 50 nm thick pentacene film grown on a sol-gel film. The pentacene film grown on the sol-gel film shows different molecular arrangements than those of the pentacene film on the thermally grown SiO₂.

10 Figure 3e is a high resolution AFM image of pentacene on sol-gel and Figure 3f shows the surface profile of the pentacene on sol-gel of Figure 3e and indicates a terrace height of about 1.5 nm and orientation of the pentacene molecule relative to the substrate. The pentacene thin films deposited on sol-gel dielectrics exhibited a grain size of ~ 1.0 μm and each grain has a terrace-structure, with a series of 12 to 14 terraces.

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Contact angle measurement of the surface of the sol-gel and thermally grown SiO₂ samples yielded wetting angles of 50° and 40° respectively, thus indicating that the sol-gel surfaces are more hydrophobic than the thermally grown oxides. The contact angle of sol-gel may increase to around 80° when the sol-gel is subjected to heat treatment in
20 an ultrahigh vacuum.

Figure 4 is a graph of an X-ray diffraction scan of 50 nm thick pentacene film deposited on:

(a) a thermally grown SiO₂ (black line); and

(b) a sol-gel film (grey line).

All peaks correspond to (00 l) planes, indicating that all crystals are oriented to their (00 l) planes parallel to the substrates and come from the substrate-induced thin film phase. This is characterized by an inter-planar spacing of 15.5 Å in the pentacene film.

- 5 The small contribution of the triclinic bulk phase exhibits a vertical periodicity of 14.5 Å.

The dielectric properties of sol-gel films were investigated using a conventional metal-insulator-semiconductor ("MIS") structure. Figure 5 shows high frequency capacitance-
10 voltage curves measured at room temperature in vacuum (10^{-5} mbar). The device exhibits typical MIS characteristics with accumulation and depletion regions. In the accumulation region, a capacitance of 24 nF was observed that corresponds to a dielectric constant, $k=11$, which is much higher than the dielectric constant for thermally grown SiO₂ ($k=3.9$). Higher observed dielectric constants of sol-gel films
15 may be attributed to the presence of polar molecules trapped inside the sol-gel film and/or -OH bonds inherently present in the sol-gel film structures. Polar molecules such as water and organic reactants contribute to the increase in the dielectric constant. A clockwise hysteresis and capacitance-voltage curve shifts toward negative voltages indicate the presence of the trap states and mobile ions. The trapping sites are expected
20 to be at the interface of sol-gel. The mobile ions such as Cl⁻, H⁺ and OH⁻ originating from the sol-gel synthesis also contribute to the observed hysteresis.

As stated above the control sample is a thermally grown SiO₂ dielectric consisting of 30 nm thick thermally grown SiO₂ dielectric with W= 500 μm and L= 150 μm. The

electrical characteristics of the control sample are shown in Figure 6a and 7a. Transfer characteristics of the control sample were measured by sweeping the gate voltage (V_g) from 1 to -5 V (forward bias) and -5 to 1 V (reverse bias) at constant drain-source voltage (V_{ds}) of -5V. The carrier mobility was calculated in the saturation region from the plot of the square root of the drain current (I_d) versus V_g in forward bias (Figure 7a). From the electrical characteristics, parameters such as carrier field mobility, threshold voltage, sub-threshold swing and on/off ratio were determined. These are given in Table 1 below. The control sample exhibited a carrier mobility of $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage of -1.61 V, a sub-threshold swing of 250 mV/ decade, and an on/off ratio of 10^5 . These parameters are quite typical for the pentacene OTFT with thermally grown SiO_2 as the gate dielectric.

To evaluate the quality of sol-gel gate dielectric OTFT devices consisting of 399 nm spin coated sol-gel film, 50 nm thick thermally grown pentacene film, and thermally evaporated gold contact were fabricated (e.g. see Figure 1a). The output and transfer characteristics of OTFT are presented in Figures 6b and 7b and included in Table 1 below. Carrier field mobility, threshold voltage, sub threshold swing and on/off ratio were determined as $2.08 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$, -1.76 V, 750 mV/ decade, 10^3 respectively from forward bias I_d - V_g curve. The sol-gel OTFTs showed hysteresis behavior both in the drain-source voltage sweep and the gate-source voltage sweep. Table 1 is a summary of the parameters extracted from the OTFTs fabricated using thermally grown SiO_2 , sol-gel, thermally grown SiO_2 + sol-gel dielectric.

