
CHAPTER 2

Low Voltage Operable Eco-Friendly Water-Induced LiO_x Dielectric Based Organic Field Effect Transistor.

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CHAPTER 2

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2.1 Introduction

There is a significant amount of interest in the potential of utilizing solution processed low voltage operable organic field effect transistors in large-area electronics applications, sensors, displays, and electronic bar codes. To reduce power consumption in battery-operated and portable sensors, the development of low-voltage organic field effect transistors (OFETs) is a must[68], [69]. To develop low voltage OFETs many solution-processed high k inorganic dielectric like HfO₂, hafnium oxynitride (HfON), ZrO₂, Al₂O₃, and barium zirconate titanate have been explored as the dielectric in OFETs [70]–[73]. Inorganic dielectrics despite very high k values are difficult to incorporate with organic semiconductors due to various problems like surface charge traps and roughness[2]. Recently many groups have reported various combinations with lithium oxide (LiO_x) for low voltage inorganic semiconductor-based thin film transistors[74]–[76]. However, to our knowledge, there isn't such report available for the use of LiO_x dielectric in OFETs.

The floating film transfer method (FTM), which uses the transfer of self-assembled organic semiconductor (OSC) film from the liquid surface (organic/water surface) to the substrate, has gained popularity because of the ease of large area processing, no requirement for sophisticated instruments and minimal wastage of costly OSCs materials[44], [47], [77]–[79].

Water based synthesis of Metal oxide dielectrics decreases the processing cost of the device and is environmentally friendly in comparison to costly organic solvents and additives. The water-processed synthesis is regarded to be safer, healthier, and more eco-friendly than the frequently used toxic organic-related solvents like dimethylformamide (DMF) and 2-methoxy ethanol. Additionally use of toxic Organic additives requires higher annealing temperature leading to increased surface roughness and film porosity which increases the leakage current density and degrades overall device performance [36] –[80].

This chapter reports eco-friendly water-processed DPP- DTT (poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5di(thien-2-yl) thieno [3,2-b]-thiophene)]) based OFETs using water-processed LiO_x as the gate dielectric. We prepared the precursor solution of LiO_x from lithium nitrate using deionized water (DI) water as the solvent and used it during the coating process without utilizing any harmful organic solvents or additives. We have also used DI water as the lifting solvent for the floating film transfer method. The maximum processing temperature in the whole experiment was not more than 300 °C.

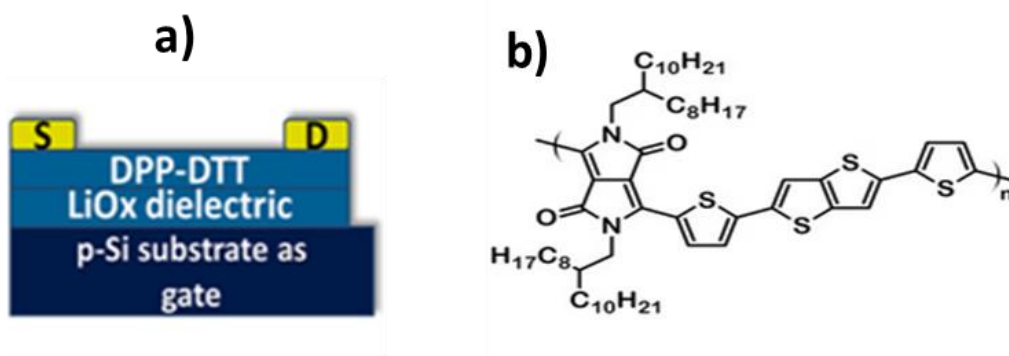


Fig. 2.1 a) Schematic of the device. b) structure of DPP-DTT.

