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Electronic Supplementary Information

Sol-Gel Titanium-Silicon Oxide/Organic Hybrid Dielectric for Low-Voltage Organic Thin Film Transistors

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Experimental

Materials

All the solvents and reagents were purchased from Sigma-Aldrich, Merck and Alfa Aesar and used without further purification.

Sol precursor preparation

To prepare the precursor for *h*TSO hybrid film, 3.44 g (0.0165 mol) of tetraethyl orthosilicate (TEOS; $Si(OC_2H_5)_4$) was dissolved in 25 ml of anhydrous ethanol, followed by 0.17 ml of nitric acid (HNO_3; 60%) as catalyst and 0.5 ml of DI water, while stirring at room temperature for 30 min. Then, 5.62 g (0.0165 mol) of tetrabutyl orthotitanate (TOBT; $Ti(OC_4H_9)$) was added drop-wise into the solution followed by 2 ml of hexylene glycol. After reacted for another 30 min, the volatile component in the homogenous solution was removed by vacuum evaporation. The product was further diluted with propylene glycol monomethyl ether (~ 230 mg ml^{-1}) and filtered through a 0.45 μm PTFE filter before coating.

Device fabrication and measurement

Heavily doped n-type Si wafer was diced and cleaned in sulfuric acid/hydrogen peroxide (7:3 v/v) at 110 ^oC for 40 min, rinsed thoroughly with DI water, dried under nitrogen and used immediately. The *h*TSO dielectric films were deposited by spin-coating the precursor sol onto cleaned Si substrate (6000 rpm, 60 s), then cured under ultraviolet light and baked at 150 ^oC for 1 h before cooled to room temperature. The as-fabricated *h*TSO films were then immersed in an octadecylphosphonic acid (ODPA) solution (5 mM in 2-propanol) for 16 hr, followed by rinsing with 2-propanol and blow dried with nitrogen. OTFTs were fabricated by vacuum deposition of a 50 nm pentacene film from the heated quartz crucible onto the dielectric layer at a rate of 0.1 Å s^{-1} and a pressure of 5×10^{-6} torr with 90 °C substrate temperature. Following that, source and drain electrodes were defined on top of the pentacene layer by evaporating a 50 nm thick gold film at 0.5 Å s^{-1} through a shadow mask. The channel width (W) and length (L) are 50 μm and 1000 μm, respectively. To investigate the capacitance and leakage current, parallel-plate capacitors were fabricated by depositing the top Au electrodes (square-shaped area of 1 × 1 mm^2) onto a Si substrate (bottom electrode) having dielectric film fabricated as above. An Agilent E4980A LCR meter was used for the characterization of capacitance at 1 kHz. All OTFTs electrical characteristics were measured under N_2-atmosphere using a Keithley 4200-SCS semiconductor parameter analyzer. The saturated field effect mobility (μ) and threshold voltage (V_{th}) was estimated in the saturation region from the slope and x-intercept, respectively, of the linear fit of $(-I_d)^{1/2}$ versus V_g data, using the following Eq. (S1):

$$I_d = \frac{W}{2L} C_i \mu \left(V_g - V_{th}\right)^2 \tag{S1}$$

where C_i is the dielectric capacitance. The subthreshold swing (SS) is calculated by taking the inverse slope of a plot of logarithmic I_d versus V_g in field effect transistor operating region. Assuming that both the density of deep bulk trap and density of interface trap are of independent energy, the trapping density (N_{trap}) can be extracted from SS using Eq. (S2):

$$N_{trap} = \frac{C}{q}\left[\frac{q\, SSlog\, e}{k_B T} - 1\right] \tag{S2}$$

where k is the Boltzmann's constant and T is the temperature in Kelvin. More than 10 device cells were tested from at least two different batches and reproducible data were obtained.

Characterization

Fourier transform infrared spectroscopy (FTIR; PerkinElmer Spectrum One spectrophotometer) was performed to investigate the chemical structures. Film thickness was measured with DEKTAK 150 Surface Profilometer (Veeco). The chemical composition of *h*TSO film was measure by X-ray photoelectron spectroscopy (XPS; Thermo VG Scientific Sigma Probe spectrometer) using Al Kα radiation (1486.6 eV). A carbon 1s peak at 284.8 eV was used as a reference for calibration. The atomic force microscope (AFM, Seiko SPA400) was operated under tapping mode at room temperature to investigate the surface roughness. Etched silicon tips with a typical resonant frequency of 160 kHz were employed. The contact angle was measured using a high-resolution drop shape analysis system (DSA 10-MK2, KRUESS) under laboratory conditions. Five measurements were made on different area of the sample. The surface energy was evaluated by the method proposed by Owens and Wendt (Eq. (S3)) using the measured contact angles with water and diidomethane in static mode:

$$1 + cos\,\theta = \frac{2(\gamma_s^d)^{1/2}(\gamma_L^d)^{1/2}}{\gamma_L} + \frac{2(\gamma_s^p)^{1/2}(\gamma_L^p)^{1/2}}{\gamma_L} \tag{S3}$$

where γ_s^d and γ_s^p are the dispersion and polar components of surface energy. γ_L^d and γ_L^p are fluid dispersion and polar components of surface energy. The total surface energy γ^s is obtained by summing the dispersion and polar components.

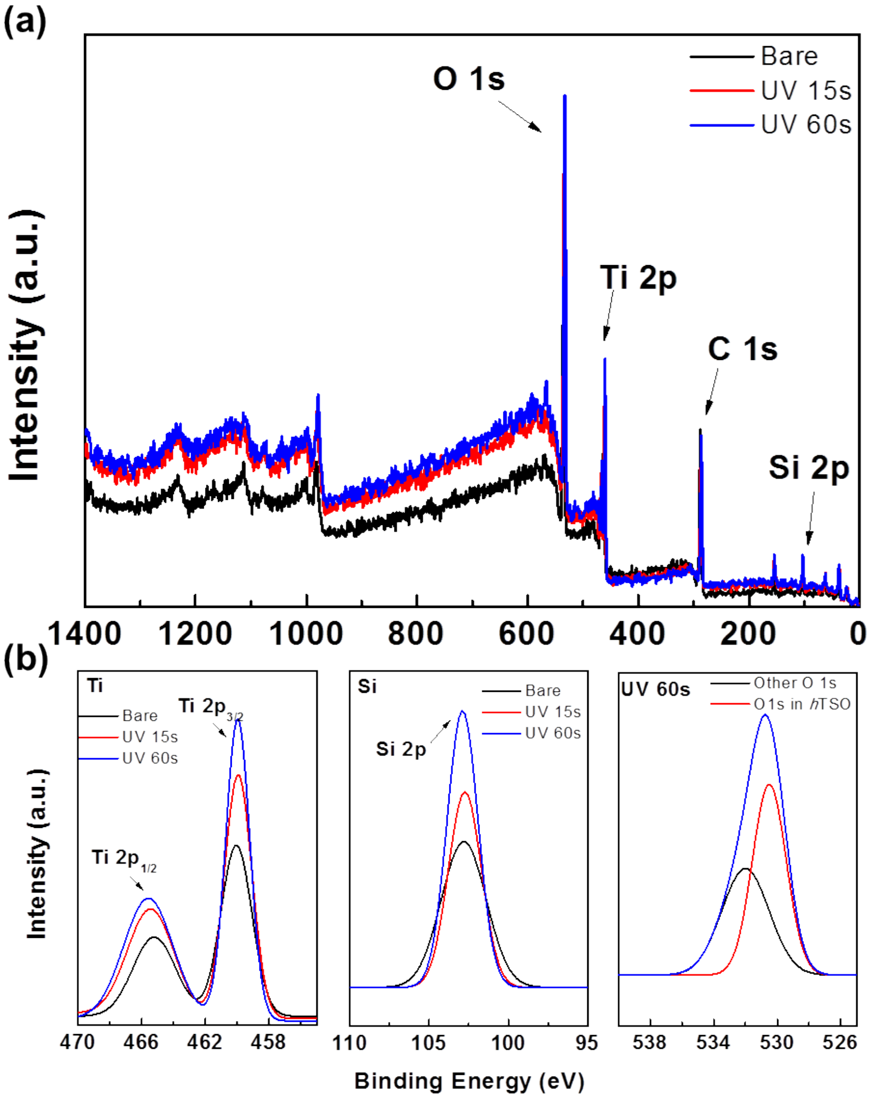

Fig. S1 (a) X-ray photoelectron spectroscopy (XPS) analysis showing the composition of *h*TSO film. (b) Ti 2p, Si 2p and O 1s core level photoemission spectrum of the *h*TSO film.