Dielectric	μ_h (cm^2/Vs)	V_t (V)	s.s (mV/decade)	I_{ON}/I_{OFF}	$I_{D, SAT}/W$ ($\text{A}/\mu\text{m}$)	C_i (F/cm^2)
SiO ₂ (30 nm)	0.12	- 1.61	250	1.4×10^5	-3.88×10^{-10}	1.5×10^{-8}
Sol-gel (399 nm)	2.08	- 1.76	750	1.00×10^3	-3.33×10^{-9}	2.44×10^{-8}
SiO ₂ (18nm)+Sol- gel (391nm)	0.67	- 1.10	300	2.64×10^5	-9.04×10^{-10}	2.2×10^{-8}

Table 1

- 5 Sol-gel OTFTs with thermally grown SiO₂ blocking layer were fabricated that consisted of 391 nm spin coated sol-gel films, on an 18 nm thick thermally grown SiO₂ layer that acts as a 'blocking' layer (e.g. Figure 1g). The output and transfer characteristics are shown in Figures 6c and 7c as well as in Table 1 above. They show excellent transistor characteristics at -5V. The value of on/off ratio reaches to 2.64×10^5 , carrier mobility
- 10 of $0.67 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, threshold voltage of -1.10 V, and a sub threshold swing of 300 mV/decade. The on/off ratio is improved by a factor of 100 compared to OTFT device without thermally grown SiO₂ blocking layer. The mobility value is also improved by factor of 5 compared to the control sample OTFT.

Solution processed sol-gel OTFT fabrication may be by preparing a 0.3 wt % solution of poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] ("PQT-12") (Figure 8a) in dichlorobenzene at about 70 °C. The resulting solution was subject to ultrasonic

5 agitation while being cooled to room temperature. The solution was filtered using a 1µm filter and then spin coated on a n-type Si substrate with 45nm thermally grown SiO₂ (Th-Ox) to form a PQT-12 semiconductor layer that was 20 nm thick (Figure 8d). The PQT-12 semiconductor layers were then dried in a vacuum and annealed at the PQT-12's liquid-crystalline phase transition temperatures of 120–140 °C. Subsequently,

10 the gold source and drain electrodes were vacuum deposited onto the PQT-12 semiconductor layer through a shadow mask, thus creating an array of OTFTs with various dimensions. Gate width varied from 500 to 4000 µm, while gate length varies from 100 to 200 µm.

15 The electrical characteristics of the control sample SiO₂ dielectric and spin coated PQT-12 are shown in Figures 8b and d as well as Table 2 below. The control sample SiO₂ dielectric exhibited a carrier mobility of 0.005 cm² V⁻¹ s⁻¹, and an on/off ratio of 6x10⁵. For the spin coated PQT-12, I_g (@V_g = -5V) was 1.02 x 10⁻¹¹ A and the integration time was normal. The gate leakage in I_dV_g was taken from I_dV_d measurements. For the top

20 contact, W/L were 500/150; µ was 0.005 cm²/Vs; V_t was 3.94V; s.s was 1205 mV/decade; I_{on}/I_{off} was 6.96 x 10⁵; I_{d,sat} (@V_g = -20V) was -4.62 x 10⁻⁸ A; I_{d,sat}/W (@V_g = -20V) was -9.23 x 10⁻¹¹ A/µm; and the integration time was normal.

Figure 9c shows OTFT devices that were fabricated using a 365 nm spin coated sol-gel film on a 45 nm thick thermally grown SiO₂ layer. The Th-Ox acts as a blocking layer to improve gate leakage. As shown in Figures 9a and b, as well as Table 2 below, The OTFT exhibited a carrier mobility of $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an on/off ratio of 1×10^5 . The mobility is increased by 7000% compared to the control sample. For the spin coated PQT-12, I_g (@ $V_g = -5\text{V}$) was $6.00 \times 10^{-10} \text{ A}$ and the integration time was normal. The gate leakage in $I_d V_g$ was taken from $I_d V_d$ measurements. For the top contact, W/L were 500/150; μ was $0.35 \text{ cm}^2/\text{Vs}$; V_t was 0.50V; s.s was 633 mV/decade; I_{on}/I_{off} was 1.74×10^5 ; $I_{d,sat}$ (@ $V_g = -20\text{V}$) was $-1.46 \times 10^{-7} \text{ A}$; $I_{d,sat}/W$ (@ $V_g = -20\text{V}$) was $-2.91 \times 10^{-10} \text{ A}/\mu\text{m}$; and the integration time was normal.

