

Solution Processed PTB7 Thin Film Devices for Photodetection and Ammonia Sensing Applications



**Thesis submitted in partial fulfillment
for the Award of Degree**

DOCTOR OF PHILOSOPHY

BY

JOGENDRA SINGH RANA

**DEPARTMENT OF ELECTRONICS ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI-221005, INDIA**

ROLL No. 18091506

2023

DECLARATION BY THE CANDIDATE

I, *Jogendra Singh Rana*, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of *Prof. Satyabrata Jit* and co-supervision of *Dr. Santanu Das* from *December 2018* to *December 2023* at the *Department of Electronics Engineering, Indian Institute of Technology (BHU), Varanasi*. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma elsewhere. I declare that I have faithfully acknowledged and accredited to the research communities wherever their works have been cited in the accomplishment of this thesis. I further declare that I have not intentionally copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports, dissertations, theses, *etc.*, or available at websites and have not included them in this thesis or cited as my own work.

Date: *21/12/2023*

Place: *Varanasi*

Jogendra

Signature of the Student

Jogendra Singh Rana

CERTIFICATE BY THE SUPERVISORS

It is certified that the above statement made by the student is correct to the best of my/our knowledge.

Satya
21.12.23

Prof. Satyabrata Jit
(Supervisor)

Department of Electronics Engineering
IIT(BHU), Varanasi 221005

Santanu

Dr. Santanu Das
(Co-Supervisor)

Department of Ceramic Engineering
IIT(BHU), Varanasi 221005

Ajesh
26/04/2024
(Head)

Department of Electronics Engineering
IIT(BHU), Varanasi 221005

आचार्य व विभागाध्यक्ष/PROFESSOR & HEAD
इलेक्ट्रॉनिकी अभियांत्रिकी विभाग/Department of Electronics Engineering
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.)/Indian Institute of Technology (BHU)
वाराणसी/Varanasi-221005 (INDIA)

This thesis is dedicated to

[बाबा काशी विश्वनाथ]

[संकट मोचन हनुमान]

[बाबा कालभैरव]

[मां अन्नपूर्णा]

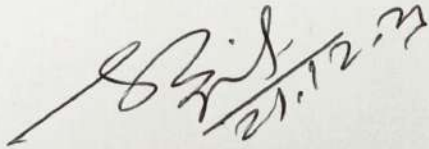
This thesis is dedicated to

[My Beloved Parents]

CERTIFICATE

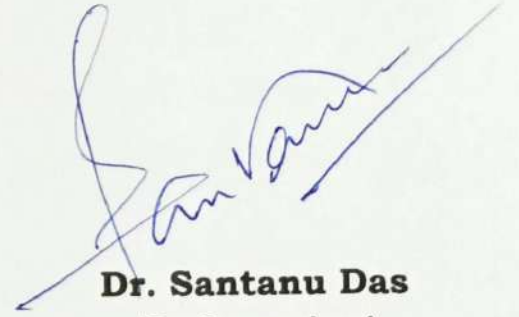
It is to certify that the thesis titled "*Solution Processed PTB7 Thin Film Devices for Photodetection and Ammonia Sensing Applications*" being submitted by "*Jogendra Singh Rana*" to the Indian Institute of Technology (Banaras Hindu University) Varanasi, for the award of the Degree of Doctor of Philosophy (Ph.D.) in the Department of Electronics Engineering is a record of bonafide research work carried out absolutely by him under our supervision and that this work has not been submitted to any other university/institute for the award of any degree or diploma.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.



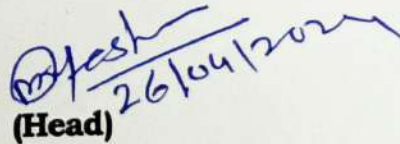
Prof. Satyabrata Jit
(Supervisor)

Department of Electronics Engineering
IIT(BHU), Varanasi 221005



Dr. Santanu Das
(Co-Supervisor)

Department of Ceramic Engineering
IIT(BHU), Varanasi 221005



(Head)

Department of Electronics Engineering
IIT(BHU), Varanasi 221005

आचार्य व विभागाध्यक्ष/PROFESSOR & HEAD
इलेक्ट्रॉनिकी अभियांत्रिकी विभाग/Department of Electronics Engineering
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.)/Indian Institute of Technology (BHU)
वाराणसी/Varanasi-221005 (INDIA)