In brief, this chapter presents a water processed LiO_x dielectric film and W-FTM transferred organic semiconductor film of DPP-DTT. The fabricated devices showed average mobility of

0.14 (± 0.035) $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$, on/off ratio of $\sim 10^4$, a good Subthreshold swing of 186 (± 15) mV/decade and surface charge trap density (N_{it}) of $4.63 (\pm 0.42) \times 10^{12} \text{cm}^{-2} \cdot \text{eV}^{-1}$, the threshold voltage of around -1.12 (± 0.3). This chapter has four sections including this one. The subsequent sections include device fabrication steps (section 2.2) followed by result and discussion in section 2.3 and conclusion summarizing key findings in section 2.4

2.2 Experimental Details

The DPP-DTT (Mw. =100,105) was procured from Ossila Ltd. UK. Lithium nitrate, Chloroform, and Dichlorobenzene were purchased from Sigma Aldrich. Heavily doped p-type silicon substrate was diced and cleaned using the standard cleaning process[36], [76] and used as a gate electrode using the bottom gate and top contact structure. 0.12M lithium nitrate solution, prepared in DI water by stirring overnight, was spin-coated on the plasma-cleaned substrate at 5000 rpm and baked at 80 °C for 5 min before heating at 300 °C for 2 hours. Thereafter the coated film went under HMDS (Hexamethyldisilane) vapor treatment for 2 hours at 90 °C. The HMDS treated substrate was rinsed with ethanol and dried on the hot plate at 120 °C for 10 minutes. 10 mg/ml DPP-DTT was dissolved in a solution made up of chloroform and dichlorobenzene in the volume ratio of 8:2 for 6 hours using a stirrer. 10 μL of the DPP-DTT solution was dropped gently over the water surface in a Petri dish and a floating film of DPP-DTT was obtained as shown in figure 2.2 (a) which was stamped onto the HMDS treated LiO_x film and then dried at 120 °C for 30 minutes. Then 50 nm gold source drain electrodes (W/L =1000 μm /30 μm) were deposited using a metal mask from Ossila Ltd. in the thermal evaporator (Hind Hivac 1242D) maintained at the high vacuum of 2×10^5 mbar at 0.02 nm/sec.