In Figure 10c there is shown an OTFT device fabricated using a 365 nm spin coated sol-gel film on a 45 nm thick thermally grown SiO₂ as blocking layer, a 10 nm thick poly- α -methylstyrene ("PAMS") (Figure 10d) layer as a capping layer, and the PQT-12 layer. As shown in Figures 10b and c as well as Table 2 below, the OTFT exhibited a carrier mobility of $0.019 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an on/off ratio of 1×10^6 . The mobility is increased by 380% compared to the control sample. For the spin coated PQT-12, I_g (@ $V_g = -5\text{V}$) was $-3.79 \times 10^{-12} \text{ A}$ and the integration time was normal. The gate leakage in $I_d V_g$ was taken from $I_d V_d$ measurements. For the top contact, W/L were 500/150; μ was $0.019 \text{ cm}^2/\text{Vs}$; V_t was -1.97V; s.s was 584 mV/decade; I_{on}/I_{off} was 1.04×10^6 ; $I_{d,sat}$ (@ $V_g = -20\text{V}$) was $-3.08 \times 10^{-9} \text{ A}$; $I_{d,sat}/W$ (@ $V_g = -20\text{V}$) was $-6.15 \times 10^{-12} \text{ A}/\mu\text{m}$; and the integration time was normal. Table 2 below is a summary of the parameters extracted from the OTFTs fabricated using Th-Ox (thermally grown SiO₂), Th-Ox + Dielectric (Sol-Gel), Th-Ox + Dielectric + PAMS (poly- α -methylstyrene).

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Dielectric Thickness (nm)	μ (cm ² /V s)	V_t (V)	$s.s$ (mV/decade)	I_{ON}/I_{OFF}	$I_{D, sat}$ (A)	C_i (F/cm ²)
45 nm (th-ox)	0.005	-3.94	1205	6.96×10^5	-4.62×10^{-8}	7.13×10^{-8}
45nm (th-ox) + 365nm (Dielectric)	0.35	-0.50	633	1.74×10^5	-1.46×10^{-7}	1.66×10^{-8}
45nm (th-ox)+ ~365nm (SG) + ~10nm PAMS	0.019	-1.97	584	1.04×10^6	-3.08×10^{-9}	2.47×10^{-8}

10

Table 2

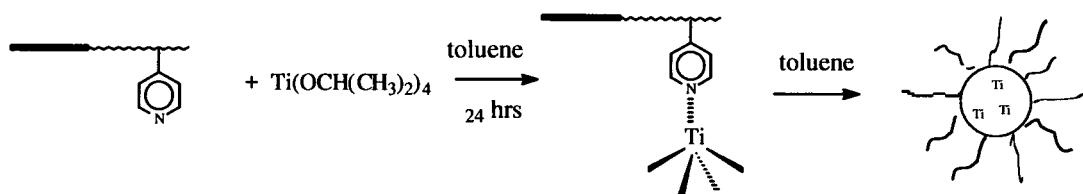
In Figure 11, there is shown an OTFT device fabricated using a 69 nm spin-coated sol-gel film on a 35 nm thick sputtered silicon nitride, a monolayer of octyltrichlorosilane (OTS) layer as capping layer, and the PQT-12 layer on aluminized polyester flexible substrate. As shown in Figure 11 and Table 3 below, the OTFT exhibited a carrier mobility of 0.64 cm²/V s, and an on/off ratio of 5×10^3 . Table 3 is a summary of the parameters extracted from the OTFTs fabricated using silicon nitride+sol-gel+OTS on aluminized polyester flexible substrate.

