High Performance, Low Operating Voltage n-Type Organic Field Effect Transistor Based on Inorganic-Organic Bilayer Dielectric System

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Abstract. The performance of organic field-effect transistors (OFETs) fabricated utilizing vacuum deposited n-type conjugated molecule N,N'-Diocotadecyl-1,4,5,8-naphthalenetetracarboxylic diimide (NDIOD2) were investigated using single and bilayer dielectric system over a low-cost glass substrate. Single layer device structure consists of Poly (vinyl alcohol) (PVA) as the dielectric material whereas the bilayer systems contain two different device configuration namely aluminium oxide/ Poly (vinyl alcohol) (Al\(_2\)O\(_3\)/PVA) and aluminum oxide/Poly (methyl methacrylate) (Al\(_2\)O\(_3\)/PMMA) in order to reduce the operating voltage and improve the device performance. It was observed that the devices with Al\(_2\)O\(_3\)/PMMA bilayer dielectric system and top contact aluminum electrodes exhibit excellent n-channel behaviour under vacuum compared to the other two structures with electron mobility value of 0.32 cm\(^2\)/Vs, threshold voltages \(-1.8\) V and current on/off ratio \(\approx 10^4\), operating under a very low voltage (6 V). These devices demonstrate highly stable electrical behaviour under multiple scans and low threshold voltage instability in vacuum condition even after 7 days than the Al\(_2\)O\(_3\)/PVA device structure. This low operating voltage, high performance OTFT device with bilayer dielectric system is expected to have diverse applications in the next generation of OTFT technologies.

1. Introduction

Organic field-effect transistors (OFETs) are the basic elements of organic electronic and optoelectronic applications. Due to their low-cost, large-area fabrication possibility, in near future OFET technologies are expected to build a new alternative market compared to conventional inorganic technologies in the mainstream electronics. Generally, OFETs are operated within large operating voltage range, which is one of the major limitations in finding their application in futuristic electronics [1-3]. Hence, an ideal OFET should have low operational voltage, high electrical stability and lifetime for real-life application, such as radio frequency identification (RFID) tag, sensor, electro-optical switch etc. It has already been reported that in order to achieve excellent device performance with low operating voltage, high-k inorganic dielectrics have been traditionally used [4, 5]. The popular choice has always been Al\(_2\)O\(_3\) because of its high insulating property and low-cost deposition technique [6, 7]. However, the single Al\(_2\)O\(_3\) film shows huge leakage current because of the inferior film forming
quality. In contrast, Poly(vinyl alcohol) (PVA) and Poly(methyl methacrylate) (PMMA), the polymer dielectric materials, have emerged as the viable choice since they can be processed through solution processing methods, thereby reducing the overall cost of device fabrication. However, PVA-based OFETs often suffer from relatively low stability and large drain current ($I_{DS}$) hysteresis, which could be possibly associated due to the presence of -OH groups on the PVA surface [8]. On the other hand, due to the remarkable film forming ability and non-interacting nature of PMMA, it can be used to achieve high quality films in the organic-organic interface. However, these dielectric materials possess very low capacitance value, requiring very high threshold and operating voltages for device operation. Considering the advantages of polymer dielectric for better interfacial effect and high-k inorganic dielectric for low voltage operation, the concept of hybrid bilayer dielectric was proposed and introduced in OFETs.

In this study, we reported the fabrication and characterization of vacuum deposited NDIOD2 molecule containing 1, 4, 5, 8-Naphthalene diimides (NDI) substituted with octadecylamine (OD) chains, on Al2O3/PMMA bilayer dielectric system to achieve incredibly low threshold and operating voltages. The result was compared with our previous report containing single layer PVA gate dielectric on the glass substrate [9]. Al2O3 was used as a high dielectric constant material, whereas the role of PMMA was to provide a smoother interface to the organic semiconductor film. Devices having top contact aluminum electrode architectures exhibit excellent n-channel behavior with threshold voltage as low as 1.8 V. The ON/OFF current ratios of the devices were observed to be of the order of $10^4$ up to an operating voltage of 6 V. Moreover, the devices exhibit remarkable stability under repeated scans and low threshold even after prolonged storage compared to Al2O3/PVA dielectric system. Thus, without compromising the carrier mobility (0.32 cm$^2$/V s) low-cost and environmentally friendly n-channel OTFT can be accomplished with drastic reduction in the operating voltage to 6 V from 50 V, by utilizing a combination of inorganic-organic (Al2O3/PMMA) bilayer dielectric system. This high performance OTFT device with 6 V operating voltage, with bilayer dielectric system is expected to have diverse applications in next generation of OTFT based technologies.

2. Experimental Section

2.1. Chemicals and solvents
1, 4, 5, 8-Naphthaleneteracarboxylic dianhydride, octadecylamine, quinoline, zinc acetate, PMMA (MW=550000 g/mol), and aluminum wire (99.999% purity) were used as received from Sigma Aldrich. PVA (MW= 1, 15,000 g/mol) and anisole were purchased from Loba Chemie (99% purity) and used as received. Microscope glass slides (thickness 1-1.2mm) purchased from Jain Scientific Glass Works, India, was used as the device substrate without any surface modification. NDIOD2 molecule was synthesized following the procedure reported previously [9].