LIST OF FIGURES

| | |
|--|----|
| Figure 1.1 Band gap of metals, semiconductors, and insulators. | 3 |
| Figure 1.2 Broad area applications of semiconductor materials. | 4 |
| Figure 1.3 Classification of semiconducting materials. | 4 |
| Figure 1.4 Broad area applications of organic semiconducting material-based devices. | 7 |
| Figure 1.5 Splitting of molecular orbitals in organic semiconducting materials [28]. | 11 |
| Figure 1.6 HOMO and LUMO levels and bandgap representation in organic/inorganic semiconducting materials [29]. | 12 |
| Figure 1.7 Chemical structure of PTB7. | 14 |
| Figure 1.8 Classification of photodetectors. | 15 |
| Figure 1.9 Figure of merits of photodetector. | 15 |
| Figure 1.10 Structures used for photodetectors. | 17 |
| Figure 1.11 Classification of gas sensors. | 18 |
| Figure 1.12 Figure of merits of gas sensors. | 19 |
| Figure 1.13 Gas sensing mechanism: (a) physisorption and (b) chemisorption. | 21 |
| Figure 1.14 Various steps involved in device fabrication and characterization. | 22 |
| Figure 1.15 Various thin film deposition techniques. | 23 |
| Figure 1.16 Spin coating and FTM method of thin film deposition. | 24 |
| Figure 1.17 Resources used in fabrication and characterizations of devices used in this thesis. | 25 |
| Figure 1.18 Photodetectors market demand forecast and analysis 2023-2027. | 30 |
| Figure 1.19 Gas sensor market size, growth, trends, report 2023-2032. | 31 |
| Figure 2.1 Fabrication steps used for device fabrication. | 38 |
| Figure 2.2 Fabricated device image and device schematics are shown (a) and (b). | 38 |
| Figure 2.3 AFM image of the polymer thin film (a) 2D and (b) 3D for surface morphology analysis. | 39 |
| Figure 2.4 (a) UV-Vis spectrum of the polymer film and (b) band gap calculation. | 39 |
| Figure 2.5 (a) I-V measurements of the fabricated device under dark/illuminated conditions, (b) wavelength-dependent responsivity curve of the fabricated device for visible range from 400 to 900 nm. | 40 |
| Figure 2.6 (a) Specific detectivity curve of the fabricated device for visible light spectrum, and (b) EQE curve of the fabricated device with wavelength ranging from 400 nm to 900 nm. ... | 41 |
| Figure 2.7 (a) Transient analysis of the fabricated device and (b) rise time and fall time | |

| | |
|---|----|
| calculation from single peak of wavelength 665 nm..... | 42 |
| Figure 2.8 Energy band representation of the fabricated device structure (a) before equilibrium (b) at equilibrium under dark conditions and (c) under light illumination. | 43 |
| Figure 3.1 Steps of floating film transfer method. | 49 |
| Figure 3.2 (a) Schematic of device structure, (b) 3D AFM image of the polymer film..... | 49 |
| Figure 3.3 (a) Energy band diagram of the fabricated device representing the HOMO and LUMO energy levels of polymer before biasing, (b) UV absorbance spectra of the polymer thin film, (c) UV absorbance spectra of the Al contact. | 51 |
| Figure 3.4 Current - Voltage plot of the as-fabricated device with varying incident white light irradiation and device image in inset. | 51 |
| Figure 3.5 (a) Device current as a function of incident optical power, (b) responsivity and Specific detectivity plot of the fabricated device with respect to the power intensity of incident white light..... | 52 |
| Figure 3.6 (a) Transient response characteristics of the fabricated photodetector at -2 V under the illumination of 12.98 mW/cm ² white light power, (b) rise time and fall time calculation of the fabricated device..... | 53 |
| Figure 4.1 Hydrothermal method of ZnO nanorods synthesis. | 58 |
| Figure 4.2 In-house developed gas sensing setup. | 59 |
| Figure 4.3 XRD of ZnO nanorods. | 60 |
| Figure 4.4 (a) High-resolution SEM image of PTB7 deposited ZnO nanorods with the HRSEM image of the ZnO nanorods in the inset, (b) 3-D AFM image of the polymer film on ZnO nanorods, (c) cross-sectional view of the pristine ZnO nanorods, and (d) cross-sectional view of the PTB7 decorated ZnO nanorods. | 61 |
| Figure 4.5 (a) Current-voltage characteristics of PTB7-ZnO NRs device with varying ammonia concentration. (b) comparison of the current-voltage characteristics of ZnO NR device with and without PTB7 layer under 20-ppm ammonia..... | 62 |
| Figure 4.6 (a) Gas response of the PTB7-ZnO NR device with varying gas concentration from 2 ppm to 50 ppm, (b) comparison of gas response of only ZnO NR device and PTB7-ZnO NR device at 20 ppm ammonia. | 62 |
| Figure 4.7 (a) Transient gas response characteristics of the proposed PTB7- ZnO NR device at 2 V for different concentrations of ammonia gas varying from 2 ppm to 50 ppm, (b) enlarged view of the transient gas response at 20 ppm for analyzing the response and recovery times. | 63 |
| Figure 4.8 (a) Gas response analysis for different values of relative humidity, (b) selectivity | |

