

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**FABRICATION AND CHARACTERIZATION OF NEW
GENERATION ORGANIC FIELD EFFECT TRANSISTORS**

BETÜL CANIMKURBEY
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS

GEBZE

2017

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**FABRICATION AND CHARACTERIZATION
OF NEW GENERATION ORGANIC FIELD
EFFECT TRANSISTORS**

BETÜL CANIMURBEY
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS

THESIS SUPERVISOR
PROF. DR. SAVAŞ BERBER
II. THESIS SUPERVISOR
PROF. DR. ZAFER ZİYA ÖZTÜRK

GEBZE

2017

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

YENİ NESİL ORGANİK ALAN ETKİLİ
TRANSİSTÖRLERİN ÜRETİMİ VE
KARAKTERİZASYONU

BETÜL CANIMKURBEY
DOKTORA TEZİ
FİZİK ANABİLİM DALI

DANIŞMANI
PROF. DR. SAVAŞ BERBER
II. DANIŞMANI
PROF. DR. ZAFER ZİYA ÖZTÜRK

GEBZE

2017



DOKTORA JÜRİ ONAY FORMU

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 29/06/2017 tarih ve 2017/35 sayılı kararıyla oluşturulan jüri tarafından 17/07/2017 tarihinde tez savunma sınavı yapılan Betül CANIMKURBEY' in tez çalışması Fizik Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

JÜRİ

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. Savaş BERBER

ÜYE

: Prof. Dr. Mevlüt KARABULUT

ÜYE

: Prof. Dr. Lütü ARDA

ÜYE

: Yrd. Doç. Dr. Serkan BÜYÜKKÖSE

ÜYE

: Yrd. Doç. Dr. Erhan GENGEÇ

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun

..... tarih ve/..... sayılı kararı.

İMZA/MÜHÜR

Doç. Dr. Arif Çağdaş AYDINOĞLU
Gebze Teknik Üniversitesi
Fen Bilimleri Enstitüsü Müdürü

SUMMARY

This work outlines our findings in understanding and characterizing the injection and transport mechanisms of charge carriers in solution processed polymer composite dielectrics organic field effect transistors. One of the aim of this study is to prepare dielectric composites to obtain better mechanical and electrical properties. Composite materials based on inorganic fillers dispersed within insulating polymer matrix have wide range of application. For this purpose, dielectric composites with inorganic fillers like Ta_2O_5 , Al_2O_3 , were prepared. Ta_2O_5 : PMMA, Al_2O_3 : PVA, Ta_2O_5 : Gel PMMA composites at different compositions were prepared by dispersing inorganic high- κ dielectrics (Ta_2O_5 , Al_2O_3) in organic dielectric solution material. Their electrical and optical properties were investigated.

Another aim of this study is to fabricate and characterize OFETs which have composite material as dielectric layers. While doing this, composite dielectric layer was deposited on semiconductor layer using spin coating technique. P3HT:PCBM, CuPc were used as semiconductor layer. OFETs with Ta_2O_5 :PMMA dielectric layer, show ambipolar properties. This behavior is explained due to the presence of high permittivity metal oxide particles and the interfacial Maxwell-Wagner polarization with the polymer matrix and filler.

Key Words: Organic Field Effect Transistors (OFETs), composite dielectrics, ambipolar OFET, high- κ dielectrics.

ÖZET

Bu çalışma, çözelti tabanlı polimer kompozit dielektriklere sahip organik alan etkili transistörlerde yük taşıyıcılarının enjeksiyon ve iletim mekanizmalarının anlaşılması ve karakterizasyonundaki bulgularımızı özetlemektedir. Bu çalışmanın amaçlarından biri daha iyi mekanik ve elektriksel özellikler elde etmek için dielektrik kompozitlerin hazırlanmasıdır. Dielektrik polimer matrisleri içine dağılmış inorganik dolgu maddelerine dayanan kompozit malzemeler geniş bir uygulama yelpazesine sahiptir. Bu amaçla, Ta_2O_5 , Al_2O_3 gibi inorganik dolgular içeren dielektrik kompozitler hazırlanmıştır. Farklı kompozisyonlardaki Ta_2O_5 : PMMA, Al_2O_3 : PVA, Ta_2O_5 : Gel PMMA kompozitleri, yüksek dielektrik sabitli (κ) inorganik dielektriklerin (Ta_2O_5 , Al_2O_3) organik dielektrik çözeltiler içinde dağılmasıyla hazırlanmıştır. Onların elektriksel ve optik özellikleri araştırılmıştır.

Bu çalışmanın bir diğer amacı, dielektrik tabakanın kompozit malzeme olduğu OFET' lerin üretimi ve karakterizasyonudur. Bunu yaparken, kompozit dielektrik tabaka spin kaplama tekniği kullanılarak yarıiletken tabaka üzerine kaplanmıştır. P3HT:PCBM, CuPc yarıiletken tabaka olarak kullanılmıştır. Ta_2O_5 :PMMA dielektrik tabakası ile yapılan OFET' ler, ambipolar özellikleri göstermiştir. Bu davranış, yüksek dielektrik sabitine sahip metal oksit partiküllerinin varlığından ve polimer matrisi ile dolgu maddesi arasındaki Maxwell-Wagner (Arayüzey) polarizasyonu nedeniyle olduğu açıklanmıştır.

Anahtar Kelimeler: Organik Alan Etkili Transistörler (OAET), Kompozit dielektrikler, ambipolar organik alan etkili transistörler, yüksek dielektrik sabitli dielektrikler.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisors, Prof. Savaş BERBER Prof. Dr. Zafer Ziya ÖZTÜRK for their guidance and excellent helps during PhD. I also would like to thank them for treated me like someone from the family.

I am much indebted to Assist. Prof. Serkan BÜYÜKKÖSE, Dr. Arif KÖSEMEN, Dr. Muhammad YASİN, Dr. Elif ALTÜRK PARLAK who shared their profound scientific knowledge with me. His support, suggestions and encouragement will complete this work.

I am grateful to Prof. Dr. Mevlüt KARADOĞAN for their precious advice in my thesis

I wish to express my endless and sincere thanks to Gökhan BAYRAM, Hakan YILDIRIM and Dr. Zühal ALPASLAN KÖSEMEN for their immortal friendship and being a part of my life.

Finally, my deepest thanks are to my family, especially my mother Müzeyyen CANIMKURBEY, my father Selahattin CANIMKURBEY and my brothers for their patient and love.

This thesis is supported by National Scholarship Program for Graduate Student TÜBİTAK (2211/A) in PhD thesis.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	v
ÖZET	vi
ACKNOWLEDGEMENTS	vii
TABLE OF CONTENTS	viii
SYMBOLS and ABBREVIATIONS	x
LIST OF FIGURES	xi
LIST OF TABLES	xv
1. INTRODUCTION	16
2. ORGANIC FIELD EFFECT TRANSISTORS	18
2.1. Working Principle of OFETs	18
2.2. Device Structures	20
2.3. Importance of Gate Dielectric for OFET	21
2.4. Composites and Nanocomposites	23
2.5. Important of Injecting Electrodes	23
2.6. Charge transport in organic semiconductors	24
2.7. Organic Materials	25
2.8. Important Parameters for OFETs	27
2.8.1. Mobility	27
2.8.2. Threshold voltage	28
2.8.3. Hysteresis/bias-stress	29
2.8.4. Gate leakage	30
2.8.5. Subthreshold slope	30
3. EXPERIMENTAL METHODS	31
3.1 OFET Fabrication	31
3.1.1. Preparation of Glass ITO Substrate	31
3.1.2. Preparation of Source/Drain Electrodes with Photolithography	32
3.1.3. Preparation of Active Layer Thin Films	34
3.2. Device Characterization	35
3.2.1. OFET Characterization	35

3.2.2. Dielectric Characterization	37
4. FABRICATION AND INVESTIGATION OF P3HT: PCBM BULK HETEROJUNCTION BASED ORGANIC FIELD EFFECT TRANSISTORS USING DIELECTRIC LAYERS OF PMMA:Ta ₂ O ₅ NANOCOMPOSITES	40
4.2 Introduction	40
4.3 Experimental Details	41
4.3. Results and Discussion	43
4.4. Conclusion	49
5. MEDIUM BAND GAP POLYMER BASED SOLUTION PROCESSABLE HIGH DIELECTRIC CONSTANT COMPOSITE GATE INSULATORS FOR ORGANIC FIELD EFFECT TRANSISTORS	51
5.1. Introduction	51
5.2 Experimental Details	53
5.3 Results and Discussion	54
5.4 Conclusion	61
6. SOLUTION PROCESSABLE HIGH DIELECTRIC CONSTANT NANOCOMPOSITES BASED ON Al ₂ O ₃ NANOPARTICLES FOR ORGANIC FIELD EFFECT TRANSISTORS	63
7. EFFECT OF Ta ₂ O ₅ INORGANIC PARTICLES ON POLYMER GEL DIELECTRIC BASED OFET PERFORMANCE	69
7.1. Introduction	69
7.2. Experimental Details	70
7.3 Results and Discussion	71
8. SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF GRAPHENE OXIDE FILMS	74
8.1 Introduction	74
8.2. Experimental procedure	75
8.2.1. Synthesis of graphene oxide	75
8.2.2. Structure fabrication	76
8.3. Characterization	76
8.4. Results and Discussion	77
8.5. Conclusion	84
9. CONCLUSION	85
REFERENCES	88
BIOGRAPHY	106

SYMBOLS and ABBREVIATIONS

<u>Symbols and Abbreviations</u>	<u>Explanations</u>
W	: Channel Width
L	: Channel Length
μ	: Mobility
ϵ	: Dielectric Constant
ϵ_0	: Dielectric Constant of Free Space
C_i	: Capacitance
Z	: Impedance
CuPc	: Copper(II) Phthalocyanine
OFET	: Organic Field Effect Transistor
OLED	: Organic Light Emitting Diode
OPV	: Organic Photovoltaic
P3HT	: Poly(3-hexylthiophene-2,5-diyl)
PCBM	: Phenyl C ₆₁ Butyric acid Methyl ester
PMMA	: Poly Methyl Methacrylate
PVP	: Poly(4-vinylphenol)
CVD	: Scanning Electron Microscope
SEM	: Scanning Electron Microscope
AFM	: Atomic Force Microscope
XRR	: X-Ray Reflection
AFM	: Atomic Force Microscope
ITO	: Indium Tin Oxide
HOMO	: Highest Occupied Molecular Orbital
LUMO	: Lowest Unoccupied Molecular Orbital
P-SBTBDT	: Poly (selenophene, benzotriazole and dialkoxy substituted [1,2-b:4, 5-b'] dithiophene

LIST OF FIGURES

<u>Figure No:</u>	<u>Page</u>
2.1: Schematic structure of organic field effect transistor.	18
2.2: a) Schematic structure of organic field effect transistor and linear regime b) start of saturation regime at pinch-off c) Saturation regime.	19
2.3: Schematic diagrams of OFET geometry.	22
2.4: Schematic structure of P-SBTBDT.	25
2.5: Structure of a) P3HT, b) PCBM, c) CuPc, d) PMMA, e) PVA.	27
2.6: Extrapolation of V_{th} from the $I_{DS}-V_{GS}$ transfer characteristic. The inset shows the section of the $I_{DS}-V_{GS}$ output Characteristic Where the transfer characteristic is taken.	28
2.7: Schematic transfer characteristic exhibiting hysteresis.	29
3.1: a) Pre-patterned 50 μm channel length substrate consist of interdigitated ITO fingers dimensions b) The Pre-patterned OFET substrate.	31
3.2: a) Spin coating of photoresist b) Annealing for removal solvent c) Photolithography tool d) Dissolving photoresist layer in a developer.	32
3.3: Steps of the photolithography process with positive photoresist.	33
3.4: Interdigitated source/drain electrodes which fabricated photolithography method.	34
3.5: Mbraun high vacuum system to evaporate small molecule polymers.	34
3.6: Keithley 4200 Semiconductor Characterization System.	35
3.7: A sample device transfer measurement showing both the saturation and linear characteristic.	36
3.8: The output characteristic of OFET.	37
3.9: Circuit diagrams for the modeling of material proper.	39
4.1: A schematic illustration of OFET devices.	42
4.2: SEM images taken from the surface of PMMA: Ta ₂ O ₅ based dielectric films with varying wt% concentrations of Ta ₂ O ₅ .	43
4.3: Cross-section SEM images of PMMA: Ta ₂ O ₅ based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Ta ₂ O ₅ .	44

4.4:	Dielectric constant (ϵ') versus frequency graph for PMMA: Ta ₂ O ₅ based dielectric films for different concentrations of Ta ₂ O ₅ .	45
4.5:	a) Tan δ versus logarithmic frequency graph and b) Conductivity versus frequency graph for PMMA: Ta ₂ O ₅ based dielectric films for different concentrations of Ta ₂ O ₅ . The inset displays the extended diagram from low frequency region for clarity.	45
4.6:	XRR curves acquired from PMMA: Ta ₂ O ₅ based dielectric films with Ta ₂ O ₅ concentrations of a) 0 wt% and b) 50 wt%.	46
4.7:	Output I-V characteristics of OFETs with PMMA: Ta ₂ O ₅ based dielectric films for different concentrations of Ta ₂ O ₅ changing from 0 wt% to 50 wt%	48
4.8:	Transfer I-V characteristics of OFETs with PMMA: Ta ₂ O ₅ based dielectric films for different concentrations of Ta ₂ O ₅ changing from 0 wt% to 50 wt%.	50
5.1:	A Schematic Illustration of OFET Devices and Chemical Structure of P-SBTBDT.	53
5.2:	Variations of conductivity with respect to frequency for Ta ₂ O ₅ :PMMA based dielectric films with varying concentrations of Ta ₂ O ₅ . The inset figure displays the extended graph for low frequency region.	54
5.3:	a) Temperature dependence of the conductivity (σ) plotted as $\ln(\sigma)$ versus $1/T$. b) The E_a activation energies obtained from the linear fits in a) for the filling ratios of 0, 10, 50, 70 wt. %.	55
5.4:	Cole-cole plots of dielectric constants for PMMA:Ta ₂ O ₅ based nanocomposite dielectric films with varying concentrations of Ta ₂ O ₅ . The inset figure on the right shows the frequency dependent real part of permittivity. The inset figure on the left side shows the equivalent circuit of nanocomposite thin films.	56
5.5:	SEM images for the surfaces of PMMA:Ta ₂ O ₅ based dielectric films with a) 0 wt.%, b) 3 wt.%, c) 7 wt.% d) 10 wt.%, e) 20 wt.% and f) 50 wt.% concentrations of Ta ₂ O ₅ .	57
5.6:	AFM images taken from the surface of a) P-SBTBDT, b) PMMA:Ta ₂ O ₅ based dielectric films with 0 wt.%, c) 10 wt.% and d) 50 wt.% concentrations of Ta ₂ O ₅ .	58

5.7:	Schematic view of OFET devices are on the left (a,c), and The corresponding energy level diagrams are on the right (b,d).	58
5.8:	Output I-V characteristics of OFETs having semiconducting layer of P-SBTBDT and dielectric films of PMMA:Ta ₂ O ₅ with a) 0 wt.% and b) 50 wt.% concentration of Ta ₂ O ₅ .	59
5.9:	Transfer characteristics of the devices with a) 0 wt.% and b) 50 wt.% concentration of Ta ₂ O ₅ .	60
6.1:	Variation of a) Real and b) Imaginary parts of dielectric constant with frequency for Al ₂ O ₃ :PVA nanocomposites with different wt % of Al ₂ O ₃ .	63
6.2:	Cole-cole plots of dielectric constants for PVA:Al ₂ O ₃ based nanocomposite dielectric films with varying concentrations of Al ₂ O ₃ .	65
6.3:	Output and transfer I-V characteristics of OFETs with PVA: Al ₂ O ₃ based dielectric films for 0 wt% concentrations of Al ₂ O ₃ .	67
6.4:	Output and transfer I-V characteristics of OFETs with PVA: Al ₂ O ₃ based dielectric films for 50 wt% concentrations of Al ₂ O ₃ .	67
6.5:	SEM images taken from the surface of PVA: Al ₂ O ₃ based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Al ₂ O ₃ .	68
6.6:	Cross-section SEM images of PVA: Al ₂ O ₃ based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Al ₂ O ₃ .	68
7.1:	Schematic illustration of OFET device.	71
7.2:	Capacitive properties of gel-dielectric material and thin film PMMA at different frequencies	72
7.3:	Output I-V characteristics of OFETs having semiconducting layer of CuPc and dielectric films of gel:Ta ₂ O ₅ with (a) 0 wt.% and (b) 50 wt.% concentration of Ta ₂ O ₅ .	73
8.1:	Schematic view of parallel plate structures and b) Chemical formula of GO.	76
8.2:	Experimental set up for temperature dependent electrical analysis of GO films. PC: Computer Station, IA: Impedance Analyzer, NH: Novotherm Heating System, NM: Novotherm Microprocessor Controller Unit.	77
8.3:	a) Surface and b) 3D AFM profiles, c) Absorption and d) Transmittance spectra of GO films	78

8.4:	a) Real and b) Imaginary dielectric constants, and c) Loss tangent plots of GO film as a function of frequency at given temperatures.	79
8.5:	Plot of AC conductivity of GO film as a function of temperature at 100 Hz.	80
8.6:	AC conductivity of GO film as a function of frequency at given temperature values, inset: comparison of GO film AC conductivity at room temperature and 100°C as a function of frequency.	82
8.7:	Complex impedance spectra/ Nyquist plots of GO film at various temperatures, inset: equivalent RC network.	83

LIST OF TABLES

<u>Table No:</u>	<u>Page</u>
2.1: Summary of electrochemical properties of P-SBTBDT.	25
5.1: OFET characteristics and effective capacitances for the different wt/wt ratio of Ta ₂ O ₅ : PMMA films in ambient condition.	61
6.1: Dielectric Parameters of Al ₂ O ₃ :PVA nanocomposites.	65

1. INTRODUCTION

We live in an increasingly electronic world, with computers occupying a central part of our lives. Economic, health, and national security rely on and are positively impacted by electronic technology. Various resources and methodologies used to fabricate electronic devices raise urgent questions about easy process. Although silicon technology is the basis of today's electronic and has solved many of the challenges associated with our increased use of electronics, there are limits to what silicon can do. Different types of organic materials have worked by scientists on electronics. These materials include small molecules and polymers; fullerenes, nanotubes, graphene, and other carbon-based molecular structures; ensembles of molecules and molecular structures; and hybrid materials [1]. These materials afford electronic structures unique properties impossible to obtain with silicon alone, creating untold potential for novel functionality.