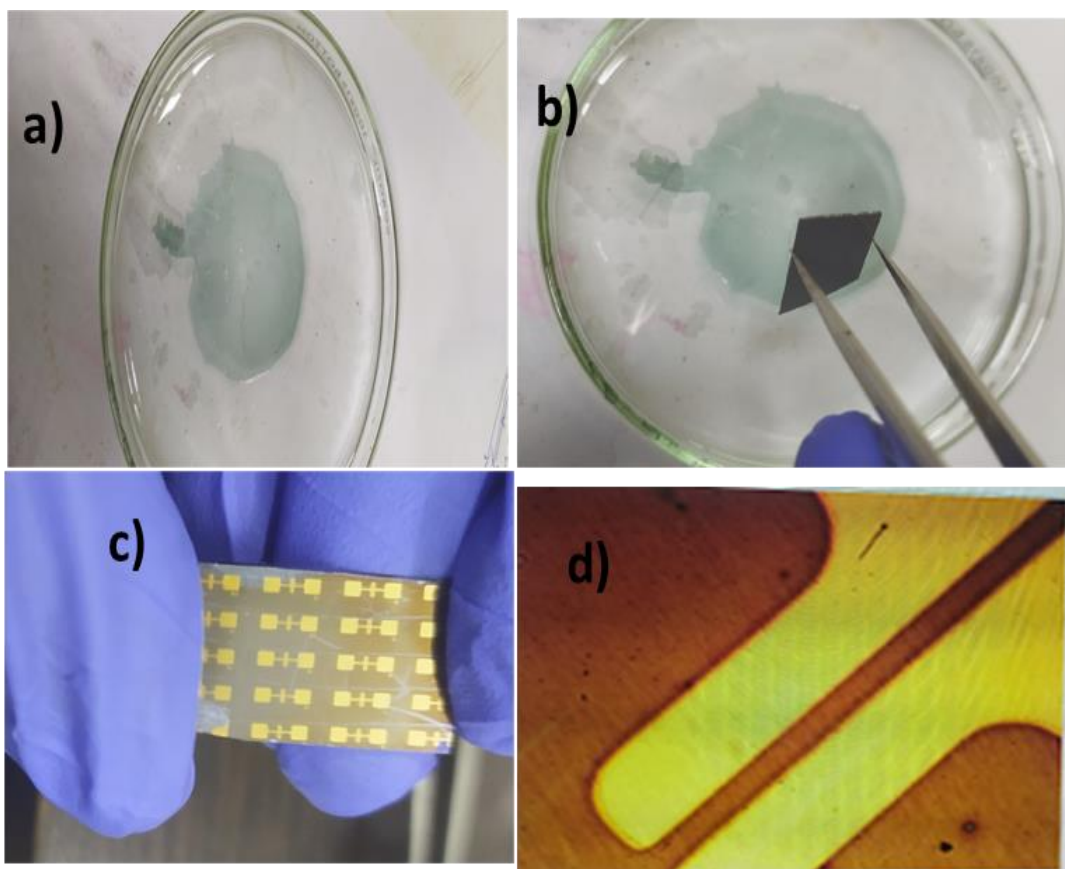


Fig. 2.2. a) Floating film of DPP-DTT over DI water. b) transfer of Floating film to the substrate. c) the fabricated device. d) optical micrograph of the device channel.

2.3 Results and Discussion

2.3.1 Surface morphologies of Dielectric and Organic semiconductor

Surface morphologies of DPP-DTT film lifted from the water surface and HMDS treated LiO_x film was performed by atomic force microscopy (NTEGRA Prima) and depicted in fig. 3. (a) and (b). The roughness parameters of the HMDS-treated dielectric film have been summarized in the table 2.1. The root mean square roughness of HMDS-treated LiO_x film and DPP-DTT film was 0.169 nm and 2.948 nm respectively. A smoother dielectric surface reduces carrier scattering centers and interface charge traps leading to a favorable interface between OSC and the dielectric layer [36], [81].