2.2. Characterization details
The thin films of NDIOD2, deposited by thermal evaporation technique, was measured by Veeco Dektak 150 Surface Profilometer. All AFM images were recorded by Agilent 5500-STM instrument under non-contact mode. Gaussian 03 software was used to perform the DFT simulation of the material. CH Instrument was used to perform the electrochemical analysis of NDIOD2. Finally, all the electrical properties were recorded by Keithley 4200 semiconductor characterization system (SCS).
3. Result and Discussion

3.1. Band gap analysis

Figure 1. Illustration of energy level diagram of NDIOD2 molecule as estimated from DFT calculation.

Figure 2. Cyclic voltammetric curve of NDIOD2 molecule thin film with ferrocene as the reference.

The geometrically optimized chemical structure of NDIOD2 obtained from DFT calculation by considering B3LYP/6-31G(d) basis set along with its energy level diagram and the cyclic voltammetric curve of NDIOD2 molecule are represented in Figure 1 and 2 respectively. The HOMO and LUMO energy values of NDIOD2 molecule, estimated by electrochemical analysis using onset calculation of Equations (1) and (2) are given below-[10]

\[
E_{\text{HOMO}} = -(E_{\text{OX,onset} \text{,} \text{eV}} + 4.8) \\
E_{\text{LUMO}} = -(E_{\text{RED,onset} \text{,} \text{eV}} + 4.8)
\]

where, -4.8 eV is the absolute HOMO level of ferrocene, acting as the internal reference. The estimated HOMO and LUMO energy levels and the band gap of the material were summarized in Table 1.

| $E_{\text{HOMO}}^{(CV)}$ | $E_{\text{LUMO}}^{(CV)}$ | $E_{g}^{(CV)}$ b | $E_{g}^{(Th)}$ c |
|--------------------------|--------------------------|------------------|------------------|
| -6.414                   | -3.394                   | 3.02             | 3.61             |

a Energies are in eV.
b Electrochemical band gap.
c Theoretical band gap was calculated by using DFT calculation.

3.2. Device fabrication method on PVA single layer dielectric configuration

OTFTs based on NDIOD2 molecule were fabricated following the procedure reported in our previous study [9]. Glass slides were used as substrates onto which an aluminum gate (thickness 100 nm) was deposited by thermal evaporation method through a shadow mask. Further, a solution of PVA dielectric in de-ionized water (10 wt. %) was spin-coated on top of the aluminum film and dried for 1 h at 100 °C in a vacuum oven. The thickness of the PVA film was approximately 1µm, measured by
surface profilometer, which showed capacitance of \( \sim 8.854 \text{ nF.cm}^{-2} \). Following this, a 60 nm thick (\( \pm 10 \text{ nm} \)) NDIOD2 thin film was thermally deposited at room temperature, at a pressure of \( 10^{-6} \text{ mbar} \). Finally, square shaped aluminum source and drain contacts having thickness \( \sim 100 \text{ nm} \) were thermally evaporated to characterize the electrical parameters of the OFETs (using a Keithley 4200 semiconductor characterization system (SCS)) under vacuum. The schematic structure of the device and the AFM images of PVA dielectric as well as the NDIOD2 molecule on top of PVA dielectric layer using glass substrate are shown below in Figure 3 and 4 respectively.

**Figure 3.** Schematic of the device structure with single layer PVA dielectric system.

**Figure 4.** AFM image of (a) PVA dielectric thin film (~1 \( \mu \text{m} \)) and (b) PVA/NDIOD2 semiconductor on the glass substrate.

3.3. **Device fabrication method on Al\textsubscript{2}O\textsubscript{3}/PVA and Al\textsubscript{2}O\textsubscript{3}/PMMA bilayer dielectrics configurations**

Anodization is a very good, effective and solution based technique to grow metal oxide films with nanometer control. The high capacitance, pinhole-free Al\textsubscript{2}O\textsubscript{3} gate insulators can be fabricated by electrochemical oxidation (or anodization) of the gate metal on desired substrates, such as, glass and flexible transparent sheets etc. In addition, this process can yield a high-quality metal-oxide insulator at room temperature with very low cost and less time.

**Figure 5.** Anodic oxidation setup for aluminum.
In this method we used cleaned glass slides (size: 15 mm × 25 mm) to serve as device substrates, onto which >200 nm thick aluminum gate with dimensions 1 mm × 20 mm was deposited by thermal evaporation method through a shadow mask. The film was then anodized with a constant current density of 0.06 mA cm$^{-2}$ and a voltage of 10 V in a 0.001 M citric acid monohydrate electrolyte solution at 25°C (room temperature) using a square-shaped platinum mesh as counter electrode to form a ~13 nm thick Al$_2$O$_3$ layer over the aluminum film gate electrode. Figures 5, 6 and 7 demonstrate the anodization setup which was used for growing Al$_2$O$_3$ film, the typical anodization graph and the AFM images of aluminum film before and after anodic oxidation.

