

Interface Engineering of Functional Material Thin Films for Electronic and Optoelectronic Applications



THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF
DEGREE

Doctor of Philosophy

By

Subhajit Jana

SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005

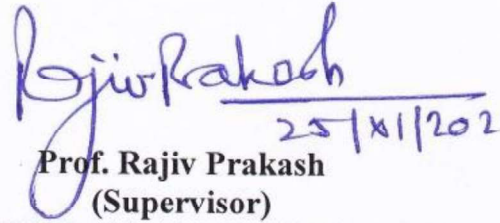
Roll No. 17111015

2022

CERTIFICATE

It is certified that the work contained in the thesis titled “*Interface Engineering of Functional Material Thin Films for Electronic and Optoelectronic Applications*” by ‘*Subhajit Jana*’ has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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.


25/11/2022

Prof. Rajiv Prakash
(Supervisor)

**School of Materials Science & Technology,
Indian Institute of Technology,
Banaras Hindu University,
Varanasi–221005**

Professor/आचार्य

School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

DECLARATION BY THE CANDIDATE

I, “*Subhajit Jana*”, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of “*Prof. Rajiv Prakash*” from “*July 2017*” to “*November 2022*”, at the “*School of Materials Science and Technology*”, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully 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 and have not cited as my own work.

Date: 02.12.2022
Place: IIT (BHU), Varanasi

Subhajit Jana
Signature of the student
(*Subhajit Jana*)

Certificate by the Supervisor

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

Rajiv Prakash
25/11/2022
Prof. Rajiv Prakash
(Supervisor)
Professor/आचार्य
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

Chunika
01/12/22
Coordinator
School of Materials Science & Technology,
IIT (BHU), Varanasi
Coordinator/समन्वयक
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: *Interface Engineering of Functional Material Thin Films
for Electronic and Optoelectronic Applications*

Name of the Student: *Subhajit Jana*

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the “*DOCTOR OF PHILOSOPHY*”.

Date: *02.12.2022*

Place: IIT (BHU), Varanasi

Subhajit Jana

Signature of the Student

(*Subhajit Jana*)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use, provided that the source and the Institute's copyright notice are indicated.

Acknowledgement

*The work presented in this thesis would not have been possible without my close association with many people who were always there when I needed them. I take this opportunity to acknowledge them and extend my sincere gratitude for helping me make this thesis a possibility. At this moment of accomplishment, first of all, I would like to pay homage to the founder of Banaras Hindu University, **Pandit Madan Mohan Malviya Ji**, who made this glorious temple to realize spiritual, technical, and scientific knowledge about this vast existing universe.*

*I embrace the opportunity to express my deep gratitude to my supervisor **Prof. Rajiv Prakash**, School of Materials Science & Technology, IIT (BHU), Varanasi, for his constant guidance, valuable suggestions, and kind encouragement during my association with his research group. His innovative research approach is a source of inspiration, and this approach is reflected in his simple but straightforward writing style, which I want to carry forward in my career. His scholarly suggestions, prudent admonitions, immense interest, constant help, and affectionate behavior have inspired me. His calmness, knowledge, and patience over the last five years will remain a happy memory.*

*I am thankful to my RPEC members, **Dr. B. N. Pal** and **Dr. I. Sinha**, and our foreign collaborators **Prof. Takaaki Manaka** and **Prof. Joydeep Dutta**, for their knowledgeable, motivational, and umpteen suggestions throughout this research work. Most of the results described in this thesis would not have been obtained without close collaboration with **Prof. Shyam S. Pandey**. His encouragement, support, wise guidance, precious ideas, and suggestions enabled me to develop an understanding of the subject. Moreover, I am pleased to gratefully acknowledge **Prof. Akhlesh Lakhtakiya** for his generous support, motivation, and guidance in maturing my team management and leadership capability in a scholastic aptitude.*

*I want to express my sincere and wholehearted gratitude to **Prof. P. Maiti**, **Dr. C. Upadhyay**, **Dr. C. Rath**, **Dr. Akhilesh Kumar Singh**, **Dr. Ashish Kumar Mishra**, **Dr. Sanjay Singh**, **Dr. Shravan Kumar Mishra**, **Dr. Nikhil Kumar**, and **Dr. Ravi Panwar** (School of Materials Science and Technology, IIT-BHU, Varanasi) for discussion during seminars and valuable suggestions given by them.*