Organic materials are being studied and developed for their potential to build devices with a flexibility [2]. So, electronic devices that bend, twist, and conform to any surface. Devices made with organic materials also have the potential to interface with biological systems in ways not possible with inorganic materials such as an artificial skin with a tactile sensitivity approximating real skin [3]. Potential applications of organic electronics span a broad range of fields, including medicine and biomedical research, environmental health, information and communications, and national security [4]. Because of the low cost and easy fabrication of organic-based electronic devices, organic electronics also promise to expand the use of electronic technology in resource-limited areas of the world. Not only organic materials promise more innovative and accessible electronic technologies, they also promise more sustainable electronic technologies. The intention is not that organic electronics will replace silicon-based electronics. Indeed, organic molecules and materials are often used in combination with inorganic materials to expand electronic landscape with new materials that make electronics more functional, accessible, and sustainable [5].

Today, the major focus of research and development in organic electronic is on three main types of existing applications: displays and lighting, transistors, and solar cells [6]. Organic Field Effect Transistors (OFETs) have several unique properties not shared by silicon transistors, most notably their flexibility. Because OFETs can be

fabricated at or near room temperature, they enable the fabricating of integrated circuits on plastic or other flexible substrates that would otherwise not withstand the high-temperature conditions of inorganic-based device process [7]. OFETs are also highly sensitive to specific biological and chemical agents, making them excellent candidates for biomedical sensors and other devices that interface with biological systems.

With the synthesis of new organic materials, charge-carrier mobilities have improved for small-molecule OFETs from $< 1 \text{ cm}^2/\text{Vs}$ in 2000 to greater than $1.0\text{-}3.0 \text{ cm}^2/\text{Vs}$ in 2010 [8]. Initially, the improved mobilities were obtained only under very clean conditions in ultrahigh vacuum chambers. However, recent results suggest that high-performance OFETs can be fabricated using simple and relatively inexpensive techniques, such as solution processing. Despite this progress, several challenges remain before OFETs will become a widespread commercial reality. For example, only recently have scientists demonstrated the fabrication of thermally stable flexible OFETs. Organic field-effect transistors (OFETs) has been interested in the development of innovative optoelectronics products, such as backplanes for flexible displays and low cost circuits for sensors applications [9]. The discovery of electrical conductivity in polymers enabled the production of organic electronic devices such as OFETs, OLEDs and OPVs. OFETs were first reported in 1986 and since then many advances in device performance have been made [10, 11]. The possibility of printing flexible electronic devices using OFETs has stimulated research devoted to discovering organic semiconductors with high conductivity and to optimizing device performance [12-14].

As gate dielectric materials, high- κ inorganic metal oxides are ideal candidates for fabricating high capacitance OFETs capable of low-voltage operation, which require generally expensive deposition equipment and usually require high temperature annealing processes [15]. On the other hand, easily processable organic materials have low dielectric constants and good mechanical properties, but require large gate dielectric thicknesses due to high leakage currents [16]. A new approach is to combine inorganic and organic materials as gate dielectrics. Composite materials ideally combine high permittivity and high breakdown strength of the inorganic materials and mechanical flexibility, easy processability of the organic counterparts [17].

2. ORGANIC FIELD EFFECT TRANSISTORS

In this chapter, the basic structure and working principle of an organic field-effect transistor, their current voltage characteristics, and how to extract information from them will be briefly introduced. It has been used different organic molecules which is given some background details on these molecules and give an overview of their chemical and physical properties below.

2.1. Working Principle of OFETs

An organic field-effect transistor requires a semiconducting layer, gate dielectric and source/drain electrodes. The thin semiconductor layer, which is separated from a gate electrode by the insulating gate dielectric; source and drain electrodes of width W (channel width) separated by a distance L (channel length) that are in contact with the semiconductor layer (Figure 2.1). In OFETs, the semiconductor layer is usually vacuum sublimed, spin-coated, or drop-cast depending on the semiconductor. The gate electrode can be a metal or a conducting polymer. As gate dielectrics, SiO_2 , Ta_2O_5 , Al_2O_3 , Si_3N_4 , or poly (methyl methacrylate) (PMMA), poly(4-vinylphenol) (PVP) are commonly used depend on the transistor structure [18-20]. The source and drain electrodes, which inject charges into the semiconductor, are usually high work function metals such as gold [21-23].

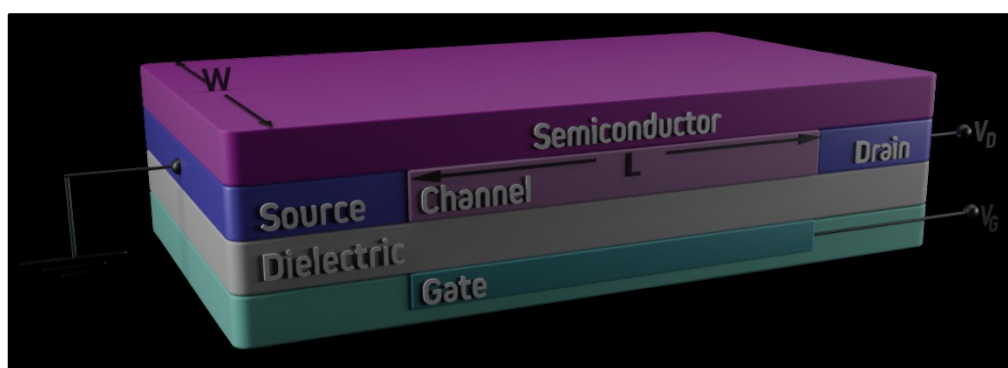


Figure 2.1: Schematic structure of organic field effect transistor.

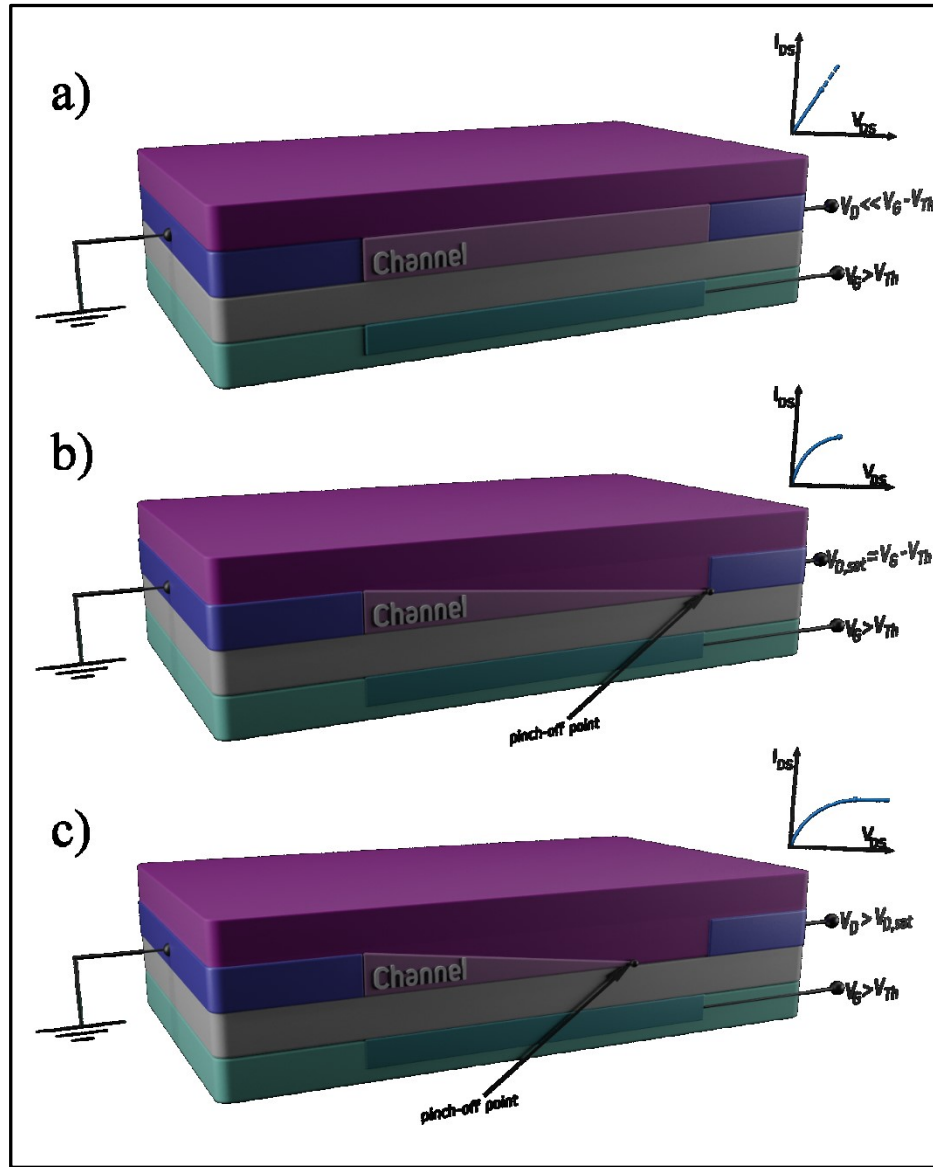


Figure 2.2: a) Schematic structure of organic field effect transistor and linear regime b) start of saturation regime at pinch-off c) saturation regime.

The potential difference between the source and the gate is usually called the gate voltage (V_{GS}), while the potential difference between the source and the drain is referred to as the source-drain voltage (V_{DS}). The source is the charge-injecting electrode, because it is always more negative than the gate electrode when a positive gate voltage is applied, electrons are injected, and more positive than the gate electrode when a negative gate voltage is applied, holes are injected [24].

The basic operate regimes and associated current-voltage characteristics of an organic field-effect transistor is given in figure 2.2 (a-c). When a positive gate voltage is applied, it will induce electrons at the insulator/semiconductor interface. For

negative V_G , positive charges (holes) will be accumulated. The number of accumulated charges is proportional to V_{GS} and the capacitance C_i of the insulator. However, all induced charges aren't mobile. So, it won't contribute to the current in an organic field-effect transistor. Gate voltage (effective gate voltage is $V_G - V_{Th}$) has to be applied higher than a threshold voltage V_{Th} , because the traps need to be filled first before the additionally induced charges can be mobile [25, 26].

If source-drain bias isn't applied, the charge carrier concentration in the transistor channel is uniform. A linear gradient of charge density from the carrier injecting source to the extracting drain forms when a small source-drain voltage is applied. It is shown in Figure 2.2 (a) that the current flowing through the channel is directly proportional to V_{DS} in linear regime [27].

If the source-drain voltage is reached $V_{DS}=V_{GS} - V_{Th}$, at which the channel is "pinched off" (Figure 2.2 (b)). A depletion region is formed next to the drain because the difference between the local potential $V(x)$. Saturation current ($I_{DS,sat}$) can flow across this narrow depletion zone. Because carriers are swept from the pinch-off point to the drain thanks to comparatively high electric field in the depletion region. Further increasing the source-drain voltage will not substantially increase the current. However, it leads to an expansion of the depletion. Thus the potential drop between that point and the source electrode stays approximately the same, the current saturates at a level $I_{DS,sat}$ (Figure 2.2 (c)) [28].

2.2. Device Structures

The physical nature of the semiconductor as well as the employed gate dielectric may require or enable different device structures that can show very different transistor behavior. Thus, transistors which have same components and different geometries, can show dissimilar behavior.

The most known structures are the bottom contact/top gate (BC/TG), bottom contact/bottom gate (BC/BG), and top contact/bottom gate (TC/BG) structures in relation to the substrate. One of the major differences between these device geometries cause by the position of the injecting electrodes in relation to the gate. While charges are directly injected into the channel of accumulated charges at the semiconductor-dielectric interface in the bottom contact/bottom gate structure, the source/drain

electrodes and the channel are separated by the semiconducting layer in the other two structures. [29-31]. Other differences between transistor structures arise from the dielectric/semiconductor and electrode/semiconductor interfaces, such as different morphologies at the top and bottom surfaces of a semiconductor film (molecular orientation, roughness) or trap states [32-34].

2.3. Importance of Gate Dielectric for OFET

Charge accumulation and transport in field-effect transistors occur at very close to the interface between the gate dielectric and the semiconductor. Thus, investigation of this interface and dielectric material properties is important for the device characterization. Gate dielectric layer is one of the most important part of an OFET, which can directly affect the performance of the device [35]. Mobility, threshold voltage, capacitance, dielectric strength, on /off ratio, low hysteresis etc. are the requirements for gate dielectric layer [36]. If the dielectric layer is rough and it contains valleys at interface, these parts behave as charge trap [37]. So, dielectric and organic semiconductor layer interface with minimal concentrations of impurities is also important factor for OFET. Dielectric layer should be environmentally stable, easily processable, and compatible with subsequent processing steps.

Gate dielectrics are mainly characterized by their dielectric constant ϵ (also named k), which determines the capacitance $C_i = \epsilon\epsilon_0/d$ of a dielectric layer of thickness d (ϵ_0 is the permittivity in vacuum) and thus the amount of induced charges per applied V_{GS} [38]. If electric field is applied to dielectric material, material changes its charge distribution. Thus, high gate capacitance is also important property for gate dielectrics. Because the capacitance of the gate dielectric determines the charge density that can be induced in the semiconductor layer by applying a voltage between the gate and the semiconductor (Figure 2.3). To obtain a certain amount of charges in the transistor channel, dielectric layer thickness can be reduced or used a dielectric material with a higher dielectric constant (ϵ) [20, 36].

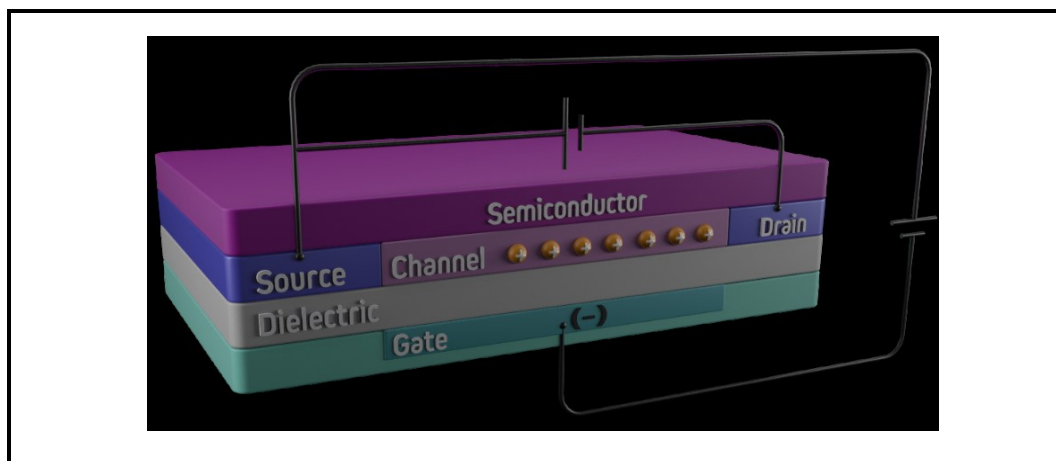


Figure 2.3: Schematic diagrams of OFET geometry.

Decreasing the operation voltage is also important for some applications of OFETs. Three important parameters which affects the operating voltage are mobility of the semiconductor, capacitance of the dielectric and geometry of the channel. The most reasonable way of them to decrease the operation voltage is increasing the capacitance of the dielectric layer by decreasing thickness of the insulator layer or usage of high dielectric constant material [37]. Because, geometry of the channel can be changed to decrease the operation voltage, but it is difficult to decrease owing to limitations of the shadow mask and printing techniques. Mobility of the semiconductor cannot be altered due to its intrinsic property of the semiconductor material.

Metal oxides with higher ϵ such as, e.g., Al_2O_3 ($\epsilon=10$) and Ta_2O_5 ($\epsilon=25$) have also been investigated as possible gate dielectrics for organic transistors [39-41]. However, SiO_2 , Ta_2O_5 , Al_2O_3 and other oxides are not ideal dielectrics for the application of organic semiconductors in flexible electronics. Because they usually need to be sputtered or anodized to obtain inferior device performance. Another method is using solution processed dielectric polymers, which do not require high temperature processing, and whose characteristics can be tuned over a wide range by changing their chemical structure [42]. Polymer gate dielectrics are easily applied in top gate transistors. But they have low dielectric constant. To overcome these disadvantages, a new approach is to combine inorganic-organic materials as gate dielectrics polymer. So, it is combined that high permittivity of the inorganic dielectric materials with high breakdown strength, mechanical flexibility, and easy processability of the organic counterparts [15].