After iodization, to further reduce the surface roughness, a 100 nm thick PVA and PMMA thin film was separately spin coated on the two device configurations, to form Al$_2$O$_3$/PVA and Al$_2$O$_3$/PMMA bilayer dielectric systems, and dried for 1 h at 120°C under nitrogen atmosphere. Both the organic dielectric solution was prepared by dissolving 30 mg/ml of PVA in de-ionized water and 30 mg/ml of PMMA in anisole. The capacitance of the Al$_2$O$_3$/PVA and Al$_2$O$_3$/PMMA bilayer dielectric systems were observed as ~6 nF.cm$^{-2}$ and ~27 nF.cm$^{-2}$ respectively, out of which Al$_2$O$_3$/PMMA is much higher than the single layer device structure. Followed by this, 60 nm (± 10 nm) the NDIOD2 active material was deposited by thermal deposition method under a base pressure of 10$^{-6}$ mbar. Further, aluminum source-drain electrodes were thermally evaporated, at room temperature, up to a thickness of 100 nm to calculate three terminal properties of the NDIOD2 material. The schematic of the device structures and the AFM images of Al$_2$O$_3$/PVA and Al$_2$O$_3$/PMMA bilayer dielectrics and NDIOD2 molecule on top of these layers using glass substrates are shown below in Figures 8 - 11 respectively.
3.4. Device Characterisation

The OFET mobility value of the NDIOD2 molecule was estimated from the saturated region by using the following Equation (3).

\[
I_{DS} = \frac{\mu W C_i}{2L} (V_G - V_{Th})^2
\]

where \(I_{DS}\), \(\mu\) and \(C_i\) represent the drain current, the field effect electron mobility and the capacitance per unit area of the bilayer gate dielectric. \(V_{Th}\) and \(V_G\) signify the threshold voltage and gate voltage respectively. Figures 12, 13 and 14 demonstrate the typical drain and transfer characteristics curve of NDIOD2 molecule on single layer PVA, bilayer Al\(_2\)O\(_3\)/PVA and Al\(_2\)O\(_3\)/PMMA dielectric system respectively. The calculated OFET parameters of the molecule are listed in Table 2.
Figure 13. (a) Drain and (b) transfer characteristics curve of NDIOD2 molecule in the Al$_2$O$_3$/PVA bilayer dielectrics system.

Figure 14. (a) Drain and (b) transfer characteristics curve of NDIOD2 molecule in the Al$_2$O$_3$/PMMA bilayer dielectrics system.

Table 2. Comparison of OFETs measurement for NDIOD2 molecule between single and bilayer dielectrics system

| Dielectric  | Thickness  | Capacitance(C$_i$) (nF/cm$^2$) | Mobility(µ) (cm$^2$/V.s) | V$_{th}$ (V) | Ion/Ioff |
|-------------|------------|---------------------------------|--------------------------|-------------|---------|
| PVA         | 1 µm       | 8.854                           | 0.68                     | 16.24       | 10$^2$  |
| Al$_2$O$_3$/PVA | 10nm/100nm | 6                               | 0.13                     | 0.99        | 10$^1$  |
| Al$_2$O$_3$/PMMA | 10nm/100nm | 27                              | 0.32                     | 1.8         | 10$^4$  |

The NDIOD2 molecules in OFET devices, sublimed at room temperatures over bilayer Al$_2$O$_3$/PMMA gate dielectric, exhibited excellent average electron mobility as 0.32 cm$^2$/V.s under vacuum with a threshold voltage of 1.8 V. The ON/OFF current ratio of the devices were observed to be of the order of $10^4$ up to an operating voltage of only 6 V. However, the device with Al$_2$O$_3$/PVA showed low threshold voltage and low electron mobility likely due to the presence of -OH group in the PVA.
dielectric which creates charge traps at the dielectric-semiconductor interface. These traps also reduce the overall stability and degrade the devices very fast (~1 day). Thus, the Al₂O₃/PMMA bilayer dielectric system demonstrates drastic improvement in the device performance due to better capacitive coupling between the gate and the channel through the dielectric layer to enhance field-effect carrier mobility and the threshold voltage compared to the PVA dielectric system.

4. Conclusion
In conclusion, we described the electrical performances of vacuum-deposited thin film based n-channel organic field effect transistors with alkyl chain-substituted NDIOD2 molecule. The devices were studied in a top contact bottom gate configuration using aluminum source/drain electrodes with PVA, Al₂O₃/PVA and Al₂O₃/PMMA as single and bilayer gate dielectric systems respectively. The devices fabricated using NDIOD2 with Al₂O₃/PMMA gate dielectric and aluminum source-drain metal electrodes exhibited excellent n-channel behavior with average field-effect electron mobility of 0.32 cm²/V s and threshold voltage of 1.8 V for channel length, L=40 µm and channel width, W=800 µm. This OFET device showed ON/OFF current ratio of 10⁴ which is much higher than PVA dielectric based devices. Also the Al₂O₃/PMMA devices demonstrated highly stable electrical behavior with no hysteresis when tested at low vacuum conditions under several scans, even after 7 days. These low cost, high performance devices are expected to open newer avenues in the field of electronic devices, energy efficient sensors and stable switching devices.

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