Acknowledgement

*I would also like to thank CIFIC, IIT (BHU) for providing experimental facilities during the entire course of research work, to mention some names, **Mr. Nirmal** for his help in my measurements. I am thankful to all non-teaching staff of SMST, IIT (BHU), and CIFIC for their cooperation at all levels, especially **Mr. Shiv, Mr. Waris, Mr. Dharmendra, and Mr. Rakesh.***

I am thankful to the unknown reviewers who have rejected my papers several times in international conferences and journals. The comments that they provided helped to polish our articles in better shape. Nevertheless, the bigger and nobler cause of thanking them is that the rejections have equipped me with a high level of patience and helped me to exercise/implement my spiritual thoughts in practice.

*My acknowledgment will never be complete without the special mention of my lab seniors who have taught me the lab culture and have lived by example to make me understand the hard facts of life. I want to acknowledge **Dr. Arun K. Singh, Dr. Akhilesh K. Singh, Dr. Ashish Kumar, Dr. Rajiv Kumar Pandey, Dr. Shashi Tiwari, Dr. Sandeep Gupta, Dr. Gopal Ji, Dr. Shraddha Singh, Dr. Monika Srivastava, Dr. Uday Pratap Azad, Dr. Narsingh Raw Nirala, Dr. Neeraj Giri, Dr. Madhu Tiwari, Dr. Kashish, Dr. Preeti Tiwari, Dr. Manish Kumar Singh, Dr. Richa Mishra, Dr. Chandrajeet Verma, Dr. Aniruddha Jaiswal, Dr. Ravi Prakash Ojha, Mr. Vineet, and Mr. Nikhil** for all their support and motivation during the initial days of my Ph.D. I can see my thesis is in good shape because of their help formatting it. I express my special thanks to my seniors, **Dr. Rajiv Kumar Pandey, and Dr. Neeraj Giri,** for their constant guidance, support, motivation, and valuable suggestions at every step of my career.*

*Also, I am thankful to my colleagues and juniors of my lab, especially **Shweta, Ajay, Radhe, Priya, Saurabh, Rajpal, Nupur, Shipra, Shania, Preetam, Gaurav, and Arya** for their helping behavior. My friends **Bishnu, Pooja, Krishna, Manish, Shanu, Nila, Arka, Amba di, and Sourav da** (from IIT (ISM) Dhanbad), **Shubham** (from KIT, Japan) and from the list is endless...thanks to one and all. Their association has made my stay at IIT (BHU) a pleasurable and memorable experience. They were always beside me during the happy and hard moments to push me and motivate me.*

I am also thankful to all I could not mention here who helped me directly or indirectly throughout the work.

Acknowledgement

*I express my indebtedness to my parents, **Smt. Rekha Jana** and **Sri. Satyabrata Jana**, my dear wife **Labanya**, my sister **Sudipta**, my brother **Soumyajit**, and other family members for their love, affection, and support during every moment in my life. Words fail me to express my appreciation to my grandparents, Late Srihari Jana and Late Sarojini Jana, for their unconditional love, continuous support, excellent care, and encouragement.*

*I gratefully acknowledge the **DST-INSPIRE** for providing me with the necessary funding and fellowship to pursue research work.*

Finally, I am grateful to Almighty for giving me the patience to make this endeavor a success.

(Subhajit Jana)

Dedicated to my Parents

*“When you want something you’ve
never had, you have to do
something you’ve never done.”*