2.4. Composites and Nanocomposites

Composites are made with the combination of two materials to give the unique properties of materials in one material. The properties of the composites depend on the type of the filler, matrix and interface between filler and polymer chains. Interface between polymer and filler is important to provide better load transfer. Size, shape, orientation and dispersion of the filler are other factors affecting the properties of the composites [43]. While the interface of fillers is close to the bulk polymer matrix in micrometers scale, they have ultra large interfacial area per volume, and the distances between the polymer and filler components are extremely short in the case of nanocomposites [44].

2.5. Important of Injecting Electrodes

In order for the current to flow through the transistor channel, injection of electrons to the LUMO level for the n-channel transistors and a hole for the p-channel transistors must be injected into the semiconductor HOMO level from the source electrode. The contacts in organic field effect transistors are based on a direct metal-semiconductor junction, without any doping, unlike silicon transistors [45-47]. So, the metal-semiconductor interface is usually treated as a Mott-Schottky barrier. Barrier height is given by the difference between the metal work function (ϕ) and the semiconductor HOMO or LUMO level. A good ohmic contact is expected when the HOMO or LUMO level of semiconductor is close to metal work function [48]. However, in the opposite case, a potential barrier is created, resulting in a poor charge injection which causes the transistor to provide extra resistance (it is known contact resistance). If contact resistance is larger than the channel resistance, it dominates the performance of this device depending on the semiconductor mobility, which affects the linear regime of the organic field effect transistors because a large part of the source-drain voltage already falls in the contacts and does not across the channel [49, 50]. It is important to compare the working function of the injection metal with the HOMO / LUMO levels of a semiconducting material. Because it can help understand whether the charge injection is likely or whether a high or low contact resistance is

expected. In the studies related to this subject, work function of gold ($\phi = 5.1$ eV) is well aligned with the HOMO level of P3HT (4.8 eV), which leads to a very low contact resistance, while almost no charge injection from aluminum ($\phi = 4.0$ eV) was observed [51].

2.6. Charge transport in organic semiconductors

In the efficient operation of modern optoelectronic devices such as light emitting diodes, field-effect transistors and organic solar cells, understanding the processes that determine charge transfer is important for designing materials with improved structure-property relationships. Organic semiconductors are hydrocarbon molecules with a backbone of carbon atoms. The carbon atom has four valence electrons, each of which can form covalent bond with other atoms, two of which are in the 2s and the other in the 2p atomic orbitals [52]. It is said that if the electrons that occupy a molecular orbital have a lower energy than they had before forming the bonds which are formed by hybridizing the atomic orbitals to form new molecular orbitals [53]. In the ground state, the orbitals contain two electrons each, while the higher energy orbitals are empty up to a certain orbital, because molecular orbitals are filled with electrons from low to high energy [54]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are separated from each other by the band gap which is known in crystalline inorganic semiconductors [55].

The simplest organic molecules are alkanes, linear chains of carbon atoms connected with single bonds and supplemented with hydrogen atoms. For each carbon atom in an alkane, one 2s and three 2p orbitals hybridize to form four new covalent σ -bonds. The electrons in a σ -bond are localized in space [52]. The electrical conductivity in organic semiconductors originates from conjugation. In a conjugated molecule, the atomic orbitals of carbon are not sp^3 hybridized. Instead, double bonds between two carbon atoms are formed by hybridization of one 2s and two 2p atomic orbitals [55]. Thus, two carbon atoms are bound via a double bond, an sp^2 -hybridization is formed. It forms three coplanar σ -bonds. One s- and two p-orbitals form three coplanar degenerated orbitals. Thus, a σ -bond between two neighboring carbon atoms is formed. Two neighboring p_z orbitals overlap with the p_z orbital of a

neighboring carbon atom to form a π -bond. The σ -bond and the π -bond together make up the double bond. In contrast to a σ -bond, the electrons in a π -bond are delocalized in space [56].

2.7. Organic Materials

As an active material, solution processed semiconducting blend of π -conjugated P3HT (poly(3-hexylthiophene-2,5-diyl)) and PCBM ([6,6]-phenyl C₆₁ butyric acid methyl ester) and P-SBTBDT (poly (selenophene, benzotriazole and dialkoxy substituted [1,2-b:4, 5-b'] dithiophene) polymers has preferred. Additionally, CuPc small molecule have used by evaporation in high vacuum. The evaporation method is applicable for very short polymer chains. Small conjugated organic molecules are used to achieve a more crystalline semiconductor.

Table 2.1: Summary of Electrochemical Properties of P-SBTBDT.

Polymer	HOMO(eV)	LUMO(eV)	E _g (eV)
P-SBTBDT	-5.17	-3.34	1.81

Schematic representation of synthesized P-SBTBDT containing benzotriazole and selenophene units, is shown in Figure 2.4 [57]. In order to overcome probable solubility problems, branched alkyl chain units were incorporated to benzotriazole moiety. It is given below HOMO and LUMO energy levels and band gap (E_g).

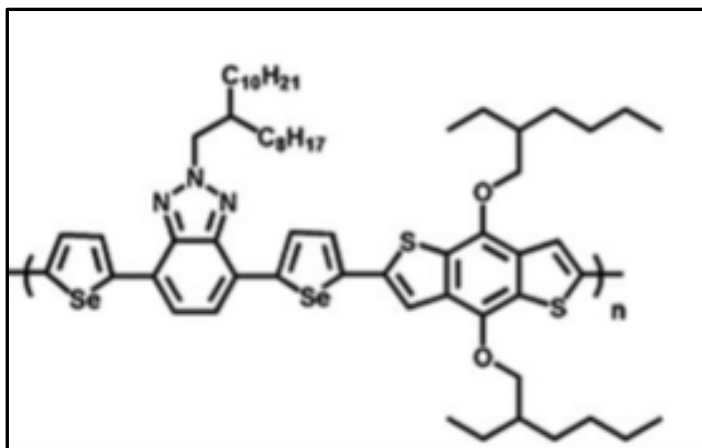


Figure 2.4: Schematic structure of P-SBTBDT.

P3HT is a derivative of polythiophene, which molecular structure is shown in Figure 2.5 (a). Polythiophene is widely used in organic electronic devices, and probably the most widely used polymer in transistors due to chemically stable conducting polymer. By adding hexyl groups as the side chains to the thiophene rings which is insoluble makes the polymer soluble in chloroform [31]. The new polymer is called poly(3-hexylthiophene) (P3HT). PCBM is one of the most commonly used electron accepting materials in organic photovoltaic devices (Figure 2.5 (b)). PCBM can be dissolved in common solvents used for donor polymers, allowing the simultaneous casting of polymer and fullerene and the formation of an efficient bulk heterojunction. When used in a device with a donor polymer, PCBM enables rapid and efficient charge transfer and exciton dissociation [58], and has a high electron mobility [59].

Phthalocyanines are another widely studied organic molecule. They consist of an alternating nitrogen carbon ring structure. The simplest phthalocyanine molecule has two hydrogen atoms in the center, which can be replaced by various metal atoms, such as Fe, Zn, Pb or Cu. Its molecular structure is shown in Figure 2.5 (c). It is one of the most investigated molecule for fabrication of OFET structures with p-type transport properties [13]. CuPc is a material with high chemical stability that is widely used in industry, e.g. as dye for plastics.

Poly (methyl methacrylate) (PMMA) and poly vinyl alcohol (PVA) are mainly used as dielectric layers in almost all reported literature. PMMA has a permittivity of approximately 3.5 [20]. Multilayer dielectric of (relatively low-k) PMMA and (high-k) tantalum pentoxide (Ta_2O_5) has been used to reduce the operating voltages of printed transistor [60].

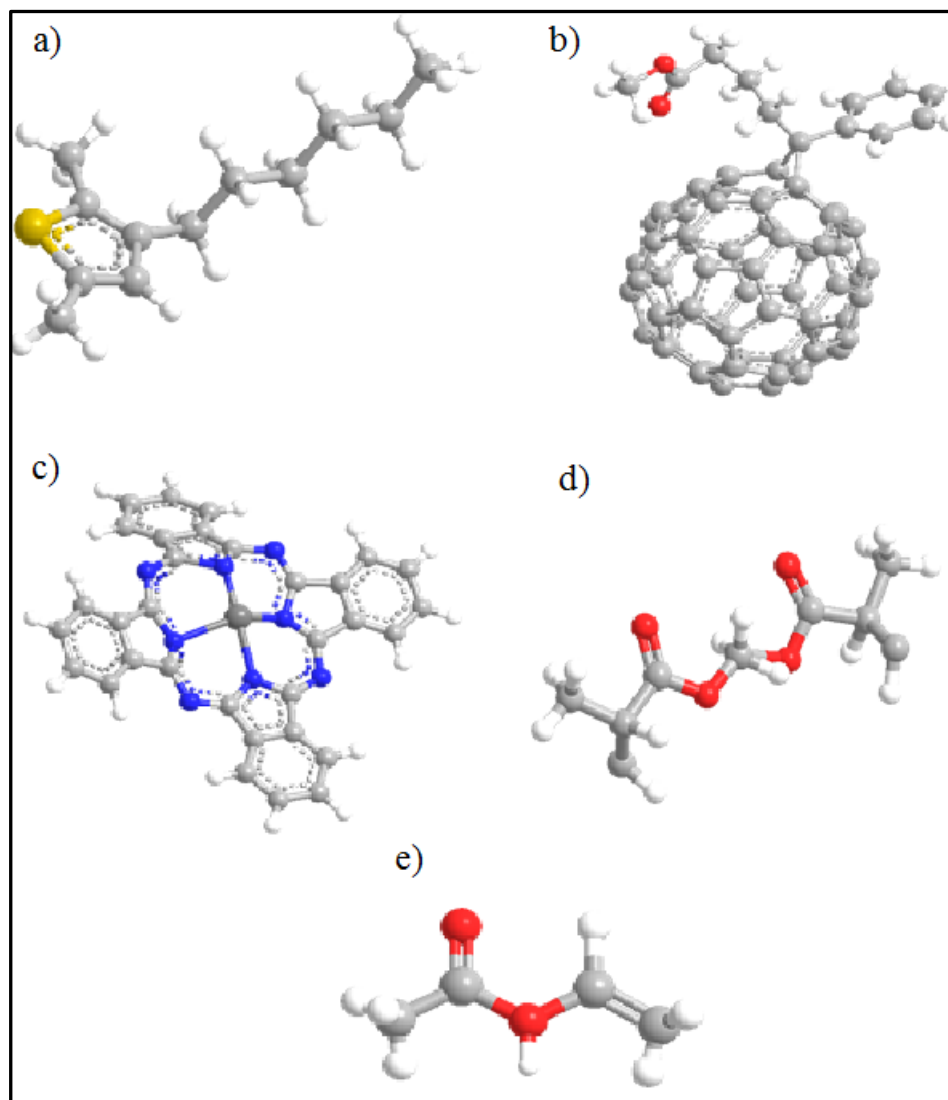


Figure 2.5: Structure of a) P3HT, b) PCBM, c) CuPc, d) PMMA, e) PVA.

2.8. Important Parameters for OFETs

2.8.1. Mobility

Mobility is the related the carrier speed in a material and the applied electric field and mobility unit is in $\text{cm}^2(\text{Vs})^{-1}$. Microscopically, carriers accelerate due to the force applied by the electric field, which occurs rapidly and across a large number of carriers. Observed macroscopically, carrier velocity is a viscous flow process in solid materials [9].

In OFETs, charge carriers are induced by a gate electrode across an insulating layer. Applying a voltage V_{DS} between the source and the drain contact gives rise to a current in the channel. In literature, mobility can be extracted from the experimental data (OFET output and transfer curves) by using current value and other OFET parameters. Typically mobility in the saturation regime of the OFET is described by [24]:

$$\mu_{sat} = \frac{dI_{DS,sat}}{dV_G} \frac{L}{WC_i} \frac{1}{V_G - V_{Th}} \quad (2.1)$$

2.8.2. Threshold voltage

Threshold voltage V_{Th} is an important parameter that needs to be controlled to ensure proper operation of the circuits. Term of threshold voltage is generally used to specify the gate voltage at which current begins to flow which in OFETs at the onset of accumulation [61]. While threshold voltage is determined, the linear part of a $\sqrt{I_{DS}} - V_{GS}$ curve extrapolated to the intercept on the V_{GS} axis (it can be seen in Figure 2.6)

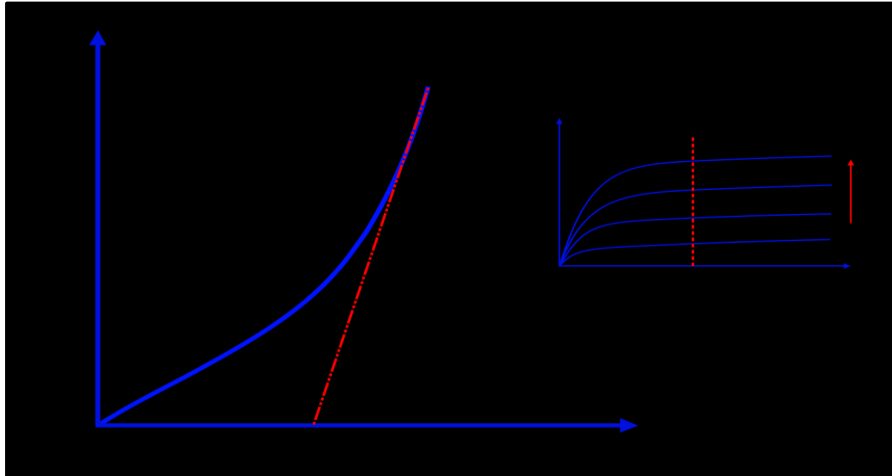


Figure 2.6: Extrapolation of V_{Th} from the $\sqrt{I_{DS}} - V_{GS}$ transfer characteristic. The inset shows the section of the $I_{DS}-V_{GS}$ output characteristic where the transfer characteristic is taken.

Threshold voltages can originate from several effects and depend strongly on the semiconductor and dielectric used. In particular; impurities, interface states, and, charge traps contribute to the threshold voltage [20].

2.8.3. Hysteresis/bias-stress

Hysteresis in OFETs can arise from a number of sources one of which is water incorporation in the gate dielectric material [62]. Organic gate dielectrics with strong polar groups can absorb water and experience a slow relaxation which can compromise device performance. When a gate dielectric is selected, attention should be paid to either eliminating this issue through selection of a less hygroscopic dielectric material (e.g. an inorganic or hydrophobic material), or by dehydrating and encapsulating the device. Slow relaxation of the gate dielectric is usually strongest in polymer-based gate dielectrics which have polar groups [63] or absorb water [64]. The relaxation of the gate dielectric invariably increases the dipole in the gate dielectric as time passes. This causes a decrease in current after a bias change which increases the current flow. Dielectric charge storage is caused by injection of charges into the gate dielectric. The driving force for the relaxation increases the field drop across the gate dielectric and decreases the field which reaches the semiconductor. This generally leads to a decrease in current after a bias change which increases the current flow.

Several studies, slow relaxation of the gate dielectric, dielectric charge storage, dielectric charge storage, have identified three major contributions to decrease term hysteretic effects [62].

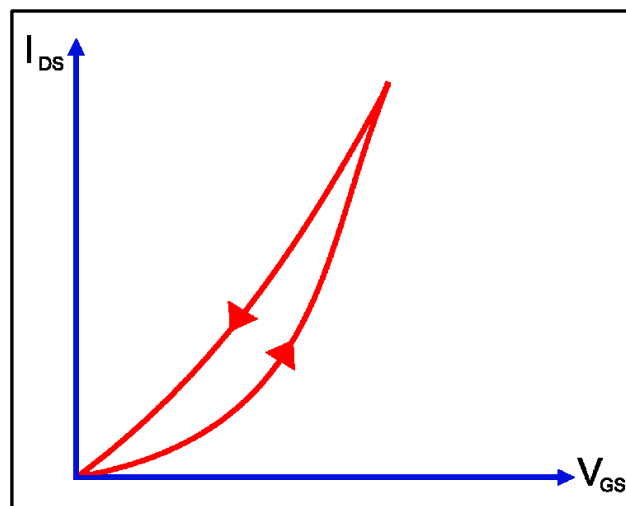


Figure 2.7: Schematic transfer characteristic exhibiting hysteresis.

2.8.4. Gate leakage

In an ideal FET with no gate leakage ($I_G = 0$) and $I_D = -I_S$. It can be seen in equation 2.2 that conservation of charge requires:

$$I_D + I_S + I_G = 0 \quad (2.2)$$

The simplest measurement of leakage is taken while $V_{DS} = 0$ over a range of V_{GS} , but the gate current can be measured over a range of bias conditions [65]. Imperfect gate dielectrics, surface conduction, bulk device transport, or a lack of semiconductor patterning can lead to gate leakage and affect the performance of many circuits.

2.8.5. Subthreshold slope

The subthreshold slope is reported at the area of maximum slope which is the inverse slope of the $\log I_D$ vs V_{GS} measured below threshold. It is typically reported in base 10 logarithmic units of mV/decade [66]. In many thin film transistors the current begins to increase again at bias points which are normally associated with cut-off. Increment in current is generally because of increased gate leakage. This may alternatively correspond to ambipolar behavior and a second region of accumulation in some materials [67] or hole and electron transporting semiconductor blends [68].

3. EXPERIMENTAL METHODS

In this dissertation, organic field effect transistors (OFETs) with P3HT:PCBM, P-SBTBDT, CuPc semiconductors which are built with the Ta₂O₅:PMMA, Al₂O₃:PVA, PC-PMMA composite gate dielectric were studied. This chapter describes the fabrication process of OFET and the various instruments and methods used for the electrical characterization of the organic dielectric and semiconductor thin films grown for OFET. Surface morphologies and cross-sectional images were obtained by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

3.1 OFET Fabrication

3.1.1. Preparation of Glass ITO Substrate

The pre-patterned OFET substrates consist of interdigitated ITO fingers (purchased from Ossila) (20 mm x 15 mm) were cleaned by using deionized water, acetone and isopropyl alcohol (purchased from Aldrich) in ultrasonic bath for 15 minutes, respectively. The structure of the interdigitated ITO substrate was given in Figure 3.1.

