Development of Organic and Organic/Inorganic Hybrid Thin Film Transistors for Sensing Applications

Thesis submitted in partial fulfillment for the award of degree

Doctor of Philosophy

By

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DEDICATION

TO THE GOD

For the shower of blessings throughout the journey and successful completion

TO MY BELOVED PARENTS AND FAMILY

For their love, support and encouragement

TO MY RESPECTED SUPERVISORS

For their sincere guidance, motivation and encouragement

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LIST OF ABBREVIATIONS

Abbreviation	Details
AFM	Atomic Force Microscopy
FTM	Floating Film Transfer Method
FETs	Field-Effect Transistors
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
LOD	Limit of detection
MOS	Metal-Oxide-Semiconductor
MW	Molecular Weight
MOSFET	Metal Oxide Semiconductor Field-Effect Transistor
OTFT	Organic Thin Film Transistor
OFETs	Organic Field-Effect Transistors
P3HT	Poly(3-hexylthiophene)
PANI	Polyanilines
PBTTT-C14	Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene]
ppm	Part per million
PQT-12	Poly(3,3"'-dialkylquaterthiophene)
QDs	Quantum Dots
SAED	Selected Electron Diffraction Pattern
SEM	Scanning Electron Microscopy
SMU	Source and Measuring Unit
TEM	Transmission Electron Microscopy
TFT	Thin Film Transistor
UV-Vis	Ultraviolet-Visible
XRD	X-ray Diffraction

LIST OF SYMBOLS

Symbol	Abbreviation
Au	Gold
Cu	Copper
α	Absorption Coefficient
C_{ox}	Capacitance per unit area of insulator
CV	Capacitance-Voltage
L	Channel Length of Transistor
W	Channel Width of Transistor
R^2	Correlation Coefficient
I_{DS}	Drain to Source Current
V_{DS}	Drain to Source Voltage
E_F	Fermi Energy Level
m	slope
σ_{rms}	root-mean-square deviation
R	Gas Response
V_{GS}	Gate to Source Voltage
μ	Mobility
t_{ox}	Oxide Gate Thickness
SS	Subthreshold Swing
SiO_2	Silicon dioxide
V_{th}	Threshold Voltage

Preface

The emergence of the Internet of Things (IoT) will significantly increase demand for sensors and actuators, which are essential physical components that are used in many different applications. Devices that respond to different gases in the environment are recognized as gas sensors. Since industrial processes, safety, and environmental monitoring are becoming increasingly crucial, there has been a steady increase in demand for gas detecting sensors across a range of fields.

π-conjugated materials are typically used as the active gas sensitive layer in organic semiconductor gas sensors, serving as both a transducer and a receptor. A three-terminal field effect transistor (FET) or a two-terminal resistor could be the device configuration. Among them, the main advantage of using organic thin film transistor (OTFT) as a gas sensor is its exceptional properties like smaller size, signal amplification, accumulation and depletion mode investigations, including the variation in threshold voltage and field effect mobility, allowed it to be employed as a multi-parametric gas sensor. However, it was necessary to optimize the active layer material which is due to the thickness, microstructure and processing dependent response of the conducting channel of OTFT that determines the gas detection performance.

This thesis presents the development and characterization of ammonia gas sensors designed to detect ammonia (NH_3) at low concentrations. The prime objective of this study is to investigate the performance of the gas sensor in terms of sensitivity, selectivity, stability, and response/recovery times, under varying environmental conditions. The outcomes of this study contribute to advancing the field of gas sensing technology, particularly in the context of ammonia detection, where there is an emergent need for cost-effective, instantaneous, and portable solutions.

Preface

This thesis work is briefly discussed in 7 chapters in which ***Chapter 1*** includes the introduction of different classes of chemical gas sensors, NH_3 gas sensors and their application in different areas. Besides, it is also discussed about different classes of materials and devices that are used for electronics based chemical gas sensors. Particularly organic materials that have been used as the sensitive layers of OTFT device architectures are discussed in detail. In addition, it also discussed the fabrication technique of OTFT channels, charge transport in OTFT channels etc.