List of Figures

Figure No.	Figure Caption	Page No.
Figure 1.1	π -conjugated backbone system in trans-polyacetylene.	2
Figure 1.2	Classifications of organic conjugated systems, (a) small molecules, and (b) semiconducting polymer.	4
Figure 1.3	(a) Aromatic and (b) Quinoid form of polythiophene, (c) positive and negative polaron and bipolaron formations in polythiophene	6
Figure 1.4	(a) Total energy curve corresponding to trans-polyacetylene chain with respect to the degree of bond length alternation Δr , (b) soliton formation on trans-polyacetylene chain, and (c) three different solitons with band structure illustration.	8
Figure 1.5	Energy level arrangement at the metal-semiconductor interface after the formation of (a) Schottky contact and (b) ohmic contact; (c) Density of states and carrier transport mechanism based on Gaussian disorder model.	12
Figure 1.6	(a) $\log J$ vs. $\log V$ plot in an Al/P3HT/ITO Schottky diode, and (b) energy level alignment of P3HT/Al junction at three different bias potential, $V=0$, $V>0$ and $V<0$ volts.	15
Figure 1.7	(a) Four different types of OFET configurations, (b) OFET transfer characteristics.	17
Figure 1.8	Schematic illustration of organic phototransistor operation.	19
Figure 1.9	Schematic representation of three model polymers, P3HT, PQT, and PBTTT.	22
Figure 1.10	(a) Three different backbone arrangements of OSPs found in thin films, (b) charge transport in OFET containing two different backbone stackings in the active semiconducting layer.	25

List of Figures

Figure 1.11	(a) Semicrystalline nature of oriented P3HT, and (b) HR-TEM image of P3HT film showing their backbone orientation within crystalline domains separated by amorphous interlamellar regions.	29
Figure 1.12	Schematic representation of FTM process.	31
Figure 2.1	(a) Conventional drop-cast FTM with its real image, and (b) conventional ribbon-FTM or UFTM (unidirectional-FTM) with its real image.	36
Figure 2.2	Schematic illustration of SVA-FTM process.	37
Figure 2.3	(a) describes the optimization of time for P3HT, (b) optimization for type of solvent vapor suitable for the solvent vapor assisted-FTM process in P3HT, and effect of 15 minutes long chloroform vapor treatment in FTM films of (c) PQT-12, (d) PTB7, and (e) DPP-DTT.	38
Figure 2.4	(a) The schematic arrangements of AFM along with different probing techniques, (b) real image of AFM, NT-MDT Russia.	40
Figure 2.5	(a) Schematic representation of X-ray beam incident on a crystallographic material, (b) Rigaku smart lab series, (c) schematic geometry of out-of-plane and in-plane GIXD measurements.	42
Figure 2.6	(a) Schematic representation of different modes in TEM (Image credit: Black Tubus) (b) Transmission electron microscope with EDX (FEI, TECHNAI G ² 20 TWIN).	45
Figure 2.7	(a) Schematic diagram of UV-Vis spectrophotometer, (b) UV-vis spectrophotometer, Shimadzu 2600 model.	46
Figure 2.8	Schematic representation of 2D positional mapping set-up.	47
Figure 2.9	(a) Schematic illustration of the experimental setup of CV (b) Autolab (PGSTAT 101, Metrohm, Netherlands).	49
Figure 2.10	Schematic diagram along with a Vacuum thermal Evaporations system (HHV, India).	53

List of Figures

Figure 2.11	Real images (in ambient) of different device measurement processes along with the device schematics.	54
Figure 3.1	Schematic representation of three model polymers with their self-assembly and film formation mechanism at air-liquid interface.	59
Figure 3.2	(a) Out-of-plane XRD spectra of P3HT, PQT and PBTTT films scanned keeping source fixed at grazing incidence angle 0.14° , (b) schematic of the XRD measurement, (c) $\ln[A^s(n)]$ vs n plot and (d) $f(n)$ vs n plot which yield us the values of M , g^2 and e_{rms}^2 .	62
Figure 3.3	(a-c) SAED patterns of the oriented thin films ($\approx 15\pm 2$ nm thick) of PBTTT, PQT and P3HT respectively, (d-f) correspond to their HR-TEM images, while the film progression direction is shown through black arrows.	65
Figure 3.4	(a-c) AFM height profile of PBTTT, PQT and P3HT thin films respectively and the black arrows are indicating the FTM film progression direction as maintained during sample preparation, (d-f) represents the work function mapping, and (g-i) shows the film thickness measurements.	66
Figure 3.5	(a) Electronic absorption spectra, (b) corresponding low-energy absorption line-shape analysis, (c) optical band gap, and (d) order-of-transition plot for self-assembled P3HT, PQT and PBTTT thin films measured over a glass substrate. Current density vs voltage characteristics [(e) J-V, (f) J-V ²] of the Schottky barrier diodes (SBDs) along with the device schematic in the inset.	69
Figure 3.6	Output and transfer characteristics of P3HT (a,b), PQT (c,d) and PBTTT (e,f) OFETs along with the schematic representation in the inset of (a).	73