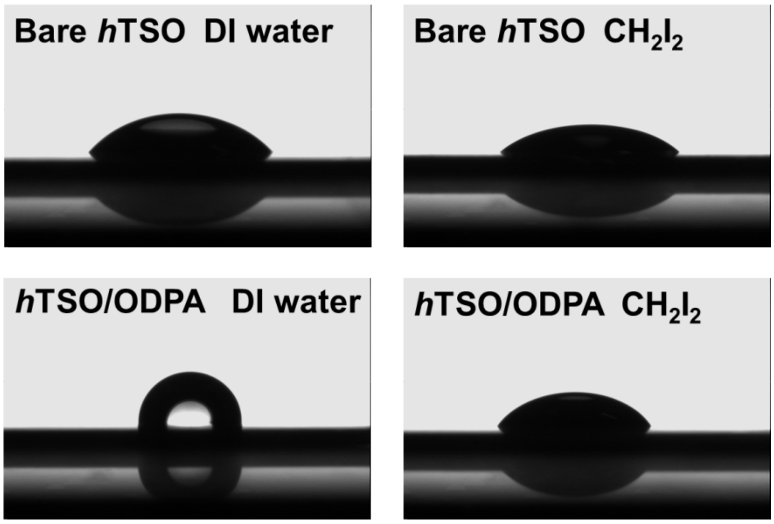

Fig. S2 (a) DI water and (b) diiodomethane contact angles on *h*TSO and *h*TSO/OPDA dielectric surface.

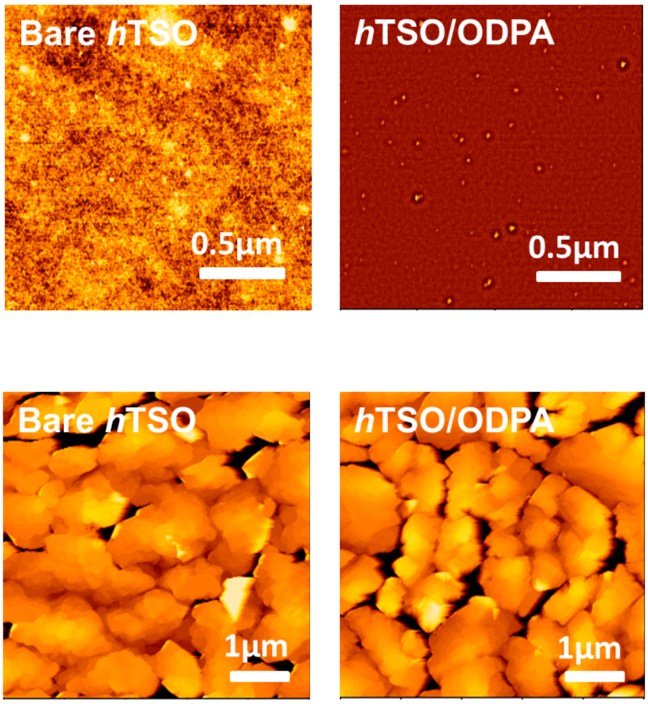

Fig. S3 AFM height images of (a) the *h*TSO and *h*TSO/OPDA surface and (b) the surface after thermally evaporating 50 nm thick pentacene on *h*TSO and *h*TSO/OPDA.

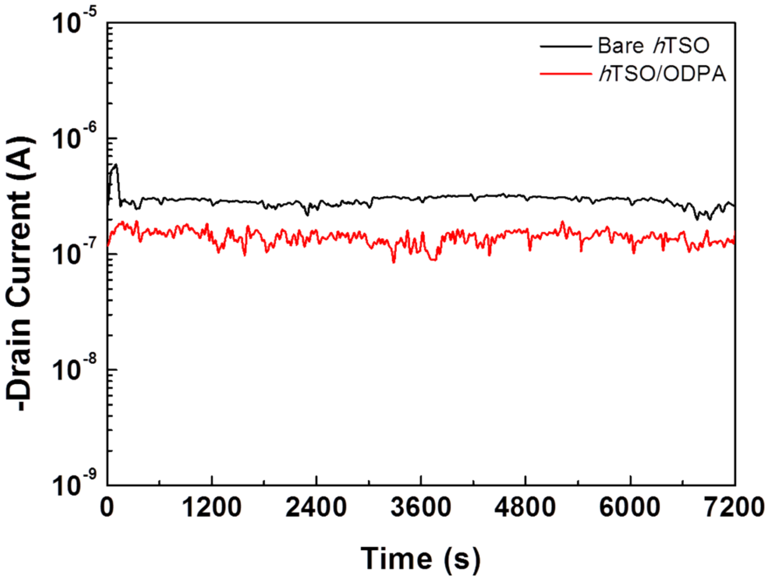

Fig. S4 I_{ON} of OTFTs based on *h*TSO and *h*TSO/OPDA dielectric as a function of the time under gate bias stress.