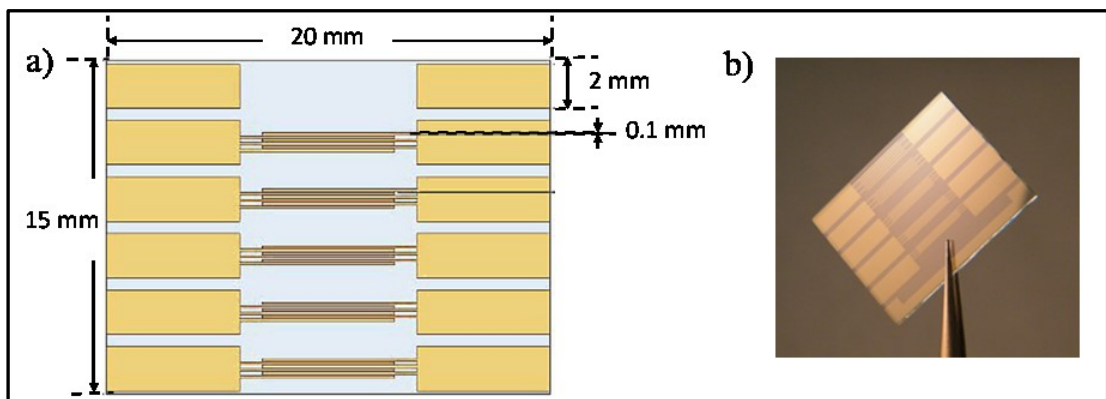


Figure 3.1: a) Pre-patterned 50 μ m channel length substrate consist of interdigitated ITO fingers dimensions b) The pre-patterned OFET substrate.

3.1.2. Preparation of Source/Drain Electrodes with Photolithography

Photolithography is composed a mainly three-step process of deposition, exposure and development, which is used to pattern a layer of photosensitive polymer, called photoresist. This photoresist layer is then either dissolved or used as a structural material, acts as a masking layer for subsequent steps that either add or remove material to the device. Solvent and a photoactive compound in photoresist, which keeps the material in a viscous solution form until deposition. Then it is evaporated causing the photoresist to solidify [69]. The solubility of the light-sensitive photoresist (in this thesis, it is used AZ5214 as a photoresist) in a developer (in this thesis, it is used AZ726 as a developer) is controlled by the ultra-violet (UV). The reaction of photoresist to UV light depends on the type of the photoresist. With positive type

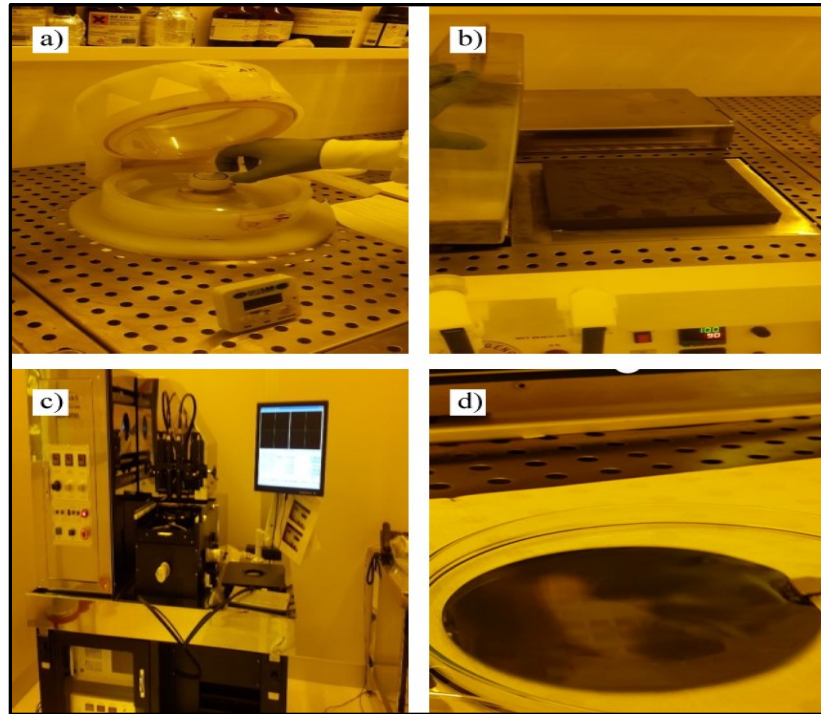


Figure 3.2: a) spin coating of photoresist b) annealing for removal solvent c) photolithography tool d) dissolving photoresist layer in a developer.

photoresist, photochemical reaction forms scissions in the polymer chain, making it more soluble in developer. The reaction is the opposite for negative type photoresist, which strengthens the polymer by UV light crosslinks, making it less soluble. The photoresist is deposited as a thin (typically 1-10 μm) layer on the wafer using a spin

coating technique (Figure 3.2 (a)). After spin coating of photoresist, to remove solvents and promote adhesion of resist layer, substrates are prebaked Figure 3.2 (b). Then, the substrates are exposed in a photolithography tool, where light is spatially patterned using an optical mask as shown in Figure 3.2 (c). Finally, the more soluble parts of photoresist layer are dissolved in a developer for several minutes (Figure 3.2 (d)). Then Au evaporated on this substrate.

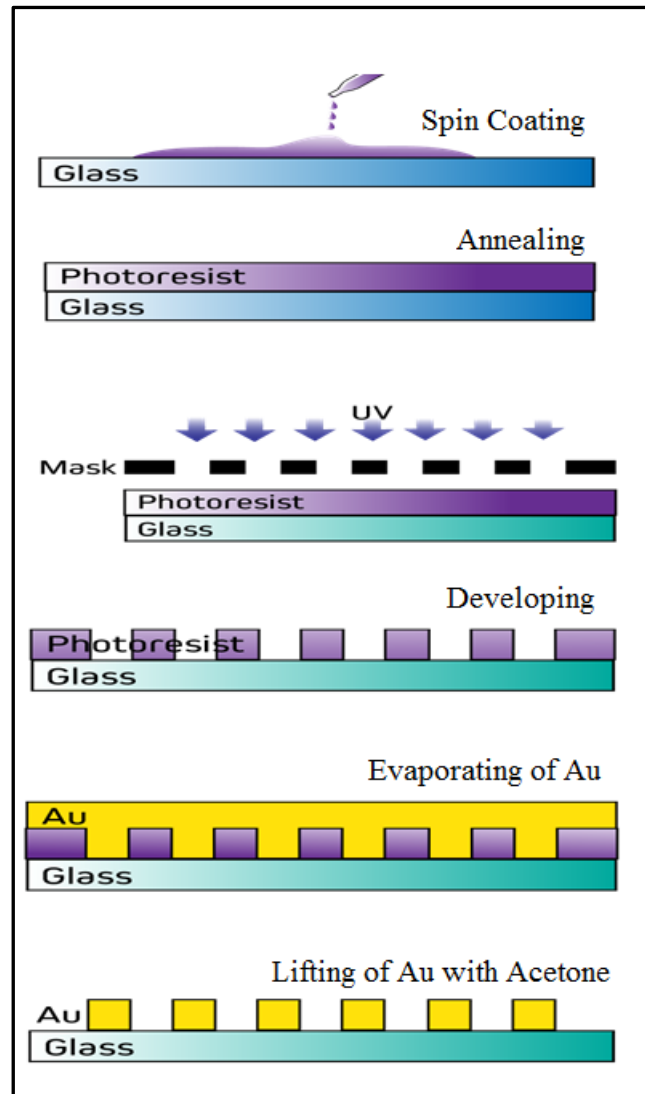


Figure 3.3: Steps of the photolithography process with positive photoresist.

It can be seen interdigitated source/drain electrodes which fabricated photolithography method (Figure 3.4)

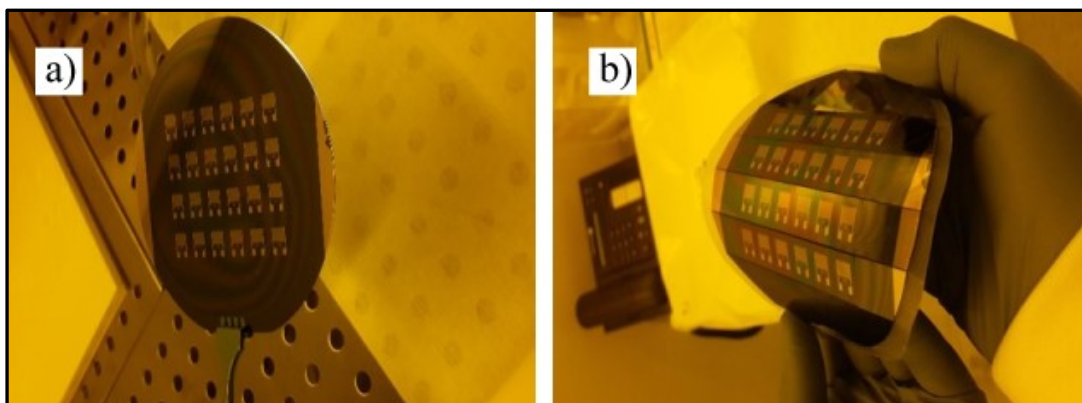


Figure 3.4: Interdigitated source/drain electrodes which fabricated photolithography method.

3.1.3. Preparation of Active Layer Thin Films

Semiconductor layers of CuPc (sublimation grade, 99.9%) which were supplied by Sigma–Aldrich, were prepared with MBraun High Vacuum System at vacuum (Figure 3.5). Semiconductor layers of CuPc were deposited at pressure of 10^{-6} torr with deposition rates of 0.1-0.2 nm/sec. The thickness of the deposited CuPc semiconductor layers was about 100 nm.

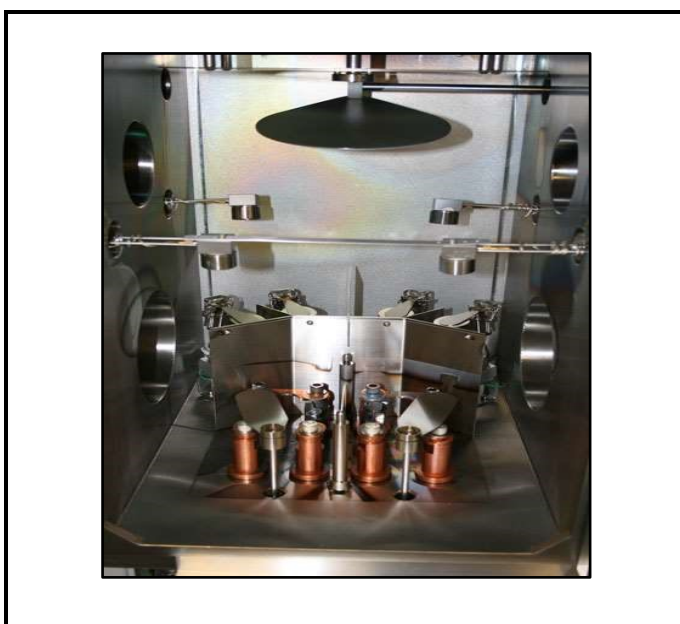


Figure 3.5: MBraun High Vacuum System to evaporate small molecule polymers.

The poly(3-hexylthiophene) (P3HT): 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6] methanofullerene (PCBM) (Sigma Aldrich) was dissolved in anhydrous dichlorobenzene (Sigma-Aldrich) at 10:10 mg/1ml. The solution was heated and ultrasonicated for 24 hours at 50°C. The P3HT solution was spin coated for 30 seconds at 2500 rpm in ambient conditions as a semiconductor layer on top of interdigitated source/drain electrode. After the spin coating the substrates were annealed for 15 minutes in 110°C.

P-SBTBDT was dissolved in anhydrous dichlorobenzene (Sigma-Aldrich) at 10 mg/1ml. Then was made spin coating for 30 seconds at 2500 rpm in ambient conditions as a semiconductor layer on top of interdigitated source/drain electrode. After the spin coating the substrates were annealed for 15 minutes in 110°C. It can be find detailed information of the semiconductor materials properties and preparing active layer in related chapters.

3.2. Device Characterization

3.2.1. OFET Characterization

All device current voltage measurements were performed with Keithley 4200 SCS (Figure 3.6). All measurements were done in ambient conditions.



Figure 3.6: Keithley 4200 Semiconductor Characterization System.

3.2.1.1. Transfer Characteristic

OFET is measured by holding V_{DS} constant and sweeping the gate voltage. At least one value of V_{DS} should be selected to test the device in the linear region. The linear region should be plotted as I_{DS} vs. V_{GS} . The saturation region characteristic can be plotted as $\sqrt{I_{DS}}$ vs. V_{GS} or on a linear curve [70]. These curves were plotted together using split axes to conserve space. The determination of threshold voltage from extrapolation from these graphs was also performed. It can be seen example for transfer characteristic in Figure 3.7 [66].

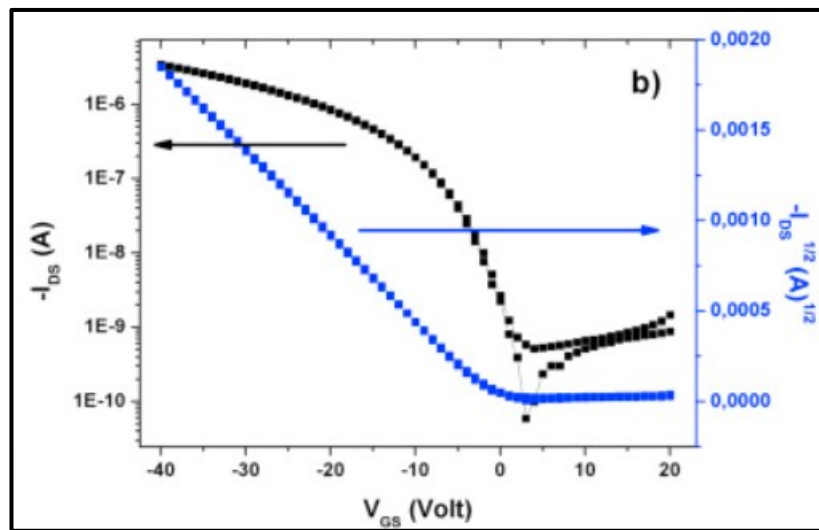


Figure 3.7: A sample device transfer measurement showing both the saturation and linear characteristic.

3.2.1.2. Output Characteristic

The output characteristic is almost universally presented as the qualitative proof that a transistor has been formed [9]. The devices were measured by changing V_{GS} different values and sweeping the drain voltage.

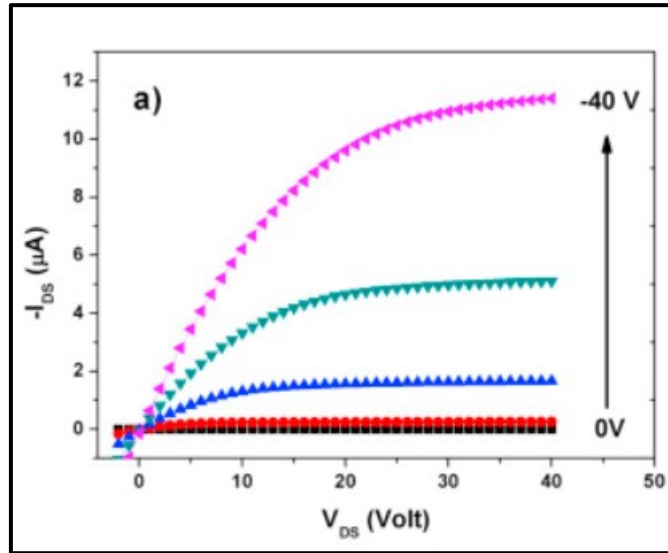


Figure 3.8: The output characteristic of OFET.

3.2.1.3 Gate Leakage

Gate leakage (I_G) can be measured plotted as a function of gate bias ($V_{DS} = 0V$).

3.2.2. Dielectric Characterization

Interest in the fundamental and application aspects of dielectric spectroscopy of polymer materials is increasing day by day. Dielectric spectroscopy is important for obtaining wealth of information about different molecular motions and relaxation process. Dielectric spectroscopy has wide frequency range, from 10^{-5} Hz to 10^{11} Hz, over which polymers respond to an applied electric field. It enables one to relate the observed dielectric response to slow (low frequency) and /or fast (high frequency) molecular events [71]. Using polymer materials in electronic interconnection devices, optoelectronic switches, printed circuit board microwave assemblies for radar, batteries, which shows the interest in the dielectric and electrical properties of the polymer.

When an electric field is applied between the faces of the capacitor with dielectrics between the plates, the atomic and molecular charges in the dielectric are displaced from the equilibrium positions and the material is said to be polarized. There are several different mechanisms that can create polarization in a dielectric material

when the field is applied [72]. One of these is electric polarization, is extremely fast; its resonant frequency is in ultraviolet or visible range of the electromagnetic spectrum. This polarization arises when electrons are displaced from their equilibrium positions with respect to the atomic nucleus and an induced dipole moment is produced. Another induced polarization is atomic polarization, and its resonant frequency is in the infrared range of the electromagnetic spectrum. This polarization is called atomic polarization, and its resonant frequency is in the infrared range of the electromagnetic spectrum. Cause of polarization in polymeric materials can be charge migration or orientation of permanent dipoles [73].