List of Figures

- Figure 4.1** (a) P3HT molecular structure, Schematic representation of conventional FTM (b) and SVA-FTM (c), and the mechanism of evaporation has been shown in both conventional (d) and solvent vapor assisted case (e). **81**
- Figure 4.2** AFM height profile for conventional FTM films (a) and SVA-FTM films (b), respectively. The black arrows in the AFM images indicate the molecular orientation (double arrow) and film progression direction (single arrow) in FTM films. (c) and (d) describes the work function mapping for the conventional and SVA-FTM films, respectively. Next, (e) shows AFM step-height scan for SVA-FTM film and corresponding height profile along horizontal (f) and vertical (g) direction. **83**
- Figure 4.3** (a) Out-of-plane XRD has been schematically shown, (b) Out-of-plane XRD pattern for both conventional and SVA-FTM films, (c) shows the $\ln[A^s(n)]$ vs n plot which gives M value and (d) represents the $f(n)$ vs n plot which yields g and e_{rms} . **85**
- Figure 4.4** Bright field HR-TEM images and respective SAED patterns for conventional FTM films (a-c) and SVA-FTM films (d-f), respectively. The film progression direction in FTM films has been shown by single arrow in black. **87**
- Figure 4.5** (a) shows non-polarised optical absorption spectra, (b) Urbach plot, (c) polarised optical absorption spectra, (f) Raman spectra, (g) cyclic voltammetry measurement for conventional and SVA-FTM films, (h) & (i) are the real images of P3HT films, and (d) & (e) represents 2D distribution of absorption maxima (or thickness) in SVA-FTM film and conventional-FTM film, respectively. **91**
- Figure 4.6** shows output and transfer characteristics of P3HT films prepared by conventional FTM (a & b) and SVA-FTM (c & d), and (e) & (g) represents schematically charge **96**

List of Figures

- transport pathways in conventional FTM and SVA-FTM films, respectively, and (f) shows electronic levels in both the films.
- Figure 5.1** (a) Ribbon-shaped FTM process, (b) Evolution of molecular arrangements in P3HT films formed through both conventional- and SM-FTM. **102**
- Figure 5.2** (a) Chemical structure of P3HT, (b) Schematic geometry of out-of-plane and in-plane GIXD measurements. (c, d) Out-of-plane and in-plane GIXD patterns of P3HT thin films prepared by conventional and subphase modified FTM. **103**
- Figure 5.3** HR-TEM images and corresponding SAED patterns of conventional-FTM films (a-c) and SM-FTM films (d-f). Non-polarised optical absorption spectra (g) and corresponding low-energy absorption line-shape analysis (h) for both conventional-FTM and SM-FTM films. **106**
- Figure 5.4** Evolution of surface topography in both films has been studied through AFM height profile (a, b), Phase profile (c, d) and work-function mapping (e, f), respectively. **108**
- Figure 5.5** (a) J-V characteristics of both P3HT films, (b) Optimization of DBSA percentage in terms of RR, (c, d) histogram of RR measured in many devices, (e) corresponding J-V² plot, (f) stability study of SBDs. **111**
- Figure 5.6** (a) Forward bias J-V characteristics fitting to estimate the overall Ohmic loss, (b) Schematic illustration of FTM dynamics in the leading edge of ribbon-shaped FTM. **112**
- Figure 6.1** (a) Non-polarized UV-vis spectra of pristine PBTTT, pristine DPPCN, and hybrid materials in solution (a), & (d), and in film (b) and (e), and the band-gap estimation **124**

