Fabrication and Characterization of Some Eco-friendly Processed Low Voltage Operable Organic Field Effect Transistors and their Sensing Applications.

Thesis submitted in partial fulfillment for the
Award of
Degree

Doctor of Philosophy

By

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This heartfelt tribute is dedicated entirely to my beloved mother, whom I affectionately called Maa. Her endless support and motivation propelled me to join this course. Even after my selection, I hesitated to pursue the Ph.D. Yet, she accompanied me (just to ascertain that I will join as 25th was the last date) to pay the fee on June 25th, 2018, ensuring I could enroll.

Her memory is interwoven with the early mornings of my childhood, resonating with the echoes of Ram Charit Manas on All India radio stations (with tuning from one station to another), and her tender voice urging me awake with, "Babua uth jao, Manas suno." She was an ardent believer in Prabhu Shree Ram and Mahadev. Her faith in Prabhu Shree Ram was so strong that on the day before her passing, seeing our solemn faces, she comforted us with, "Tumlog kyon udas ho, bhagwan hain na."

Maa dedicated her life entirely to the underprivileged around her. What was more striking that she never let anyone know that what and how she was 'helping' them. She hated the word help. The aroma of the special food she prepared, her gentle touch (Thapki), her joyful face upon hearing the sound of rain, the rain drops on leaves, sounds of falling rain through tree leaves, and the flowing rivers, will forever linger in my mind.

She taught me life's most profound lessons, and her memories and dreams will continue to motivate, sustain, and nurture me until my last breath. Never did I imagine that Maa wouldn't be with me at the time of my final Ph.D. degree. Life will never be the same without her.

In conclusion, I would say, life is fragile, and we never know what the future holds. Cherish every moment and hold onto the long-lasting memories.

‘‘कैलेंडर में तो कुछ ही माह ही बीते हैं पर मन में लग रहा है कि जाने कितने वर्ष बीत गए। कितने ठहराव छूट गए।कितने मोती बह गए।‘’

Prashant Kumar (Babua)

(For main acknowledgment please see the library copy).

Jai Shree SitaRam Ji

Dedicated

To my beloved mother Smt. Kanak Lata whose unwavering love and endless encouragement have been my guiding light and will continue to be.

Preface

This thesis explores some low voltage operable OFETs fabricated using water processed gate dielectrics and their integration with FTM transferred film from the surface of the water (W-FTM) as a liquid substrate. Furthermore, the application of Water transferred FTM film of DPP-DTT in gas sensing and NIR phototransistor have also been explored. This work contributes towards eco-friendly processing of high performance and low voltage operable OFETs and their sensing applications.

Chapter 1 covers a brief introduction to OFET devices their working, parameter extraction, and, basic charge transport in organic semiconductors. Furthermore, this chapter includes a brief review of high k dielectrics used in OFETs, a brief review of recent OFET based NO_2 sensors, a brief review of NIR OPTs, solution process techniques for OSC, a brief introduction and, mechanism of Floating film transfer method followed by the benefits of Water transferred FTM (W-FTM) Film.

Chapter 2 presents the fabrication and characterization of LiO_x based OFETs. This chapter combines the advantages of ecofriendly water induced LiO_x and W-FTM transferred DPP-DTT film. HMDS vapor treatment was used to passivate the surface traps on the LiO_x. Water processed LiO_x was deposited on the Silicon substrate which was used as a substrate as well as the gate. The organic semiconductor DPP-DTT was transferred to the annealed and HMDS treated LiO_x film from the surface of the water using the FTM method. The chapter covers leakage current behavior with respect to the applied voltage and areal gate capacitance of LiO_x film with respect to frequency. The Surface morphologies of HMDS treated LiO_x film have been studied using Atomic Force microscopy. The I_D-V_G and I_D-V_D (transfer and output respectively) characteristics have been characterized while I_D-V_G has been used to extract the performance parameters of OFETs. A repeated transfer scan for 3600 sec has been presented to see the ambient stability of the device. Current stress bias for 3600 sec continuously was studied to understand the electrical stability of the OFET. It covers the experimental details of film characterization and leakage current behavior and areal capacitance of LiO_x based dielectric characterization followed by electrical characterization and current bias stability analysis for one hour. It shows the integration of water based FTM transfer technology. The devices exhibited an average mobility (μ_{avg}) of 0.14 (±0.035) $cm^2\ V^{-1}\ sec^{-1}$and a maximum saturation mobility (μ_{max}) of 0.184 $cm^2\ V^{-1}\ sec^{-1}$. A good on/off ratio of ~ 10^4 was obtained with the threshold voltage of around -1.12 (±0.3). Moreover, LiO_x based OFET shows a good Subthreshold swing of 186 (±15) mV/decade and surface charge trap density (N_{it}) of 4.63 (±0.42) $\times 10^{12}$ $cm^{-2}.eV^{-1}$.