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Dielectric	μ_h ($\text{cm}^2/\text{V s}$)	V_t (V)	s.s (mV/decade)	$I_{\text{ON}}/I_{\text{OFF}}$	$I_{\text{D, SAT}}$ (A)	C_i (F/cm^2)
Silicon	0.64	-	300	5×10^3	-9.52×10^{-7}	1.56×10^{-7}
Nitride		0.61				
(35nm)+Sol-gel						
(69nm)+OTS						

Table 3

- 5 As shown below, for the synthesis of sol-gel polymer composite films as a dielectric layer a titania precursor – titanium isopropoxide($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) - was loaded into the core of PS-P4VP in toluene solution. The organic salt of titanium has good solubility in the micellar solution and strong interaction between pyridine and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ is expected. Coordination occurred between the Ti in the organic salt and the nitrogen in the pyridine ring.
- 10



Dielectric films can be prepared by solution spin coating, casting, or printing at low temperature and under ambient conditions. OTFTs prepared by the methods disclosed

have application in commercial products such as, for example, backplanes for organic light emitting diodes, RFID tags, organic sensors, gas sensors, bio sensors, and ASICs.

Whilst there has been described in the foregoing description exemplary embodiments of
5 the present invention, it will be understood by those skilled in the technology concerned that many variations in details of design, construction and/or operation may be made without departing from the present invention.

The Claims:

1. A method for fabricating a sol-gel film composition for use in a thin film transistor, the method comprising fabricating the sol-gel dielectric composition by solution processing at a temperature in the range 60 °C to 225 °C.
2. A method according to claim 1, wherein the sol-gel film composition is made from a precursor, the precursor comprising at least one member selected from the group consisting of: organosilicates, organosilanes, silane coupling agents, silicates derivatives, tetraalkylorthosilicate and silanes derivatives.
3. A method according to claim 1, wherein the sol-gel film composition is made from a precursor, the precursor comprising at least one member selected from the group consisting of: organosilicates, organosilanes, silane coupling agents, silicates derivatives, tetraalkylorthosilicate, silanes derivatives, metal alkoxides, metal alkoxyalkoxide; and at least one polymer consisting of at least one member of the group consisting of: poly(methyl methacrylate), poly(vinyl alcohol), polyethylene oxide-based block copolymers, and polystyrene-poly(4-vinyl pyridine) diblock copolymer.
4. A method according to claim 1, wherein the sol-gel film is fabricated from at least one of: undoped spin-on-glass, and doped spin-on-glass.
5. A method according to claim 1, wherein the sol-gel film is a mixture of one or more of: an organic polymer, an organic monomers, and organically modified sol-gels.

6. A method according to any one of claims 1 to 5, wherein the sol-gel film is doped by at least one of: a metal oxide, and a block copolymer composite with core comprising inorganic materials, metal, or metal-oxide.
7. A method as claimed in claim 6, wherein the block copolymer comprises
5 polystyrene-poly(4-vinyl pyridine).
8. A method as claimed in claim 6 or claim 7, wherein the block copolymer contains metallorganic precursors.
9. A method as claimed in claim 8, wherein the metal precursors comprise titanium isopropoxide.
10. A method as claimed in any one of claims 6 to 9, wherein the metal oxide is at
10 least one of: metal alkoxyalkoxide, and metal alkoxide.
11. A method according to any one of claims 1 to 10, wherein the sol-gel further comprises a mixture of hydrophobic molecules.
12. A method as claimed in claim 11, wherein the hydrophobic molecules comprise at
15 least one of: octadecyltrichlorosilane, hexamethyldisilazane, and derivatives thereof.
13. A method according to any one of claims 1 to 12, wherein the sol-gel film composition has a dielectric constant in the range 2 to 50.
14. A method according to any one of claims 1 to 13, wherein the sol-gel film
20 composition is formed on a substrate.
15. A method as claimed in claim 14, wherein the substrate is selected from the group consisting of: glass, plastic, quartz, metal foil, undoped silicon and heavily doped silicon.