List of Figures

	in annealed thin films of (C) pristine PBTTT and PBTTT/DPPCN(2%) and in pristine DPPCN (f).	
Figure 6.2	Schematic representation of the film formation process through ribbon-FTM (a) and the utilized organic molecules DPPCN(b) and PBTTT(c), and (d) represents FTIR spectra of pristine PBTTT, DPPCN and PBTTT/DPPCN(2%).	125
Figure 6.3	Polarized optical absorption spectra of the as-prepared thin films of PBTTT (a), DPPCN (b), and PBTTT/DPPCN hybrids (c, d, e, & f).	127
Figure 6.4	Polarized optical absorption spectra of the annealed thin films of PBTTT (a), DPPCN (b), and PBTTT/DPPCN hybrids (c, d, e, & f).	128
Figure 6.5	OFET output characteristics corresponding to pristine PBTTT (a), DPPCN (b), and PBTTT/DPPCN hybrids (c, d, e, & f).	130
Figure 6.6	OFET transfer characteristics of pristine PBTTT (a), DPPCN (b), and PBTTT/DPPCN hybrids (c, d, e, & f).	131
Figure 6.7	AFM height profile and KPFM scan along with corresponding 2D FFT in the inset for PBTTT (a & c) & PBTTT/DPPCN(2%) (b & d); Molecular orientation (double arrow) and film progression direction (single arrow) that has been estimated through the transparent polarizer sheet, is shown in the AFM images; Next, the HR-TEM images and corresponding SAED patterns has been shown for PBTTT (e) and PBTTT/DPPCN(2%) (f); Further, thin film XRD (g) and cyclic voltammetry (h) of the same systems has been shown.	133
Figure 6.8	OFET photo-response for PBTTT (a) and PBTTT/DPPCN(2%) (b).	136
Figure 6.9	Represents OFET stability (a), statistical data of saturation mobility (b), mobility anisotropy (c), variation	138

List of Figures

of exciton bandwidth along with R_{abs} value (d), optical anisotropy in terms of DR (e), and the photosensitivity with respect to the change in saturation mobility (f).

List of Tables

Table No.	Table Caption	Page No.
Table 1.1	Prospects and challenges with different thin film fabrication methods.	28
Table 3.1	Findings of peak shape analysis	62
Table 3.2	Surface roughness parameters.	67
Table 3.3	Electrical parameters of thin solid FTM films made of three polythiophene derivatives.	75
Table 4.1	Findings of XRD peak shape analysis.	86
Table 4.2	Findings of Raman peak analysis.	93
Table 4.3	Electrical parameters estimated from the parallel and perpendicular OFETs.	97
Table 5.1	Findings of out-of-plane XRD analysis.	105
Table 5.2	Electrical parameters analyzed for both conventional-FTM and SM-FTM films in SBD architecture.	112
Table 5.3	Summary of previously reported characteristic SBDs compared with our results.	114
Table 6.1	List of different functional groups found in pristine PBTTT, DPPCN and PBTTT/DPPCN(2%).	126

LIST OF ABBREVIATIONS

μA	:	Microampere
μL	:	Microlitre
$^{\circ}\text{C}$:	Degree Celsius
1D	:	One dimensional
2D	:	Two dimensional
3D	:	Three dimensional
AFM	:	Atomic Force Microscopy
Al	:	Aluminum
Au	:	Gold
cm	:	Centimeter
CV	:	Cyclic Voltammetry
DI	:	Deionized
EDS/ EDAX	:	Energy dispersive X-ray spectroscopy
eV	:	Electron volt
FTIR	:	Fourier transform infrared
FTM	:	Floating Film Transfer method
HOMO	:	Highest Occupied Molecular Orbital
h / hr	:	Hour(s)
HR-TEM	:	High resolution transmission electron microscopy
ITO	:	Indium Tin Oxide
LS	:	Langmuir Schaefer
LUMO	:	Lowest Unoccupied Molecular Orbital
Min	:	Minute(s)
M_w	:	Weight average molecular weight
M_n	:	Number average molecular weight
nm	:	nanometer

LIST OF ABBREVIATIONS

OFET	:	Organic Field Effect Transistor
OPT	:	Organic phototransistor
PDI	:	Polydispersive index
P3HT	:	Poly(3-hexylthiophene-2,5-diyl)
PBTTT	:	Poly[2,5-bis (3- tetradecylthiophen-2-yl) thieno[3,2- b]thiophene]
PQT	:	Poly(3,3'''-didodecyl[2,2':5',2'':5'',2'''- quaterthiophene]-5,5'''- diyl)
PT	:	Polythiophene
rr-P3HT	:	Regioregular- poly(3-hexylthiophene-2,5-diyl)
s	:	Second
SAED	:	Selected area electron diffraction pattern
T	:	Temperature
TBAP	:	Tetrabutyl ammonium perchlorate
TEM	:	Transmission electron microscopy
UV-Vis	:	UV Visible
V	:	Volt
XPS	:	X-ray photoelectron spectroscopy