Chapter 3 is devoted to the fabrication and characterization of ultra-low voltage operable OFETs with bilayer LiO_x/AlO_x dielectrics. DI water has been used for processing of both the dielectric layers. OPDA solution has been used as the SAM (self-assembled monolayer) layer. The same FTM approach to transfer DPP-DTT film from the water surface has been utilized for the OSC layer. The Surface morphologies of the LiO_x, AlO_x, OPDA-treated AlO_x, and Water transferred DPP-DTT film have been studied using AFM. The leakage current behavior of LiO_x and LiO_x/AlO_x bilayer has been studied along with band gap analysis using UV-vis analysis. The areal capacitance of LiO_x and LiO_x/AlO_x structure has been characterized for different frequency ranges. A detailed electrical characterization involving I_D-V_G and I_D-V_D has been carried out establishing under -1 V operation of the device. Positive bias stress, negative bias stress, and, continuous current bias stress to understand the electrical stability of the device have been carried out. An environmental stability test for six weeks has also been done and relative change in threshold voltage, Subthreshold swing, and, mobility has been plotted for 6 weeks. The device showed an on/off ratio of ~ 10^5, and a subthreshold swing of ~ 90 mV/decade approaching the theoretical limit.

Chapter 4 presents a highly sensitive and selective NO_2 sensor based on low voltage operable OFET. Here thin film has been used to improve the NO_2 sensing performance of OFETs. Water-processed AlO_x film has been deposited over the p-type silicon substrate and low-cost large area processing suitable FTM approach has been employed for OSC transfer (DPP-DTT). The film was transferred from the surface of the water as a liquid substrate. A detailed change in various parameters like mobility, threshold voltage, subthreshold swing, and trap density variation with respect to changes in different gas concentrations has been studied. A selectivity study using various other gases has been carried out. A study regarding the effect of humidity on gas sensing performance has also been done. An enhancement mechanism has been discussed along with transient analysis and comparative study with the recent reports.

Chapter 5 deals with the fabrication, characterization, and parameter extraction of ultra-low voltage operable Near Infrared Organic Phototransistors (NIR-OPTs). Biocompatible and water-soluble polyvinyl alcohol has been used as a dielectric layer while OSC has been transferred using the Floating film transfer method from the surface of the water. This report utilizes the charge trapping phenomenon at the interface of dielectric/semiconductors to enhance the performance of NIR- OPTs. The PVA dielectric has a large number of hydroxyl groups that act as electron traps. Leakage current analysis of PVA dielectric and capacitance behavior has also been studied. The UV-Vis -NIR analysis of FTM transferred DPP-DTT film was carried out. The transfer characteristics of low voltage OFET with and without exposure to NIR light (850 nm) have been studied to extract parameters like responsivity, external quantum efficiency, and detectivity. A mechanism for performance enhancement has also been discussed based on the charge-trapping effect at the semiconductor dielectric interface.

Chapter 6 summarizes the obtained experimental results followed by a brief discussion on the contribution made by this thesis and a detailed pointwise list that can be incorporated for future work that may be carried out.

Content

CHAPTER 2: Low Voltage Operable Eco-Friendly Water-Induced LiO_x Dielectric Based Organic Field Effect Transistor.

CHAPTER 3: Ultra-Low Voltage Eco-friendly Water Induced LiO_x/AlO_x Bilayer Dielectric Based OFET.

CHAPTER 4: Highly Sensitive and Selective Room Temperature Operated NO_2 Sensor Based on Eco-friendly Water Processed Low Voltage Operable OFET

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LIST OF ABBREVIATIONS

OSC	Organic Semiconductor
OFETs	Organic Field Effect Transistors
OPTs	Organic Phototransistors
NIR	Near Infra-red
SEM	Scanning Electron Microscopy
SS	Subthreshold Swing
AFM	Atomic Force Microscopy
Au	Gold
S/D	Source/Drain
SEM	Scanning Electron Microscopy
HOMO	Highest occupied Molecular Orbital
LUMO	Lowest unoccupied Molecular Orbital
PS	Polystyrene
PMMA	Polymethyl methacrylate
PVA	Polyvinyl alcohol
PQT-12	Poly(3,3‴-didodecyl[2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴-diyl), Poly(4,4″-didodecyl[2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴-diyl)
P3HT	Poly(3-hexylthiophene-2,5-diyl)
TIPS-Pentacene	6,13 Bis(triisopropylsilylethynyl)pentacene
DPP-DTT	Poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)]

PBTTT-C14	Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene]
EG	Ethylene Glycol
SC	Spin Coating
FTM	Floating Film Transfer Method
HMDS	Hexamethyldisilane
ODPA	Octadecyl phosphonic acid
SAM	Self-Assembled Monolayer
DI	De ionized
W-FTM	Water-based Floating Film Transfer Method

LIST OF SYMBOLS

Symbol	Details
V_{TH}	Threshold Voltage
V_{DS}	Drain to source Voltage
V_{GS}	Gate to source Voltage
I_D	Drain Current
$I_{D,air}$	Drain Current in air (ambient)
$I_{D,gas}$	Drain Current in gas environment
I_{ON}	On Current
I_{OFF}	OFF Current
μ	Field effect mobility
μ_{sat}	Saturation mobility
N_{it}	Interface Trap Density
$J_{Leakage}$	Leakage Current Density
C_i	Capacitance per unit area
R	Responsivity
I_{Photo}	Current under light illumination
I_{Dark}	Current under dark condition
A	Area exposed to irradiated light
D	Detectivity
W	Width of channel
L	Length of Channel
T	Temperature
k	Boltzmann constant
q	Charge on electron
k	Relative dielectric constant
t_r	Response time
t_f	Recovery/fall time