Chapter 2 summarizes the material synthesis that has been used in this thesis work. This discussion includes stepwise experimental techniques for the fabrication of OTFT sensor devices like facile thin film deposition procedure called floating film transfer method (FTM) and electrode deposition via thermal evaporator. Besides, this chapter also discussed the characterization of the materials and OTFT sensor devices including optical, structural and electronic characterizations.

Chapter 3 has been discussed about an Organic/inorganic heterojunction (PBTTT–C14/MoS_2-QDs) thin film deposition via an inexpensive and simplistic FTM thin film fabrication technique that has been used as conductive channel of an OTFT and ammonia sensitive layer of the sensor. The synthesis section of this chapter has explored the hydrothermal synthesis of MoS_2-QDs along with characterization, and the device fabrication followed by the formation of nano-composite based ammonia sensitive layers. In which heterojunction depleted zones cover a very significant part of the surface of the OTFT channel. This depleted zone of the film is more reactive to NH_3 gas that can effectively enhance the sensitivity of the device. Therefore, the sensitivity of the designed OTFT sensor in accumulation and depletion modes is examined with the important parameters. Additionally, the sensing mechanisms have also been discussed.

Conclusively, this heterojunction based OTFT sensor designed in a very easy and economical way, which can meet all the requirements needed for its practical utilization as an NH_3 sensor.

The motivation of ***Chapter 4*** is the adoption of a related quantum dot as WS_2-QDs that has higher band off-set compared to the MoS_2-QDs to form a wider depletion region in the organic/inorganic heterojunction thin film. Since WS_2 has higher energy CB w.r.t the CB of MoS_2, therefore WS_2 has a higher band off-set with PBTTT-C14 that is supposed to form a wider depleted region. That may provide better sensitivity compared to PBTTT-C14/MoS_2-QDs based sensors. Initially material synthesis, device fabrication with characterization is discussed in this chapter. Enhanced ammonia sensitivity, different important parameters in accumulation/depletion modes and device physics has been explored along with the sensing mechanism. In this chapter broadband photosensitivity of the device is also tested due to the photo-electrical conversion capability of the WS_2-QDs. Conclusively, this OTFT sensor is fulfilling the majority of the basic requirements for its use as a NH_3 sensor and broadband photo-detector in real-world applications.

Chapter 5 presented an Organic homo-junction based thin film transistor fabrication for improved NH_3 detection. A good-poor mixed solvent has been used to dissolve the PBTTT-C14 polymer that produces a fractional part of the film by crystalline fibrillar polymer on air-liquid interface. Polymeric fibrillar morphology for its higher specific surface area may provide additional sites for the ammonia molecule interactions. Ammonia detection is determined from the drain current variation with NH_3 concentration in both accumulation and depletion modes. Additionally, the variations in currents are quite linear with the ammonia concentration. The change in key parameters of the OTFT sensors and other sensing results are also explored.

Chapter 6 includes a synthesis method of Li-based high k-dielectric film for low-operating voltage OTFT fabrication. This work utilizes the fibrillar polymer layer as NH_3 sensitive film of the sensor as described in the previous chapter. The introduction of high-k dielectric with homo-junction of the polymer tuned the ammonia sensitivity of the sensor, which is compared with the previous study. In addition, the broadband photosensitivity of this device is also examined. The aim of this study is to design an affordable, low-voltage operating, solution-processed OTFT device based NH_3 sensor and photo sensor which can meet basic requirements for practical use.

Chapter 7 presents a summary of the research findings conducted during the course of the investigations. The primary objective was to explore the sensitivity, selectivity, and stability of the sensor in response to ammonia (NH_3) gas and the outcomes verified that the ammonia-sensing capabilities of organic/hetero-junction and homo-junction based OTFTs appeared promising. The future scope of this huge study is further outlined in this chapter.