LIST OF TABLES

| | |
|---|----|
| Table 1.1 Advantages and disadvantages of inorganic materials | 5 |
| Table 1.2 Comparison between small molecule and polymers type of organic materials | 9 |
| Table 1.3 Types of organic semiconducting material, some examples and their applications [22][23]. | 9 |
| Table 1.4 Comparison between organic and inorganic semiconducting materials..... | 10 |
| Table 1.5 Resistance of the device according to the type of material used and target gas | 21 |
| Table 1.6 Comparison of spin coating and FTM for thin film deposition | 25 |
| Table 2.1 Optical parameters of fabricated photodetector | 43 |
| Table 2.2 Comparison with other visible photodetector | 45 |
| Table 3.1 Comparison of the optical parameters of white light photodetectors | 54 |
| Table 4.1 Gas sensing performance of ammonia sensor | 66 |

LIST OF ABBREVIATIONS

| Abbreviation | Details |
|--------------|--|
| AFM | Atomic Force microscopy |
| DEA | Diethanolamine |
| EQE | External Quantum Efficiency |
| FETs | Field-Effect Transistors |
| FTO | Fluorine doped Tin Oxide |
| FTM | Floating-Film Transfer Method |
| HOMO | Highest Occupied Molecular Orbital |
| ITO | Indium doped Tin Oxide |
| LUMO | Lowest Unoccupied Molecular Orbital |
| NIR | Near Infrared |
| NRs | Nanorods |
| MOS | Metal-oxide-semiconductor |
| MOSFET | Metal Oxide Semiconductor Field-Effect Transistor |
| MSM | Metal-Semiconductor-Metal |
| OFETs | Organic Field-Effect Transistors |
| OLED | Organic Light-Emitting Diode |
| OTFT | Organic Thin film transistor |
| P3HT | Poly(3-hexylthiophene) |
| PBTTT-C14 | Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] |
| PEDOT | Poly(3,4-ethylenedioxythiophene) |
| PET | Poly(ethylene terephthalate) |
| PTB7 | poly ([4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b] thiophenediyl]) |
| ppm | Part per million |
| ppp | Poly-para-phenylene |
| PPT | 2,8-Bis(diphenyl phosphoryl)dibenzo[b,d]thiophene |
| PQT-12 | Poly(3, 3'''-dialkylquaterthiophene) |
| RH | Relative Humidity |
| SAED | Selected Area Electron Diffraction |
| SEM | Scanning Electron Microscopy |
| SMU | Source and Measuring Unit |
| TCE | Trichloroethylene |
| TEM | Transmission electron microscopy |
| TFT | Thin Film Transistor |
| UV-Vis | Ultraviolet-Visible |
| VLC | Visible Light Communication |
| XRD | X-ray Diffraction |
| ZnO | Zinc Oxide |

LIST OF SYMBOLS

| Symbol | Abbreviation |
|----------------|--|
| E_G | Energy Bandgap |
| E_C | Bottom of the Conduction Band |
| E_V | Bottom of the Valence Band |
| 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 |
| ϵ_r | Dielectric Permittivity of SiO_2 |
| I_{DS} | Drain to Source Current |
| I_{dark} | Current Under Dark Condition |
| I_{light} | Current Under Illumination Condition |
| I_{ph} | Photocurrent |
| V_{DS} | Drain to Source Voltage |
| E_F | Fermi Energy Level |
| S | Gas Response |
| V_{GS} | Gate to Source Voltage |
| P | Incident Optical Power |
| μ | Mobility |
| E_O | Neutral Level |
| t_{ox} | Oxide Gate Thickness |
| α_{eff} | Photo-Charge Generation Efficiency |
| R | Responsivity |
| D^* | Detectivity |
| SS | Subthreshold Swing |
| V_{th} | Threshold Voltage |
| g_m | Transconductance |
| λ | Wavelength |