The other major polarization mechanism is dipole orientation [74]. If materials that contain permanent dipoles are placed in the electric field, dipole orientation or dipole polarization is produced as a result of the alignment of dipoles in the direction of the applied field. [75]. However, unlike the electronic and atomic polarization, the polarization of permanent dipoles involves cooperative motions of molecular segments in a viscous medium with time-scales measurable by dielectric spectroscopy [76, 77].

There are two additional induced polarization for interpretation of experimental results. The first one is electrode polarization, which results from the accumulation of ions at the polymer electrode interface. The second polarization is due to the charges at the interface between components in heterogeneous systems. This polarization is called as interfacial or Maxwell- Wagner polarization [78].

Dielectric measurements can be conducted by applying voltage to the electrode interface and measuring amplitude and phase shift of the resulting current. If the input signal is the current and the output signal the voltage, the transfer function which the ratio of the output signal to the input perturbation is the system impedance [71]. The impedance, Z , is expressed as the complex number; $Z=Z'-iZ''$, where Z' and Z'' are the real and imaginary components of impedance, respectively. In addition to impedance, the complex dielectric constant (or dielectric permittivity) that can be obtained from dielectric spectroscopy [79].

The simplest equivalent circuits are obtained by combining resistance and capacitance in parallel or series. However, an R-C parallel circuit in Figure 3.8 a) is simple, it is often an adequate model of polarization by charge migration in a given frequency range. A single resistance is needed to describe the overall loss because the dissipative contributions due to electrode polarization and dipole relaxations occur at

lower and higher frequency respectively. The single capacitance embodies the overall ability of the dielectric to store the electric field by all polarization mechanism. The impedance of a parallel circuit is given by the sum of the contributions from resistance and capacitance.

$$\vec{Z} = \frac{1}{\vec{Y}} = \frac{1}{\frac{1}{R_1} + i\omega C_1} \quad (3.1)$$

where i is $(-1)^{1/2}$, ω is the angular frequency, $\omega = 2\pi f$ and RC is equal to τ , the circuit characteristic time. τ is called the relaxation time when dipole polarization form.

When resistance and capacitance are placed in series (Figure 3.8 (b)), this circuit combination leads to the classic Debye equations for a single dipole or many dipoles with a single relaxation time.

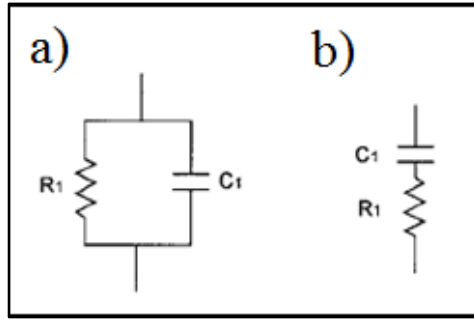


Figure 3.9: Circuit diagrams for the modeling of material proper.

Graphical representation of impedance is important, is based on the plots of imaginary versus real impedance, often called to as Cole-Cole plots. An R-C parallel equivalent circuit makes a semicircle in the complex plane, with the resistance obtained from the intersection of the semicircle and the Z' axis [71]. The other representation of impedance data consists in plotting the absolute value of impedance, as a function of the logarithm of frequency.

4. FABRICATION AND INVESTIGATION OF P3HT:PCBM BULK HETEROJUNCTION BASED ORGANIC FIELD EFFECT TRANSISTORS USING DIELECTRIC LAYERS OF PMMA:Ta₂O₅ NANOCOMPOSITES¹

4.2 Introduction

Organic Field Effect Transistors (OFETs) are of primary importance due to effective implementation of low-cost, flexible and light devices in new generation electronics [80]. Particularly, ambipolar OFETs are useful alternatives for various applications because of its operation both with negative and positive voltages. In addition to the simplification of circuit design, ambipolar character of OFETs enables the realization of low power and stable organic integrated circuits [81]. Ambipolar OFETs can be fabricated by different methods. Bilayer of electron and hole transporting materials or a single layer that is composed of their mixtures is the most used structures for ambipolar OFETs [82]. OFETs based on a single organic semiconductor with different source-drain electrode materials are also reported with ambipolar properties [83]. Another successful approach for pentacene based ambipolar devices is to use only Au as source-drain electrodes and employ poly (vinyl alcohol) (PVA) film as gate dielectric [84]. It is also shown that pentacene OFETs produced directly on SiO₂, Al₂O₃ or Ta₂O₅ with Au source-drain electrodes exhibit p-type operation [85]. Takebayashi et al. used PVA coated Au source-drain electrodes for pentacene and fabricated low voltage OFETs [86]. In these devices, Na⁺ ions in PVA change the character of the injection barrier in Au/Pentacene interface, which leads to ambipolar behavior of the devices. Bartic et al. have demonstrated low voltage OFETs with P3HT semiconducting layer and Ta₂O₅ dielectric layer which supply oxygen

¹ This chapter has been published as B. Canımkuşbey, Z. A. Kösemen, S. E. San, M.Yasin, S. Berber, A. Kösemen, “Fabrication and Investigation of P3HT:PCBM Bulk Heterojunction Based Organic Field Effect Transistors Using Dielectric Layers of PMMA:Ta₂O₅ Nanocomposites”, *Microelectronic Engineering*, (2017).

atoms during fabrication process and significantly affect the performance of the device [87].

Chemical Vapor Deposition (CVD) or Pulsed Laser Deposition (PLD) processed metal oxide dielectric films, such as Al_2O_3 , HfO_2 , Gd_2O_3 , Ta_2O_5 , BaTiO_3 , etc., have higher dielectric constants, but these materials are rather expensive and not compatible with most of the flexible substrates in printed electronics, thus, limiting large area application [88]. To overcome these disadvantages, polymer nanocomposite dielectric materials can be used with metal oxide dielectric layers. Solution processed dielectric layers such as PMMA, PVP and PVA have lower dielectric constants and gate capacitances [89-92]. Also, these layers are required to be thick enough to avoid pin holes which are generally observed in solution processed thin films. However, polymer nanocomposite based dielectric films can be easily processed even at room temperatures, making them ideal candidates for flexible microelectronic devices [93]. In recent years, much effort has been made by the researchers to tailor the properties of polymers by mixing various inorganic components to change impurity density of the film. Impurities and dopants in organic semiconductors trap one type of charge carriers [94, 95]. It has also shown that dielectric properties of solution processed PMMA films can be improved due to mixing of high- κ inorganic nanoparticles such as zinc sulphide powders and zirconium oxocluster [36].

Top-gate/bottom-contact type configuration has advantages over bottom-gate ones [96]. This structure has five times improved lifetime when compared with a conventional OFET. The top-gate insulator can be used as a passivation layer to protect the device from degradation by moisture and oxygen [97].

Thus, it is possible to develop low-cost solution process gate dielectrics with mechanical flexibility, high dielectric constants and tunable carrier density. In this work, a solution based hybrid dielectric material, containing PMMA and a high- κ Ta_2O_5 inorganic particle was reported as a gate dielectric layer of the OFETs.

4.3 Experimental Details

PMMA, P3HT, PCBM, Ta_2O_5 and butyl acetate, used for this study, were purchased from Sigma Aldrich. Glass substrates with interdigitated ITO electrodes having channel dimensions of 30mm (W) $\times$ 50 μm (L) were purchased from Ossila. P3HT: PCBM blends with 1:1 wt/wt ratio were prepared in 1,2 dichlorobenzenes (10

mg/ml) at 50°C using stirring process. P3HT: PCBM semiconducting layer with a thickness of around 150 nm was deposited on interdigitated ITO electrodes that act as source-drain electrodes. P3HT: PCBM thin films were annealed at 110°C for 30 minutes. PMMA and Ta₂O₅ (inorganic particles with diameter <20 µm) were dissolved in 1 ml butyl acetate at 0 wt%, 3 wt%, 7 wt%, 10 wt%, 20 wt%, 50 wt% concentration of Ta₂O₅ particles in PMMA and stirred for one day at room temperature until homogenous solution is obtained. To promote uniform dispersion of particles, the particle suspensions were also ultra-sonicated for 2 h. A PMMA: Ta₂O₅ dielectric layer with a thickness of about 600 nm was spin coated on the P3HT: PCBM semiconducting layer. The dielectric films were annealed at 110°C on a hot plate for 10 minutes to evaporate residual solvents in ambient conditions. This annealing parameters were selected from literature and slightly adapted for our devices taking into account evaporation time of the solvent [98]. Finally, aluminum was evaporated on dielectric layer of the sample as a top gate contact. Dielectric properties of PMMA: Ta₂O₅ composites were analyzed with metal-insulator-semiconductor (ITO/PMMA: Ta₂O₅/P3HT: PCBM) structures using HP 4194A dielectric analyzer. Figure 4.1 schematically describes the structure of the device. Electrical characterization of the

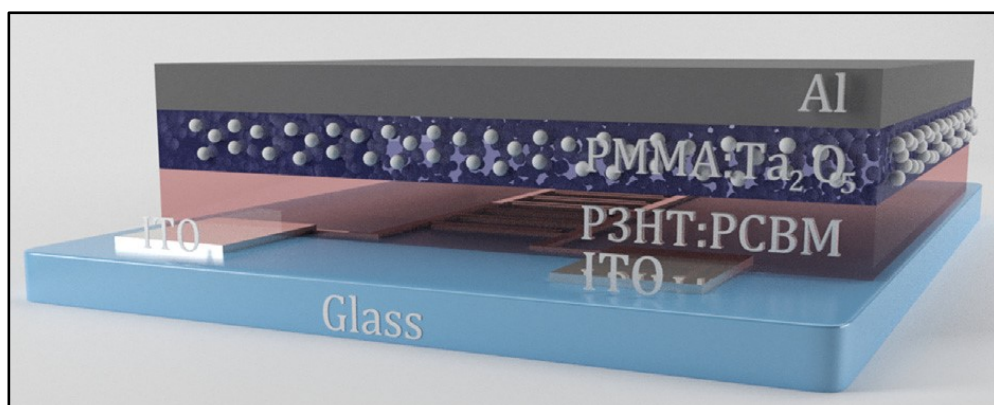


Figure 4.1: A schematic illustration of OFET devices.

fabricated OFETs was carried out using Keithley 4200-SCS at room temperature. Surface and cross sectional profiles of pure PMMA and PMMA: Ta₂O₅ composite films were analyzed using SEM (Philips XL 30 SFEG). Semiconductor-dielectric interfaces were investigated by means of X-Ray Reflectivity (XRR, Smartlab, Rigaku)

4.3. Results and Discussion

SEM was used to investigate the surface morphology and micro structural features of PMMA: Ta₂O₅ based dielectric films with varying wt/wt concentration of Ta₂O₅. SEM images of the dielectric film surface and cross-sectional profile of the semiconductor/dielectric interface are shown in Figure 4.2 and Figure 4.3, respectively. As can be seen from the Figure 4.3, SEM images did not show any significant difference regarding the morphology at the interface for varying Ta₂O₅ concentrations. In addition, PMMA forms a good interface with semiconducting films, which is very good agreement with literature [99]. As can be seen in the SEM images, agglomeration of Ta₂O₅ nanoparticles is noted in PMMA dielectric films with the increasing concentration of Ta₂O₅.

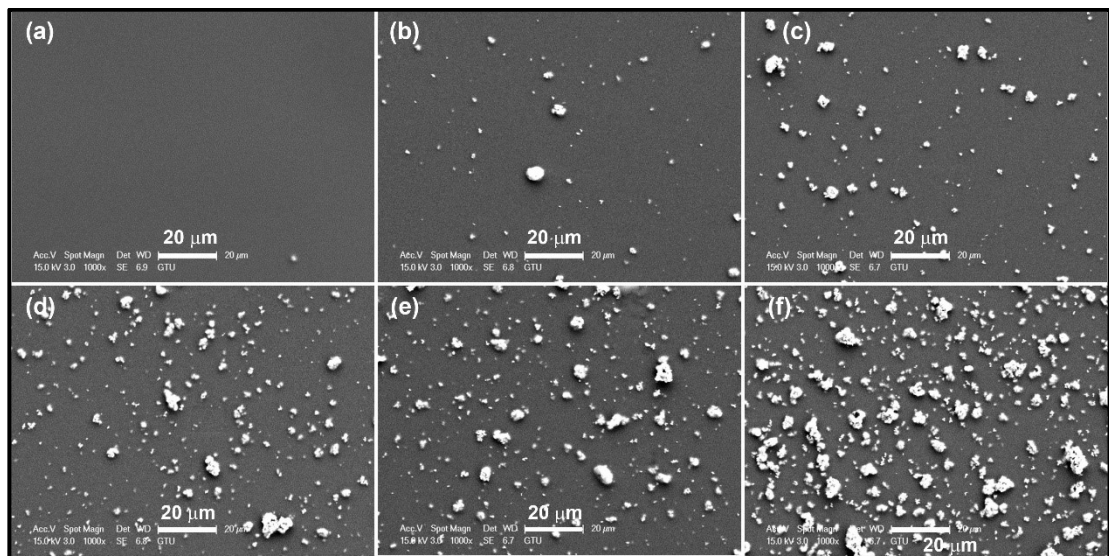


Figure 4.2: SEM images taken from the surface of PMMA: Ta₂O₅ based dielectric films with varying wt% concentrations of Ta₂O₅.

Variation in the size of Ta₂O₅ might be attributed due to difference in thickness between different regions of solution processed films.

Dielectric constant (ϵ') variation for different concentrations of Ta₂O₅ particles as a function of frequency is presented in Figure 4.4 All the samples have shown good polarization over a wide range of frequency. Dielectric constant was found to increase with increase in the concentration of Ta₂O₅. Dielectric constant value of 3.6 at 100 Hz for PMMA:Ta₂O₅ blends with 0 wt% concentration of Ta₂O₅ is in accordance with

literature [96]. Increase in the dielectric constant value with the concentration of Ta_2O_5 strongly confirms linear enhancement in both electron and hole accumulation, whereas the PMMA film showed preferential electron accumulation [100].

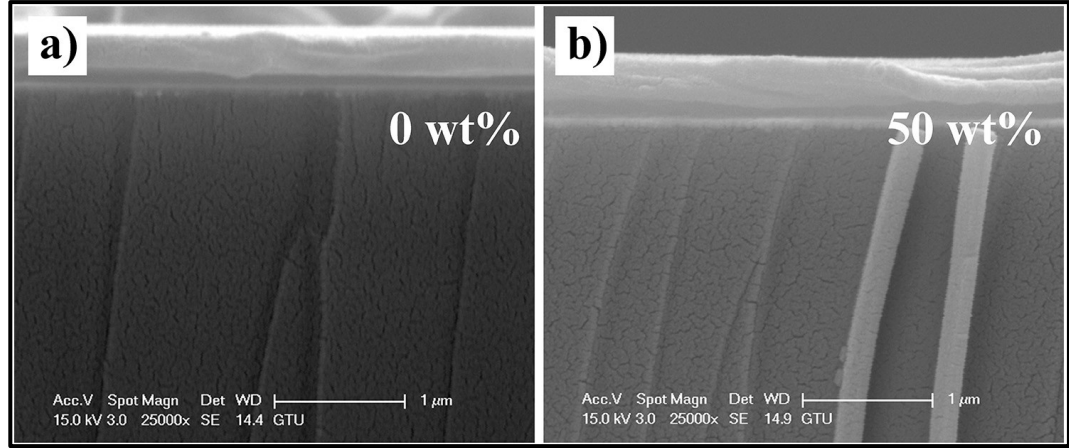


Figure 4.3: Cross-section SEM images of PMMA: Ta_2O_5 based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Ta_2O_5 .