16. A sol-gel film composition when prepared by the method of any one of claims 1 to 15.
17. A sol-gel film for use in organic thin film transistors as a dielectric film, the sol-gel film comprising at least one of: a polymer, and a co-polymer; the at least one
5 of the polymer and co-polymer containing clusters of nano-particles of at least one selected from the group consisting of: inorganic materials, metal, and metal-oxide.
18. A sol-gel film according to claim 17, wherein the sol-gel film comprises at least one member selected from the group consisting of: organosilicates, organosilanes,
10 silane coupling agents, silicates derivatives, silanes derivatives, metal alkoxides, metal alkoxyalkoxide, tetraalkylorthosilicate; and a polymer consisting of at least one member of the group consisting of: poly(methyl methacrylate), poly(vinyl alcohol), polyethylene oxide-based block copolymers, and polystyrene-poly(4-vinyl pyridine) diblock copolymer.
- 15 19. A sol-gel film according to claim 17, wherein the sol-gel film comprises at least one of: undoped spin-on-glass, and doped spin-on-glass.
20. A sol-gel film according to claim 17, wherein the sol-gel film is a mixture of one or more of: an organic polymer, an organic monomers, and organically modified sol-gels.
- 20 21. A sol-gel film according to any one of claims 17 to 20, wherein the sol-gel film is doped by at least one of: a metal oxide, and a block copolymer composite with core comprising inorganic materials, metal, or metal-oxide.
22. A sol-gel film as claimed in claim 21, wherein the block copolymer comprises polystyrene-poly(4-vinyl pyridine).

23. A sol-gel film as claimed in claim 21 or claim 22, wherein the block copolymer contains metallorganic precursors.
24. A sol-gel film as claimed in claim 23, wherein the metal precursors comprise titanium isopropoxide.
- 5 25. A sol-gel film as claimed in any one of claims 21 to 24, wherein the metal oxide is at least one of: metal alkoxyalkoxide, and metal alkoxide.
26. A sol-gel film according to any one of claims 17 to 26, wherein the sol-gel further comprises a mixture of hydrophobic molecules.
27. A sol-gel film as claimed in claim 26, wherein the hydrophobic molecules
10 comprise at least one of: octadecyltrichlorosilane, hexamethyldisilazane, and derivatives thereof.
28. A sol-gel film according to any one of claims 17 to 27, wherein the sol-gel film composition has a dielectric constant in the range 2 to 50.
29. An organic thin film transistor comprising a sol-gel film according to any one of
15 claims 16 to 28, the sol-gel film being formed as layer before the semiconductor layer and/or on substrate.
30. An organic thin film transistor as claimed in claim 29, wherein the substrate is selected from the group consisting of: glass, plastic, quartz, metal foil, undoped silicon and heavily doped silicon.
- 20 31. An organic thin film transistor as claimed in claim 29 or claim 30 having at least one property selected from the group consisting of: a sub-threshold slope less than 2 volts per decade, and an on/off ratio of at least 10^3 .

32. An organic thin film transistor according to any one of claims 29 to 31, wherein the sol-gel film is a surface modifier to enhance the transport properties in a semiconductor.
33. An organic thin film transistor according to claim 32, wherein the semiconductor is at least one of: organic, inorganic, hybrids, or mixtures thereof.
34. An organic thin film transistor as claimed in claim 32 or claim 33, wherein the semiconductor is pentacene.
35. An organic thin film transistor according to any one of claims 29 to 34 further comprising a layer of poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene].
36. An organic thin film transistor according to any one of claims 29 to 35 further comprising a capping layer of organic, inorganic, hybrids, or mixtures thereof between the sol-gel layer and the semiconductor layer.
37. An organic thin film transistor according to claim 36, wherein the capping layer is at least one of: poly- α -methylstyrene and octyltrichlorosilane
38. An organic thin film transistor according to any one of claims 29 to 36, wherein the organic thin film transistor comprises one of: a bottom gate with top contact, a bottom gate with bottom contact, top gate with top contact, a top gate with bottom contact, a top gate with top contact enhanced by surface modifier, and a top gate with bottom contact enhanced by surface modifier.
39. An organic thin film transistor comprising a sol-gel film according to any one of claims 16 to 28, wherein the sol-gel film further comprises a semiconductor comprising at least one selected from the group consisting of: a semiconductor material, a plurality of semiconductor materials, and a mixture of semiconductor materials, .

40. An organic thin film transistor according to claim 39, wherein the semiconductor is deposited on the sol-gel film.
41. An organic thin film transistor according to claim 39, wherein the semiconductor is not deposited on the sol-gel film.
- 5 42. An organic thin film transistor according to any one of claims 39 to 41, wherein the semiconductor is at least one of: organic, inorganic, hybrids, or mixtures thereof.