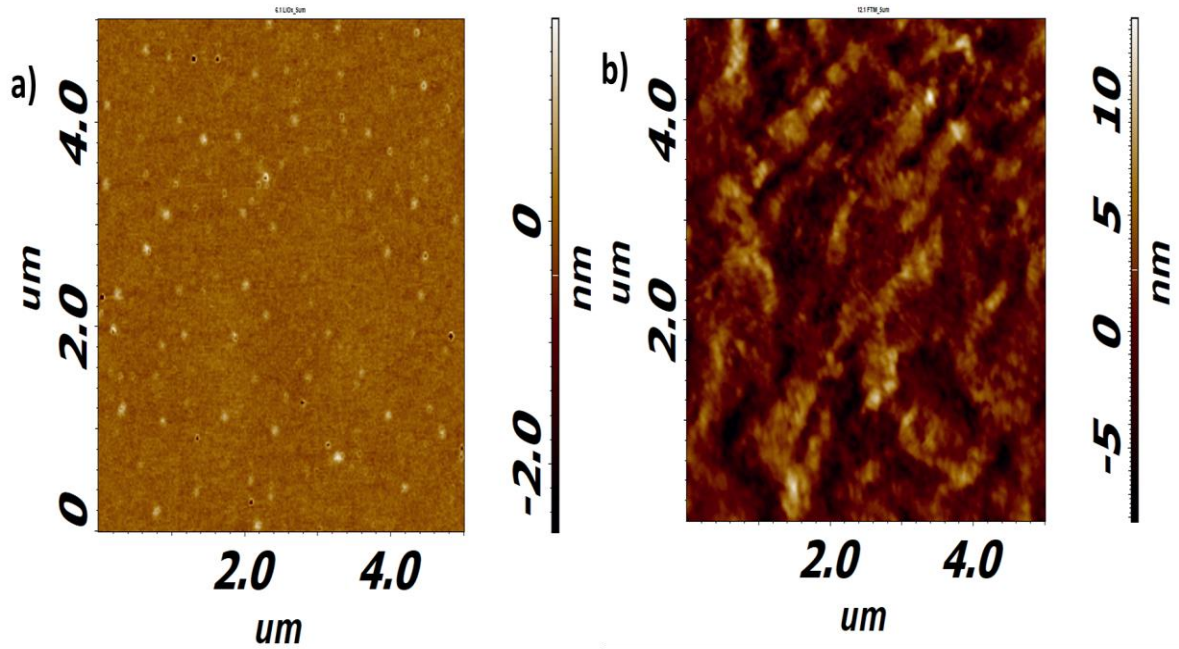


Fig. 2.3 a) Surface morphologies of DPP-DTT film lifted from water surface b) HMDS treated LiO_x dielectric.

TABLE 2.1

**ROUGHNESS PARAMETERS OF HMDS TREATED LiO_x DIELECTRIC
OBTAINED THROUGH AFM**

Roughness Parameters of LiO_x obtained from AFM	Values (nm)
Root mean square roughness (S_q)	0.169 nm
Average roughness (S_a)	0.124 nm
Area peak-to-valley height (S_t)	4.214 nm
Maximum area peak height (S_p)	1.661 nm
Maximum area valley depth (S_v)	2.553 nm

2.3.2 Dielectric Leakage Behaviour and Areal Capacitance

Metal insulator metal (MIM) structures as shown in fig. 2.4. b) were used to measure the areal capacitance (C_i) values at different frequencies which was experimentally found to be 380 (± 18) nF/cm² for plain LiO_x and 307 (± 12) nF/cm² for HMDS treated LiO_x at 1 KHz. The leakage behavior of DI water processed LiO_x thin film is plotted in fig. 2.4. a). The leakage current density (J_{leakage}) was found to be 1.6×10^{-8} A/cm² at 1 MV/cm. These leakage current density (J_{leakage}) values of LiO_x dielectric are low enough to be employed as the dielectric in low Voltage operable OFETs [81], [82].

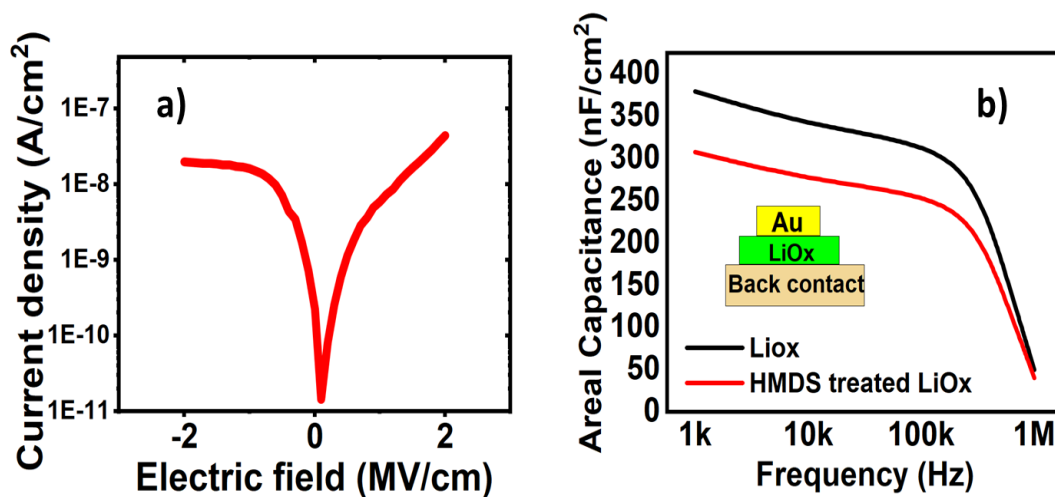


Fig. 2.4. a) Leakage current density of LiO_x dielectric film. b) Areal capacitance (C-f curve) of LiO_x film.