Frequency dependent loss tangent ($\tan \delta$) and conductivity graphs are given in Figure 4.5 (a) and 4.5 (b), respectively. Loss tangent values show the dielectric losses in a dielectric material, and decrease with the decreasing electrical conductivity in nanocomposites and vice versa [101]. Figure 4.5 (b) shows frequency dependent electrical conductivity which confirms relation between conductivity and loss tangent. The inset of Figure 4.5 (b) shows the extended diagram of low frequency region. The conductivity increases with increasing content of Ta_2O_5 filler. This behavior is in very

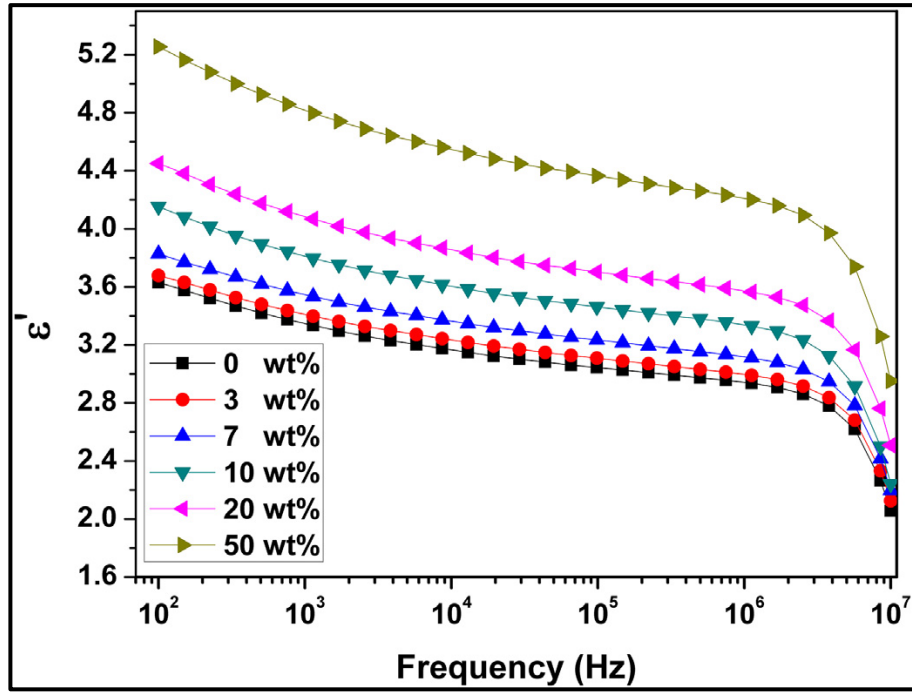


Figure 4.4: Dielectric constant (ϵ') versus frequency graph for PMMA: Ta₂O₅ based dielectric films for different concentrations of Ta₂O₅.

good agreement with literature and can be attributed to increase in number of charge carriers supplied by Ta₂O₅ filler [102, 103]. The frequency dependent AC conductivity obeys Jonscher's universal power law which is applicable for polymers.

$$\sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s \quad (4.1)$$

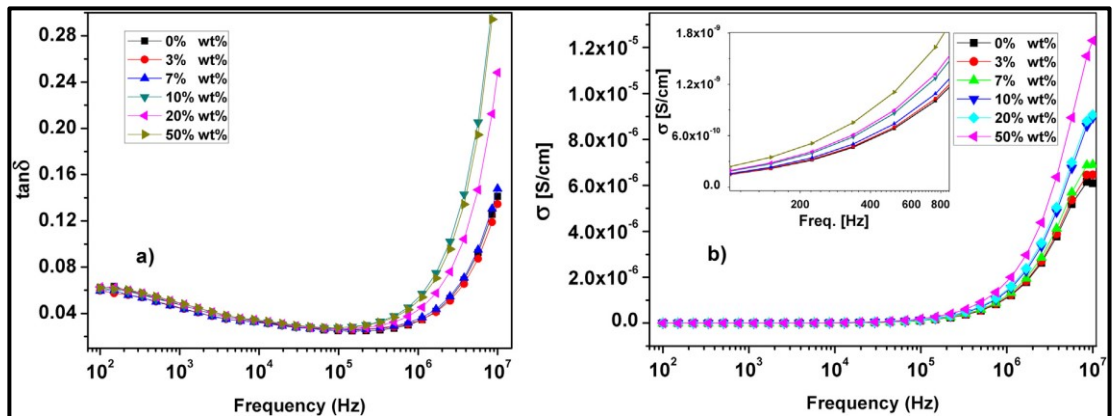


Figure 4.5: a) $\tan \delta$ versus logarithmic frequency graph and b) conductivity versus frequency graph for PMMA: Ta₂O₅ based dielectric films for different concentrations of Ta₂O₅. The inset displays the extended diagram from low frequency region for clarity.

where, A is a constant, ω is the angular frequency and s is the frequency exponent parameter [104].

In Ta_2O_5 , oxygen vacancies are the most dominant type of defect [105]. Each oxygen vacancy offers dangling bonds and donates two electrons close to the vacancy location. The dangling bonds cause electronic states within the bandgap which are able to trap excited electrons, creating many trap levels within the bandgap of Ta_2O_5 . Consequently, the presence of oxygen vacancies is expected to make Ta_2O_5 an n -type semiconductor [106]. On the other hand, the increment with source of charge carriers pave the way for ambipolar behavior of OFET.

XRR curves recorded from the deposited films are displayed in Figure 4.6. It can be noted that the critical angles (Θ_c) for the PMMA: Ta_2O_5 based dielectric films at 0 wt% and 50 wt% concentrations of Ta_2O_5 are different, thus proving change in concentration of Ta_2O_5 . According to simulations of the recorded XRR curves, these critical angle values correspond to mass densities of 0.26 g/cm^3 and 8.19 g/cm^3 for Ta_2O_5 concentrations of 0 wt% and 50 wt%, respectively.

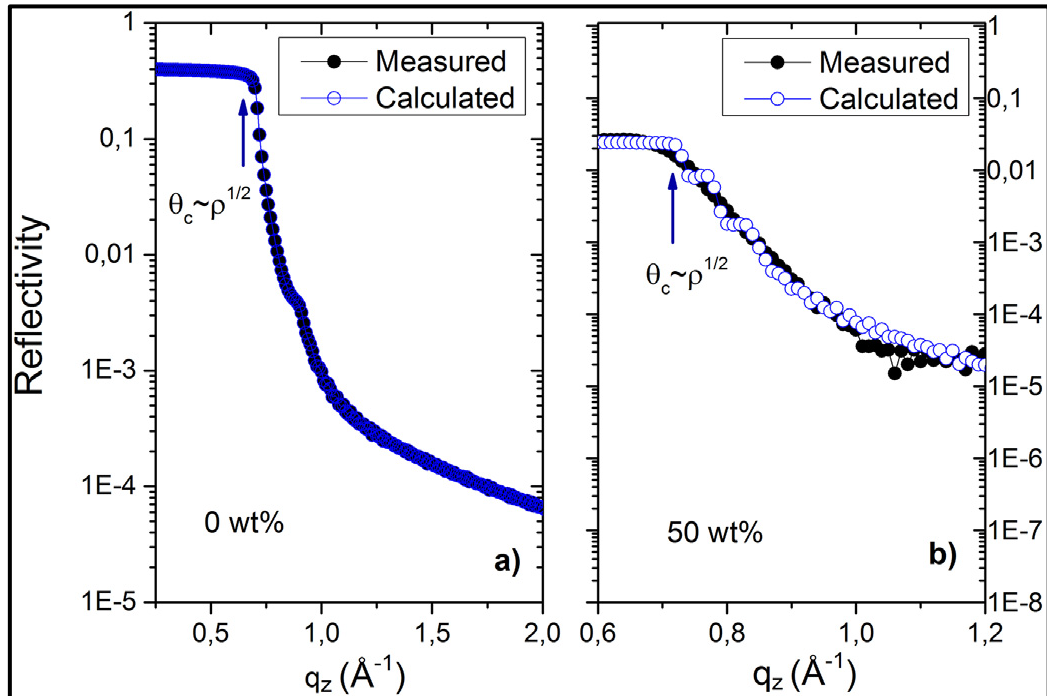


Figure 4.6: XRR curves acquired from PMMA: Ta_2O_5 based dielectric films with Ta_2O_5 concentrations of a) 0 wt% and b) 50 wt%.

Output and transfer I-V characteristics of the devices with varying wt/wt concentration of Ta_2O_5 are shown in Figure 4.7 and Figure 4.8, respectively. Drain to

source current (I_{DS}) of the devices was found increase with increase in drain to source voltage (V_{DS}). Gate to source voltage (V_{GS}) showed excellent saturation trend, following the behavior of typical OFETs. The I-V characteristics of the devices processed using 0 and 3 wt% concentration of Ta_2O_5 were found similar to the characteristics of typical p-type field effect transistors as already known for the case of P3HT:PCBM blend based transistors [107]. However, devices based on 7 wt% and higher concentration of Ta_2O_5 followed the behavior of typical ambipolar OFETs. Kinks in the output characteristics of the devices at lower gate to source voltages (as can be seen in Figure 4.7(c-f)) and increase in channel current (I_{DS}) of the devices with positive gate to source voltages (as can be seen in Figure 4.8), confirms ambipolar behavior of the devices [108, 109]. Meric et al. have developed graphene based ambipolar transistors and discussed the reasons of kinks (at lower gate to source voltages) in the I-V curves of the devices with the help of schematic drawings [110]. Recently, Yasin et al. have investigated P3HT:PCBM blends based photo-MESFETs which showed ambipolar properties similar to the investigated devices with 7% and higher wt concentration of Ta_2O_5 nanoparticles [111].

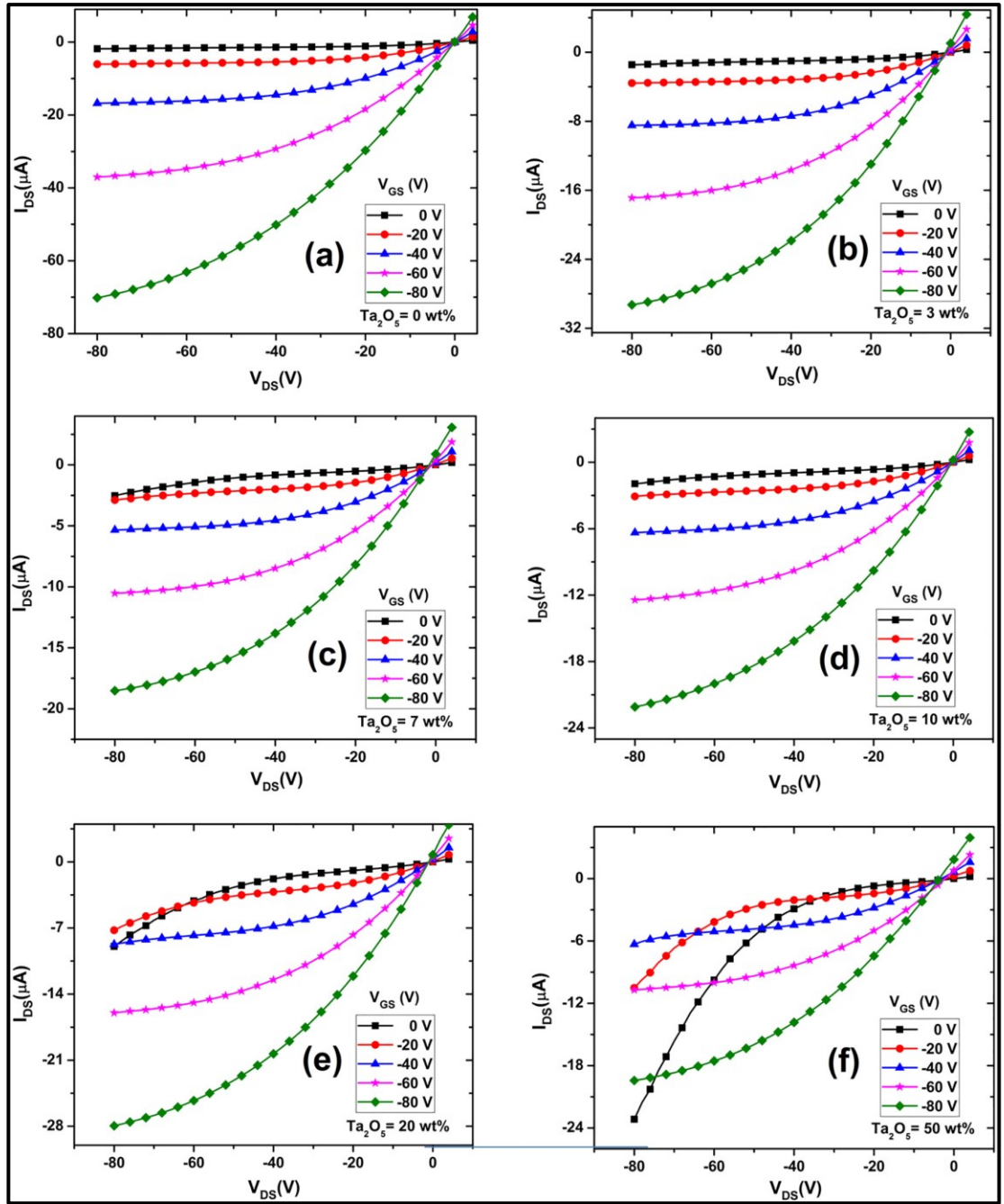


Figure 4.7: Output I-V characteristics of OFETs with PMMA: Ta₂O₅ based dielectric films for different concentrations of Ta₂O₅ changing from 0 wt% to 50 wt%.

In the saturation regime, drain to source current (I_{DS}) of the devices can be determined using following relation [112]:

$$I_{DS} = \frac{\mu W C_i}{2L} (V_{GS} - V_{th})^2 \quad (4.2)$$

where μ is the field effect mobility, C_i is the gate capacitance per unit area, W is the channel width, L is the channel length, V_{GS} is the gate to source voltage and V_{th} is the

threshold voltage. Field effect mobility of the devices in the saturation regime was obtained using following relation:

$$\mu = m^2 \frac{2L}{WC_i} \quad (4.3)$$

which is derived from equation (2). In the above relation, m is the slope of $(I_{DS})^{1/2}$ - V_{GS} curve and C_i is the capacitance per unit area [113].

It was observed that devices processed using 0 wt% and 3 wt% concentration of Ta_2O_5 followed the behavior of typical p-type OFETs with hole mobility of 2.68×10^{-3} and $3.42 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively. Whereas devices realized using 7 wt% and higher concentration of Ta_2O_5 showed electron mobility in addition to hole mobility indicating ambipolar behavior of the semiconducting layers. It was also noted that electron mobility increases with increase in the concentration of Ta_2O_5 . The hole and electron mobility values were found to be equal to 1.08×10^{-3} and $4.42 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 50% wt concentration of Ta_2O_5 , respectively.

4.4. Conclusion

In conclusion, solution processed P3HT:PCBM bulk hetero-junction based OFETs, having dielectric layer of PMMA: Ta_2O_5 nanocomposites with varying concentration of Ta_2O_5 , were successfully fabricated. The devices with 0 wt% and 3 wt% concentration of Ta_2O_5 exhibited p-type OFETs characteristics. However, devices processed with 7, 10, 20 and 50 wt% concentration of Ta_2O_5 showed ambipolar behavior with increasing trend of n-type conductivity. The hole mobility which is equal to $2.68 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 0 wt% concentration of Ta_2O_5 reduces to $1.08 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 50 wt% concentration of Ta_2O_5 . Whereas electron mobility which is negligible compared to hole mobility value at 0 wt% concentration of Ta_2O_5 rises to $4.42 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 50 wt% concentration of Ta_2O_5 . It is pertinent to mention that all the devices showed excellent saturation behavior. We conclude that the fabrication process used to prepare OFET devices is promising due to its simplicity and substrate-

independent nature. Solutions used in this work are also applicable on flexible substrates to realize large area arrays using advanced solution processing techniques such as inkjet printing. It is expected that such devices can be utilized for some industrial applications in near future with promising results and ease of processing.

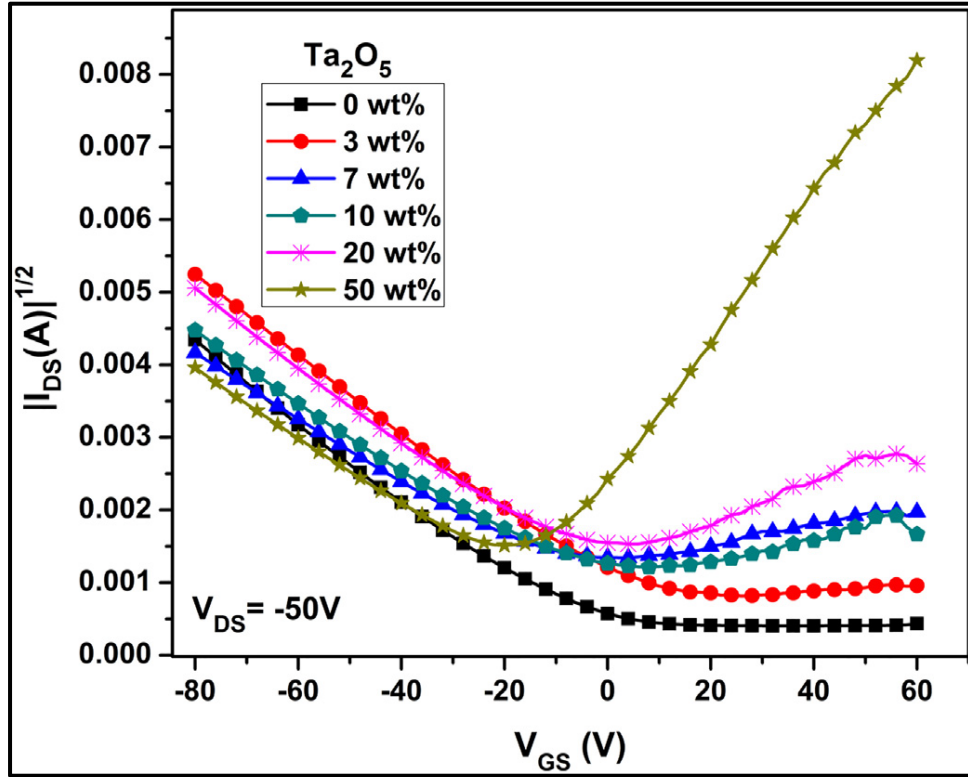


Figure 4.8: Transfer I-V characteristics of OFETs with PMMA: Ta₂O₅ based dielectric films for different concentrations of Ta₂O₅ changing from 0 wt% to 50 wt%.

5. MEDIUM BAND GAP POLYMER BASED SOLUTION PROCESSABLE HIGH DIELECTRIC CONSTANT COMPOSITE GATE INSULATORS FOR ORGANIC FIELD EFFECT TRANSISTORS²

5.1. Introduction

Organic field-effect transistors (OFETs) have advanced rapidly in recent years due to their potential applications in large-area, low-cost, flexible and printed electronics such as *e*-paper, radio-frequency identification (RFID) tags, smart cards, and biosensors [114]. For a better OFET performance, gate capacitance is one of the most important parameters that determines the charge density to be induced. One of the way to increase the capacitance is to use a high dielectric constant (κ) inorganic dielectric material, such as tantalum (V) oxide, barium titanate, barium strontium titanate etc. which were used to reduce operating and threshold voltages [115]. Higher gate capacitance enables trap states to be filled at much lower gate voltages, thus enabling higher mobility due to large number of free charge carriers induced in the channel [116].

Polymeric OFET insulators (e.g. poly (methyl methacrylate), poly-4-vinylphenol, polyvinyl alcohol, etc.), which are solution processable and have low dielectric constant (κ), have to be fairly thick to avoid pinholes [117-119]. Metal oxides (Gd_2O_3 , Al_2O_3 , Ta_2O_5 , etc.) have higher dielectric constants than those of polymers, but their vacuum evaporation or atomic layer deposition processes are rather expensive and time-consuming [120-122]. Additionally, the high processing temperature required for metal oxides is not compatible with roll-to-roll manufacturing of OFETs and the flexible polymeric substrates which are used in printed electronics [123]. To overcome these handicaps, it was proposed to combine the desirable properties of high- κ metal oxides and polymeric dielectrics such as PVP, PS, PVA, etc. [16, 124-127].

² This chapter has been submitted as B. Canımkuşbey, H. Unay, Ç. Çakırlar, S. Büyükköse, A. Çırpan, S. Berber, E. Altürk Parlak “Medium Band Gap Polymer Based Solution Processable High Dielectric Constant Composite Gate Insulators for Organic Field Effect Transistors”, Journal of Polymer Science Part B: Polymer Physics, (2017).

Deposition of the hybrid inorganic-organic dielectric layer can be achieved directly with dispersion of inorganic nanoparticles in a polymer matrix [125]. Recently, high- κ barium titanate nanoparticles were used as the nanocomposite gate insulator for solution processable, high quality, and low leakage current OFETs [128]. Titanium dioxide was also used as the nanocomposite high- κ dielectric for low voltage top-gate OFETs [129].

Ambipolar OFETs are needed in fabrication of inverters and logic circuits for digital electronics, in which both electrons and holes exist depending on the applied gate voltage [130]. To achieve an ambipolar OFET behavior, bilayer structures of n-type and p-type semiconductor layers or their mixtures are used [82]. In addition, there are some reports on ambipolar OFET devices that have source/drain electrodes with different work functions and one type semiconducting material in the accumulation channel of the OFETs [83]. Another successful approach is using only Au as the source/drain electrode with a spin-coated PVA film as the gate dielectrics. Takebayashi et al. have demonstrated ambipolar behavior using Au source-drain electrode on the pentacene active layer [86]. In their work, it has been considered that Na^+ ions in PVA modify the injection barrier in Au/pentacene interface. An enhancement of hole transport and injection for an n-type dominant polymer was also reported by using a fluorinated high- κ dielectric [131]. Impurities and dopants in the active layer act as traps for one type of the charge carriers. For example, oxygen plays a role as a p-type dopant for most of the organic semiconductors by suppressing conduction of electrons and yielding mobile holes [94, 95].

In this work, a solution processed high- κ tantalum pentoxide (Ta_2O_5): PMMA nanocomposite material was used as the dielectric layer. As an active layer P-SBTBDT material, known as a low band gap and high hole mobility semiconductor, was used [57]. Top-gated OFETs were fabricated on an interdigitated ITO coated glass substrate. The fabricated OFETs exhibited high field-induced current and air-stable ambipolar behavior with relatively high hole and electron mobilities. In addition, dielectric properties of Ta_2O_5 :PMMA nanocomposite films were investigated. Relatively high dielectric constant ($\kappa \sim 5.3$) was obtained with the 50 wt.% Ta_2O_5 :PMMA nanocomposite film.

5.2 Experimental Details

Poly (methyl methacrylate) (PMMA) ($M_w = 350,000$), tantalum pentoxide (Ta_2O_5) and butyl acetate were purchased from Sigma Aldrich. Pre-patterned substrates with interdigitated finger electrodes having channel dimensions of 30mm (W) $\times$ $50\mu\text{m}$ (L) were purchased from Ossila. Poly(selenophene, benzotriazole and dialkoxy substituted [1,2-b:4, 5-b'] dithiophene (P-SBTBDT) were synthesized using the method reported previously [57] (Figure 5.1), and dissolved in 1,2 dichlorobenzene (10 mg/ml) at 50°C using stirring process. Approximately 150 nm thick P-SBTBDT semiconducting layer was spin coated on the interdigitated ITO electrodes on glass substrates, and annealed at 110°C for 30 minutes on a hot plate. PMMA and Ta_2O_5 (inorganic particles with diameter $<20\mu\text{m}$) were dissolved in 1 ml butyl acetate at 0 wt.%, 3 wt.%, 7 wt.%, 10 wt.%, 20 wt.%, 50 wt.% of Ta_2O_5 particles in PMMA and stirred for 1 day at room temperature until homogenous solution was obtained. To promote uniform dispersion of particles, the particle suspensions were also ultrasonicated for 2 h. Ta_2O_5 :PMMA dielectric layer with a thickness of about 800 nm was spin coated on the active layer.

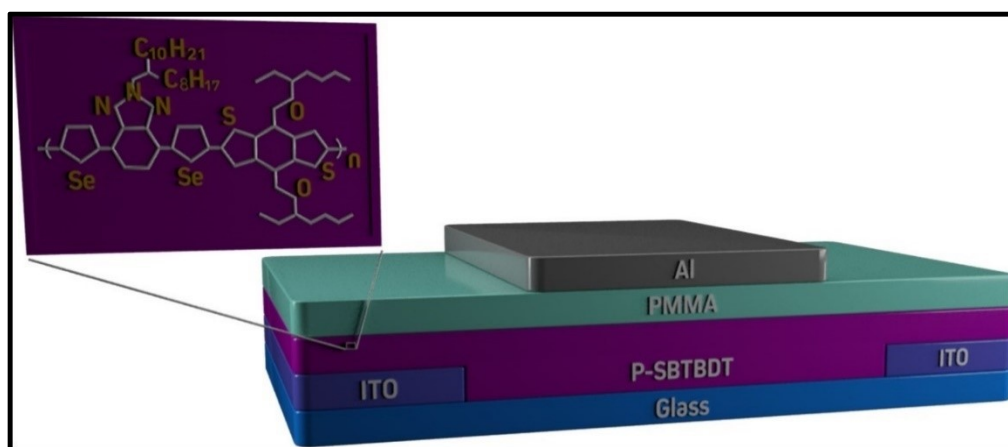


Figure 5.1: A schematic illustration of OFET devices and chemical structure of P-SBTBDT.

Finally, aluminum was evaporated on dielectric layer as a top-gate contact. Dielectric properties of Ta_2O_5 :PMMA composites were analyzed in the 100 Hz to 15 MHz range with metal-insulator-semiconductor (MIS) structures using Hewlett-Packard (4194A) impedance/gain-phase analyzer. Temperature dependence of the AC

conductivity was measured at 100 Hz over the temperature range between 303 K and 383 K. Figure 1 schematically describes the device structure. Electrical characterization of the fabricated OFETs was carried out using Keithley 4200-SCS at room temperature. Surface profiles of pure PMMA and Ta₂O₅:PMMA composite films were analyzed by using Scanning Electron Microscope (SEM) (Philips XL 30 SFEG) and Atomic Force Microscope (AFM).

5.3 Results and Discussion

Figure 5.2 shows frequency dependent electrical conductivity between 100 Hz and 15 MHz. Electrical conductivity increases with increasing content of Ta₂O₅ filler. The inset shows zoomed area in low frequency region. This increment in conductivity can be attributed to increase in number of charge carriers supplied by Ta₂O₅ filler [102, 103]. Additionally, there is a correlation between conductivity and activation energy [132].

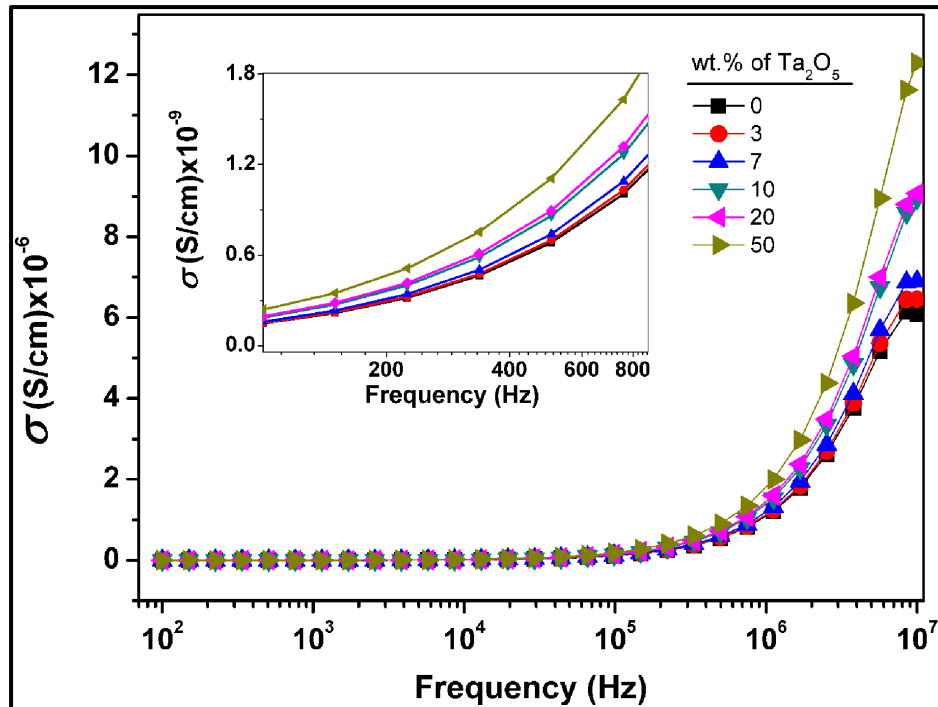


Figure 5.2: Variations of conductivity with respect to frequency for Ta₂O₅:PMMA based dielectric films with varying concentrations of Ta₂O₅. The inset figure displays the extended graph for low frequency region.

Activation energy can be calculated experimentally by using following formula [133],

$$\sigma = A \exp(-E_a/K_b T) \quad (5.1)$$

is the conductivity, A is the pre-exponential factor of conductivity, Kb is the Boltzmann constant, T is the temperature, and Ea is the activation energy.

Figure 5.3(a) shows temperature dependent conductivity. The activation energy E_a was evaluated from the linear fit of $1/T$ vs $\ln \sigma$ graph according to Equation 5.1 and filler ratio dependent E_a is given in Figure 5.3(b). It is clear from figure that activation energy value decreases with increasing the Ta_2O_5 concentration. The addition of Ta_2O_5 inorganic particle to PMMA matrix enhances the electrical conduction of PMMA due to the electronic and impurity contributions arising from the Ta_2O_5 particle.

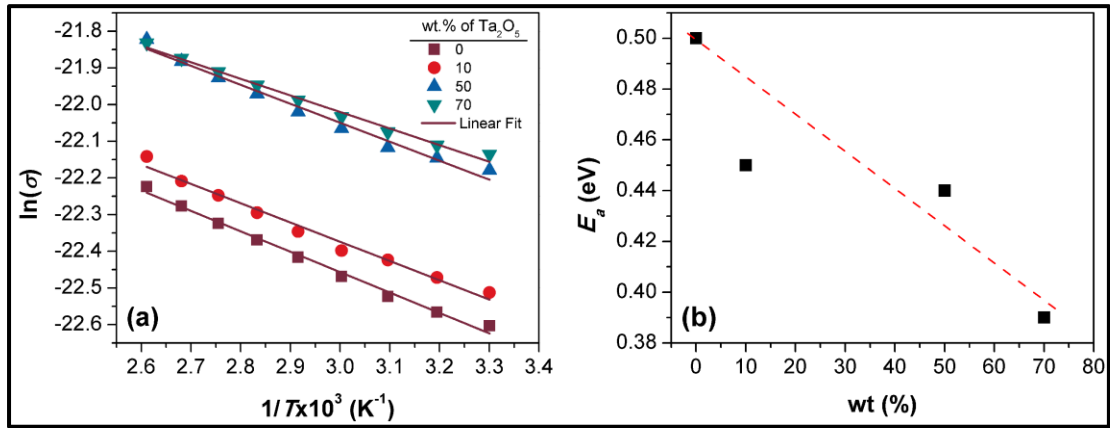


Figure 5.3: a) Temperature dependence of the conductivity σ plotted as $\ln(\sigma)$ versus $1/T$. b) The E_a activation energies obtained from the linear fits in a) for the filling ratios of 0, 10, 50, 70 wt. %.

Graphs indicate that a significant reduction in activation energy for the AC conductivity in the composite materials is achieved. Activation energy profile for AC conductivity of the composite concentrations shows that E_a levels are drastically reduced. Our results, showing that the incorporation of the additive significantly reduces the E_a for the AC conductivity of the composites, compared to the pure PMMA, are well match with the literature [134].

Cole-Cole plots for different concentration of Ta₂O₅ given in Figure 5.4 indicate depressed semicircles. The origin of the semicircular loops at lower frequencies (the right side of the ϵ' axis) is the electrode polarization at samples [135].

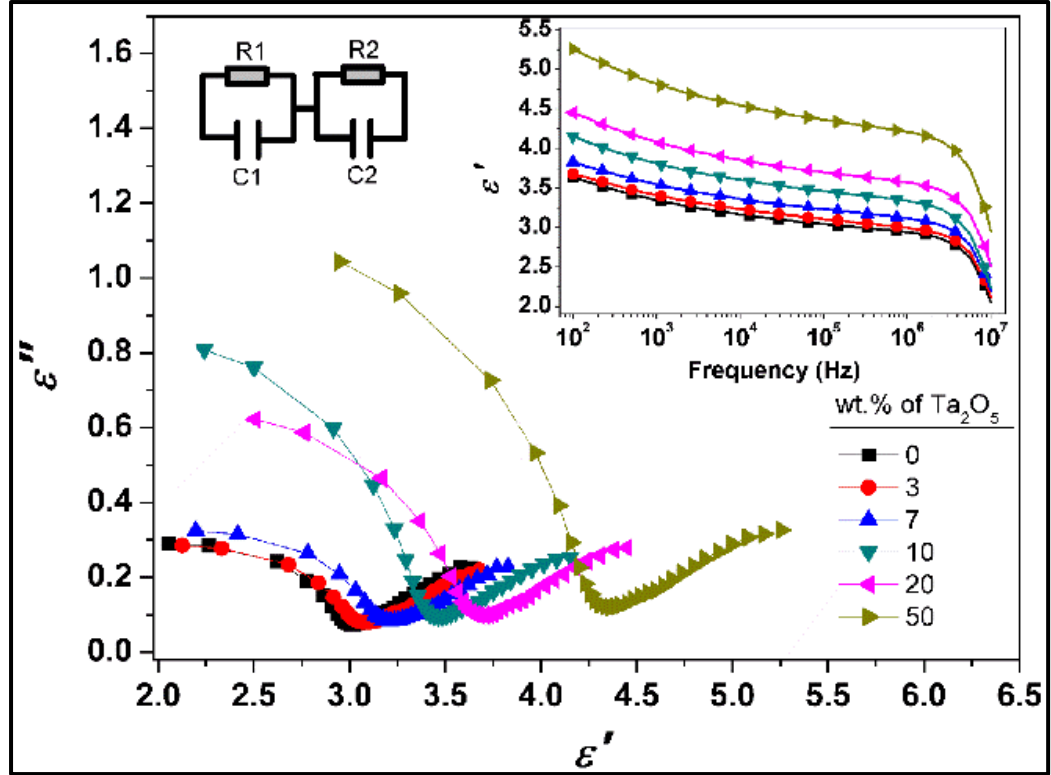


Figure 5.4: Cole-Cole plots of dielectric constants for PMMA:Ta₂O₅ based nanocomposite dielectric films with varying concentrations of Ta₂O₅. The inset figure on the right shows the frequency dependent real part of permittivity. The inset figure on the left side shows the equivalent circuit of nanocomposite thin films.

The second loops indicate bulk property of the samples [136]. Our Cole-Cole plots reveal that a non-Debye type relaxation mechanism is dominant in the system. Equivalent circuit model analysis of the Cole-Cole plots shows serial connection of two parallel Resistance-Capacitance (RC) circuit elements for the investigated samples. The inset in Figure 5.4 demonstrates that static dielectric constants measured at 100 Hz increase with increasing concentration of Ta₂O₅. The obtained dielectric constant value (3.6) for PMMA films is in very good agreement with the literature [137]. Presence of Ta₂O₅ strongly provides in both electron and hole accumulation, while PMMA film shows preferential electron accumulation as known[100].

The increment of frequency dependent dielectric constant due to the increase of filler ratio is evidently seen in Figure 5.4 inset. This behavior is explained by the

presence of higher permittivity metal oxide nanoparticles and the interfacial Maxwell-Wagner polarization of the polymer matrix and filler [138]. Shift in Cole-Cole plots of nanocomposites with different percentage of Ta_2O_5 points out the increment of dielectric constant with the increasing filler ratio [139]. Increasing filler ratio is a source of rise in oxygen vacancies. Each oxygen vacancy, which is the most dominant type of defect in Ta_2O_5 , offers dangling bonds and donates two electrons close to the vacancy location[105]. The dangling bonds result in electronic states within the band gap. These electronic states may trap excited electrons, creating many trap levels within the band gap of Ta_2O_5 . Consequently, the presence of oxygen vacancies is expected to make Ta_2O_5 an n-type semiconductor [106]. On the other hand, the increment with source of charge carriers pave the way for ambipolar behavior of OFET.

Scanning Electron Microscopy (SEM) showed surface morphology and micro structural features of Ta_2O_5 :PMMA based dielectric films with varying wt.% concentrations of Ta_2O_5 particles in Figure 5.5 SEM images of dielectric film with 0 wt.% of Ta_2O_5 shows a smooth surface. As wt.% concentration of Ta_2O_5 increases in PMMA solution processed dielectric films, the incorporation of more and more Ta_2O_5 nano-particles with varying sizes is noted in the microstructure of PMMA. It could be seen that the Ta_2O_5 particles were tended to agglomerate on the films randomly.