2.3.3 Electrical Characterizations

All electrical measurements were done using Keithley B1500A semiconductor analyzer with unencapsulated devices under ambient conditions. Fig. 2.5. (a) and (b) shows the output and transfer characteristics of DPP-DTT based OFET respectively. All the measurements of transfer characteristics and respective extraction of parameters were done at $V_{\text{DS}} = -2$ V. The maximum

slope of the linearly fitted $|I_D|^{1/2}$ against V_{GS} curve was used to extract the saturation mobility (μ_{sat}) and threshold voltage (V_{TH}) [83]. Sub threshold swing (SS) was determined by the reciprocal of the maximum slope of the semi-log plot of the transfer curve and was found to be 186 (± 15) mV/decade [84]. The devices showed I_{ON}/I_{OFF} ratio of $\sim 10^4$. Interface trap density (N_{ss}), which is indicative of a good quality interface, was found to be $4.63 (\pm 0.42) \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ [36],[85]. These measured and extracted parameters for 10 devices ($V_{DS} = -2 \text{ V}$) fabricated on the same substrate are summarized in table 2.2. In order to test the electrical stability of the device, the negative bias of $V_{DS} = V_{GS} = -2 \text{ V}$ was applied, measurements were done for 3600 sec and transfer characteristics were plotted in Fig. 2.7. The change in drain current (I_D) under negative bias stress of $V_{DS} = V_{GS} = -2 \text{ V}$ was observed for 3600 s and a decay of 19.4% was observed as shown in Fig. 2.7 Ambient stability of the LiOx based DPP-DTT OFET was carried out at different intervals of time for 3600 sec as depicted in Fig. 2.6.

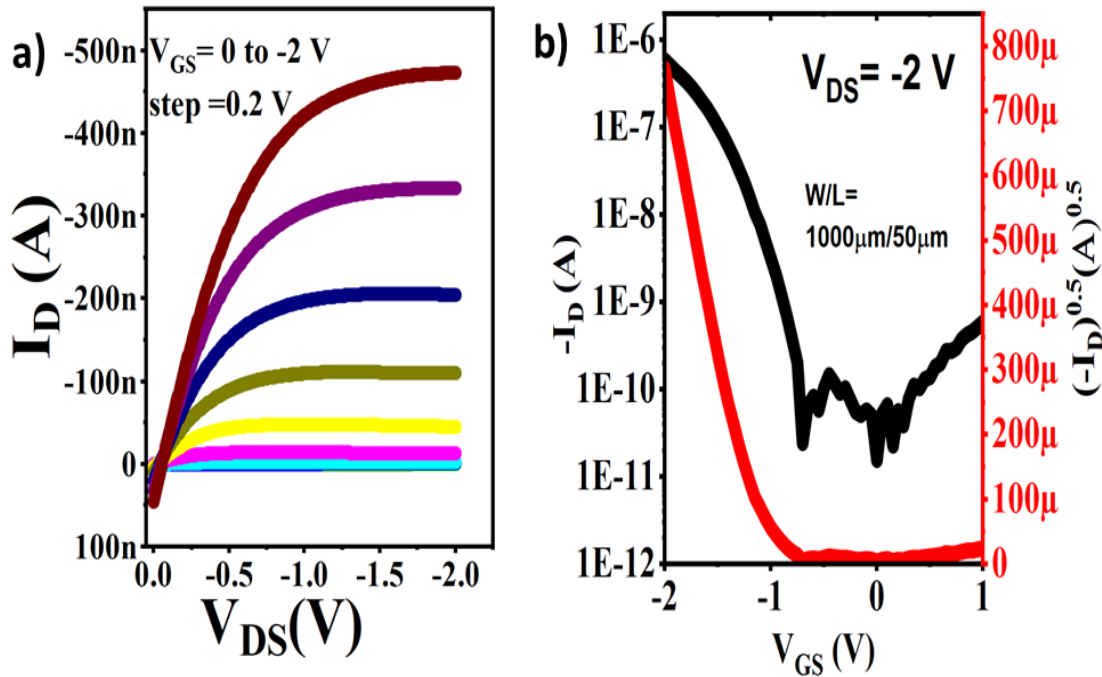


Fig. 2.5. a) Output characteristics and b) transfer characteristics of the representative device.

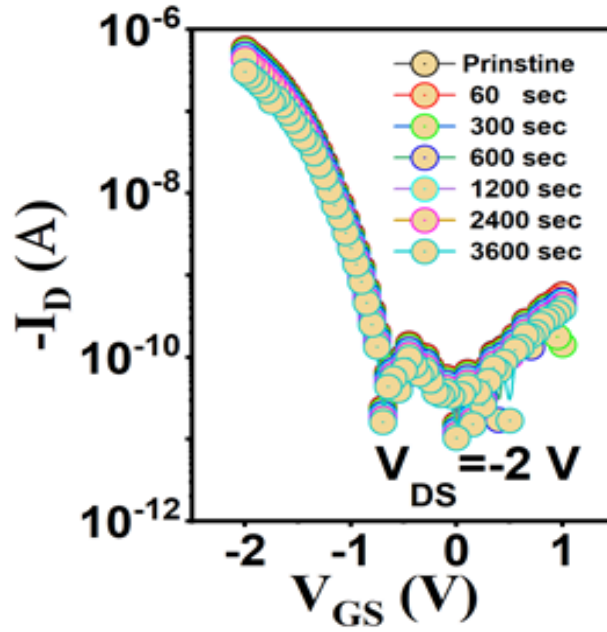


Fig. 2.6. Measured bias stability of device for 3600s.

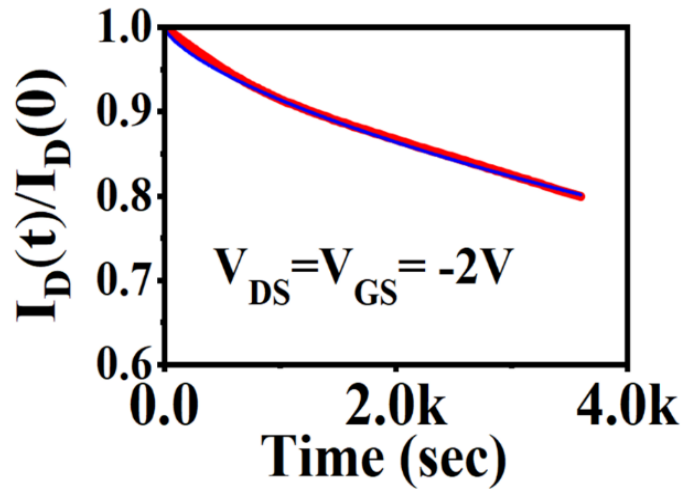


Fig. 2.7. Bias stress-induced normalized drain current decay for 3600s.

TABLE 2.2

SUMMARY OF EXTRACTED OFET PARAMAETRS FOR 10 DEVICES.

V_{TH} (V)	μ_{sat} $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$	SS (mV/decade)	N_s ($10^{12} \text{cm}^{-2} \cdot \text{eV}^{-1}$)	I_{ON}/I_{OFF}
1.12 (± 0.3)	0.14 (± 0.035)	186 (± 15)	4.63 (± 0.42)	$\sim 10^4$

2.4 Conclusion

This work uses the nontoxic and eco-friendly water-driven synthesis of LiO_x (with a maximum temperature of 300 °C) dielectric for OFETs fabrication and combines the advantages of water-induced dielectric and floating film transfer from the surface of the water instead of using toxic organic solvents. These devices exhibited maximum saturation mobility (μ_{\max}) of 0.184 cm² V⁻¹ sec⁻¹ and average mobility (μ_{avg}) of 0.14 (± 0.035) cm² V⁻¹ sec⁻¹ with the I_{ON}/I_{OFF} ratio of $\sim 10^4$ and sub threshold swing of 186 (± 15) mV/decade under -2 V operation. For electrical stability, multiple transfer scans were done for 3600 sec which produced a relative shift of 0.12 V in threshold voltage and 19.4% decay in the drain current.