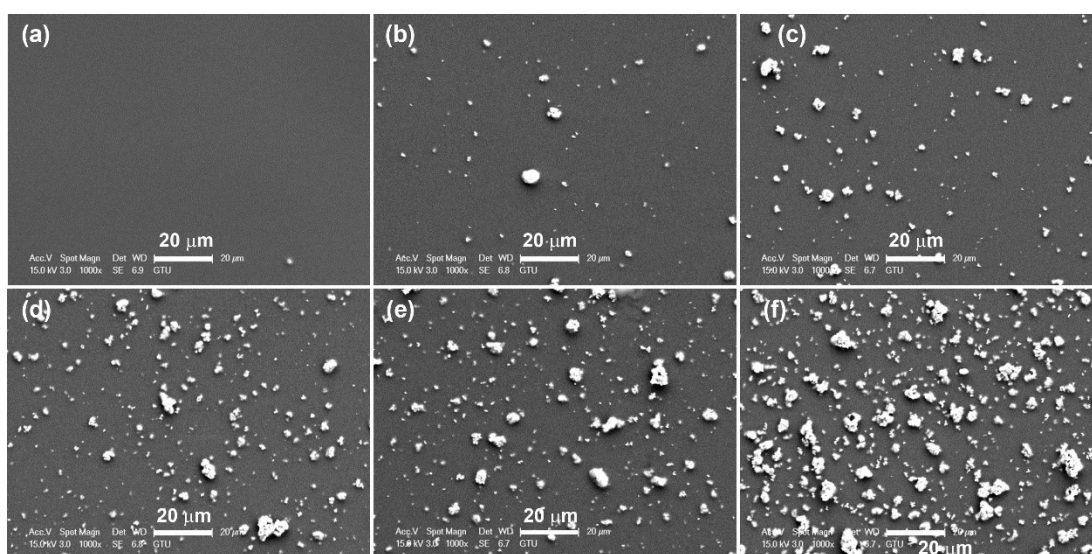


Figure 5.5: SEM images for the surfaces of PMMA: Ta_2O_5 based dielectric films with a) 0 wt.%, b) 3 wt.%, c) 7 wt.% d) 10 wt.%, e) 20 wt.% and f) 50 wt.% concentrations of Ta_2O_5 .

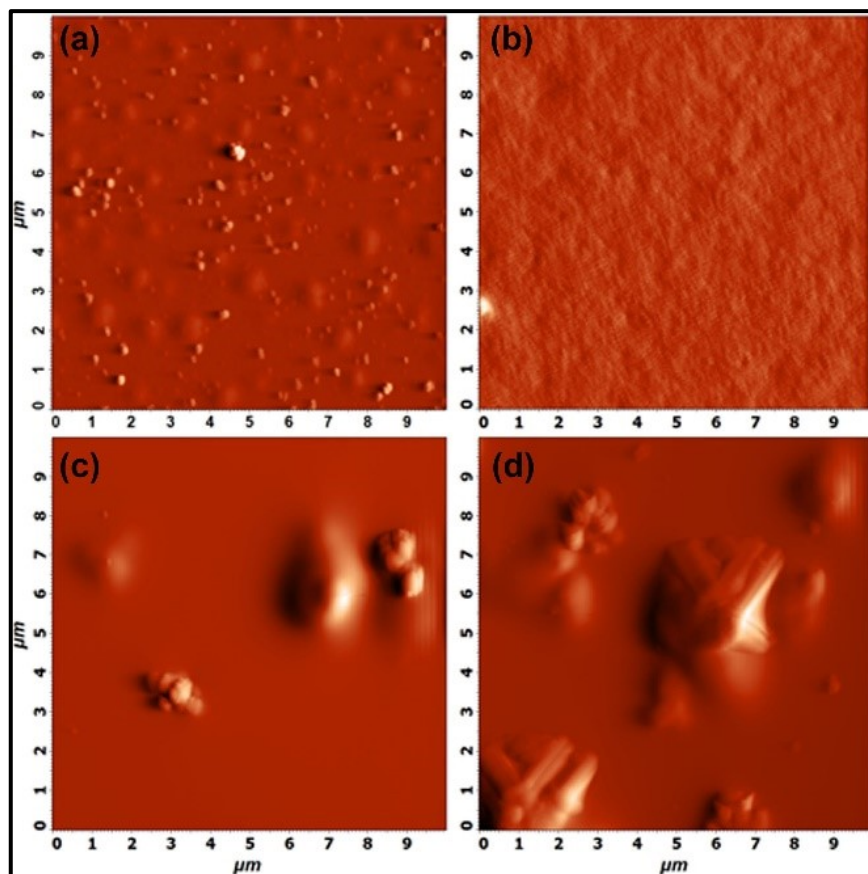


Figure 5.6: AFM images taken from the surface of (a) P-SBTBDT, (b) PMMA:Ta₂O₅ based dielectric films with 0 wt.%, (c) 10 wt.% and (d) 50 wt.% concentrations of Ta₂O₅.

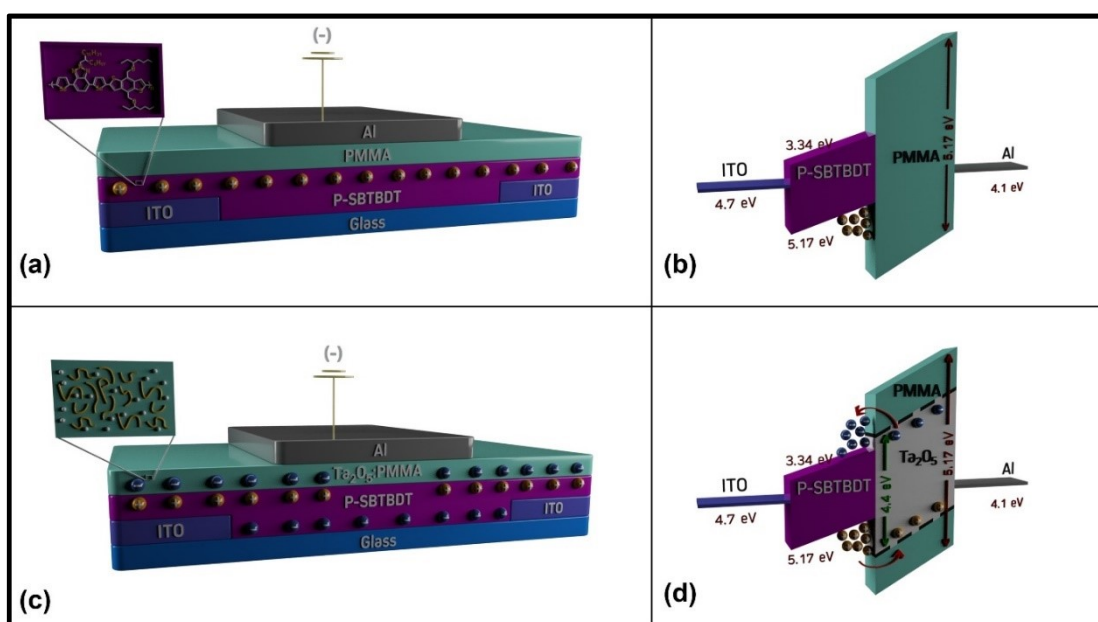


Figure 5.7: Schematic view of OFET devices are on the left (a,c), and the corresponding energy level diagrams are on the right (b,d).

The structure of a top-gate OFET comprises ITO source/drain electrodes, P-SBTBDT semiconductor layer, PMMA dielectric layer and Al gate electrode. By applying negative gate voltage, positive charges are accumulated and confined at the interface between P-SBTBDT and PMMA layer forming a conductive channel (see Figure 5.7 (a,c)). Energy level diagrams for OFET devices are illustrated in Figure 7(b,d).

Output characteristics of the OFET devices can be seen in Figure 8(a) and (b) for 0wt% and 50wt% concentration of Ta₂O₅, respectively. In semiconductor channel n type charge carriers are dominant up to -60 V_{GS} voltage. Then positive charge carriers are accumulated in semiconductor for higher voltages. This behavior can be explained by the oxygen vacancies of [140]. These vacancies donate electrons with the presence of dangling bonds, cause electronic states within the bandgap. Electronic states are able to trap excited electrons, creating many trap levels within the bandgap of Ta₂O₅. We propose that Ta₂O₅ particles located at the PMMA/P-SBTBDT interface determine the accumulation mode of OFET due to these trap levels.

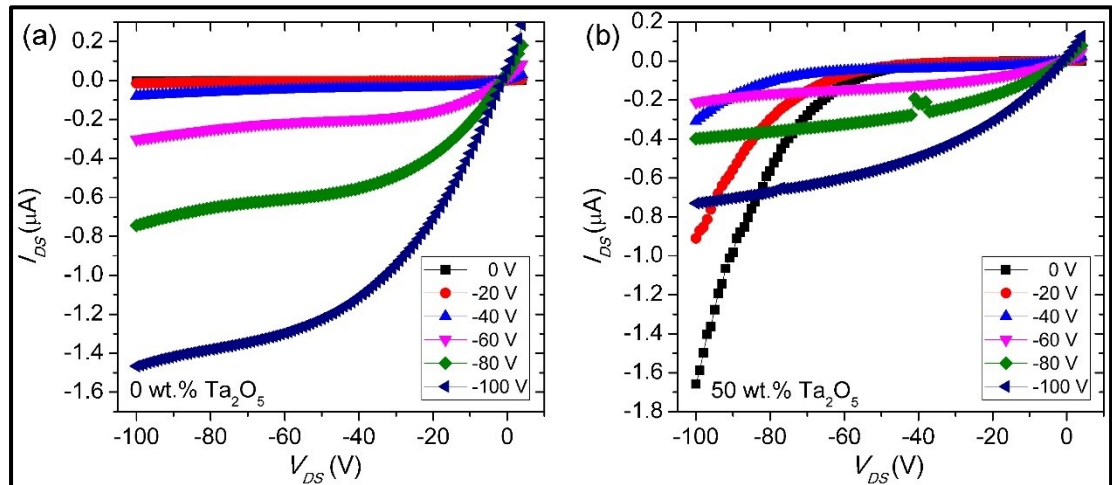


Figure 5.8: Output I-V characteristics of OFETs having semiconducting layer of P-SBTBDT and dielectric films of PMMA:Ta₂O₅ with (a) 0 wt.% and (b) 50 wt.% concentration of Ta₂O₅.

Transfer characteristics of the devices with 0 wt.% and 50 wt.% concentration of Ta₂O₅ are shown in Figure 5.9. Drain to source current (I_{DS}) of the devices was found to increase with increase in drain to source voltage (V_{DS}) and gate to source

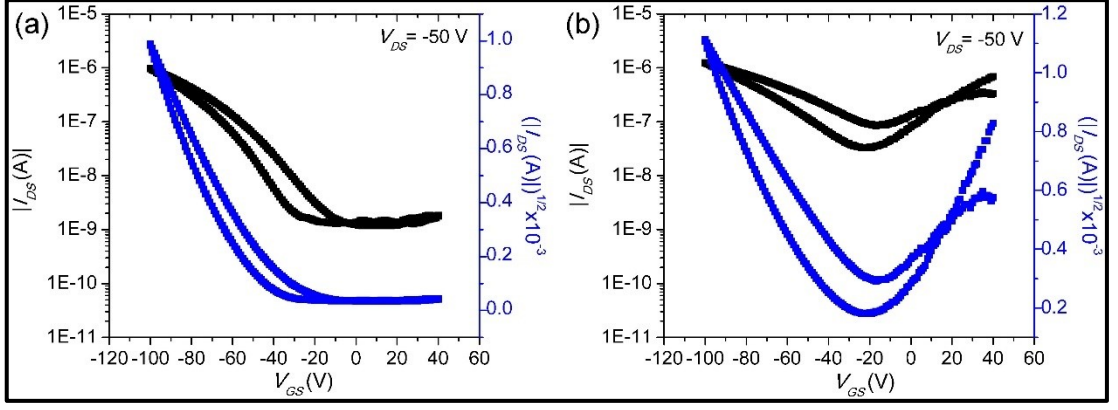


Figure 5.9: Transfer characteristics of the devices with (a) 0 wt. % and (b) 50 wt.% concentration of Ta₂O₅.

voltage (V_{GS}) with excellent saturation trend, following the behavior of typical OFETs (Figure 5.9 (a)). Although not shown in Figure 5.9, the I-V characteristics of the

devices processed using 0 wt.% and 3 wt.% concentration of Ta₂O₅ were found to be similar to the characteristics of a typical p-type field effect transistor. However, devices with 7 wt.% and higher concentration of Ta₂O₅ followed the behavior of typical ambipolar OFETs. Kinks in the output characteristics of the devices at lower gate voltages and increase in channel current (I_{DS}) of the devices with negative gate voltages confirm ambipolar behavior of the devices [108, 109]. In our previous work, we have investigated P3HT:PCBM performance as the active layer of OFETs with Ta₂O₅:PMMA blends and observed ambipolar properties similar to the investigated devices with 7 wt.% and higher concentration of Ta₂O₅ nanoparticles [141].

In the saturation regime, I_{DS} of the devices can be determined using following relation [112]:

$$I_{DS} = \frac{\mu W C_i}{2L} (V_{GS} - V_{th})^2 \quad (4.2)$$

where μ is the field effect mobility, C_i is the gate capacitance per unit area, W is the channel width, L is the channel length, V_{GS} is the gate voltage and V_{th} is the threshold voltage. Field effect mobility of the devices in the saturation regime is obtained using following relation which is derived from Equation 4.3:

$$\mu = m^2 \frac{2L}{WC_i} \quad (4.3)$$

where m is the slope of $(I_{DS})^{1/2}$ - V_{GS} curve.

It was observed that devices processed using 0 wt.% and 3 wt.% concentrations of Ta_2O_5 followed the behavior of typical p-type OFETs with hole mobility of $\sim 0.39 \times 10^{-3}$ and $\sim 0.37 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively. Whereas devices with 7 wt.% and higher concentration of Ta_2O_5 showed electron mobility in addition to hole mobility indicating ambipolar behavior of the semiconducting layers. It was also found that electron mobility increases with increase in the concentration of Ta_2O_5 . Mobility values together with other important parameters of devices can be seen in Table 1. The hole and electron mobility values were found to be equal to $\sim 0.30 \times 10^{-3}$ and $\sim 1.41 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 70 wt.% concentration of Ta_2O_5 , respectively.

Table 5.2: OFET characteristics and effective capacitances for the different wt/wt ratio of Ta_2O_5 : PMMA films in ambient condition.

Ta_2O_5 concentration (wt.%)	$\mu_{\max}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-3}$	V_{th} (V)	$I_{on/off}$ (A)	ϵ_{eff}	C (nF/cm^2)
0 (Pure PMMA)	$\mu_h=0.39$ $\mu_e= -$	$V_{th(h+)}=42$ $V_{th(e-)}= -$	$\sim 10^2$ - 10^3	3.63	0.93
3	$\mu_h=0.37$ $\mu_e= -$	$V_{th(h+)}=34$ $V_{th(e-)}= -$	$\sim 10^2$ - 10^3	3.68	0.78
7	$\mu_h=0.37$ $\mu_e= -$	$V_{th(h+)}=34$ $V_{th(e-)}= -$	$\sim 10^2$ - 10^3	3.83	0.82
10	$\mu_h=0.36$ $\mu_e=1.34$	$V_{th(h+)}=34$ $V_{th(e-)}=8.5$	$\sim 10^2$ - 10^3	4.32	1.47
20	$\mu_h=0.32$ $\mu_e=1.37$	$V_{th(h+)}=34$ $V_{th(e-)}=8.5$	$\sim 10^2$ - 10^3	4.45	1.35
50	$\mu_h=0.30$ $\mu_e=1.41$	$V_{th(h+)}=34$ $V_{th(e-)}=8.5$	$\sim 10^2$ - 10^3	5.26	1.60

5.4 Conclusion

In summary, we have fabricated solution processed P-SBTBDT organic semiconductor based OFETs, using dielectric layer of Ta_2O_5 :PMMA nanocomposites

with varying concentration of Ta₂O₅. Fabricated OFETs with 0 wt.% and 3 wt.% concentrations of Ta₂O₅ exhibited p-type behavior while the rest of the devices demonstrated ambipolar behavior with an increasing trend of n-type conductivity with the increasing concentration of Ta₂O₅. Hole mobility reduces with increase in concentration of Ta₂O₅. Whereas electron mobility is raised to $4.42 \times 10^{-3} \text{ cm}^2/\text{Vs}$ at 50 wt.% concentration of Ta₂O₅. All the devices showed excellent saturation behavior. Broadband dielectric analysis revealed that the nanocomposites with higher concentration not only showed increment in dielectric constants, but also a rise in conductivity due to the increment of charge carriers. We conclude that solutions used in this work are also applicable on flexible substrates to fabricate large area arrays. It is pertinent to mention that such devices can be utilized for some industrial applications in near future.[82]

6. SOLUTION PROCESSABLE HIGH DIELECTRIC CONSTANT NANOCOMPOSITES BASED ON Al₂O₃ NANOPARTICLES FOR ORGANIC FIELD EFFECT TRANSISTORS

The dielectric properties and AC electrical conductivity of Pure PVA and Al₂O₃ nanoparticle doped PVA films were analyzed by HP 4194A Impedance Analyzer within the frequency range of 100 Hz– 15 MHz at room temperature. The complex dielectric constant, $\epsilon^*(\omega)$ is defined as,

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) \quad (6.1)$$

where $\epsilon'(\omega)$ is the real and $\epsilon''(\omega)$ is the imaginary part of the dielectric constant. The angular frequency (ω), referred as the radial frequency; $\omega = 2\pi f$, dependent real part of the dielectric constants was given in Figure 6.1(a).

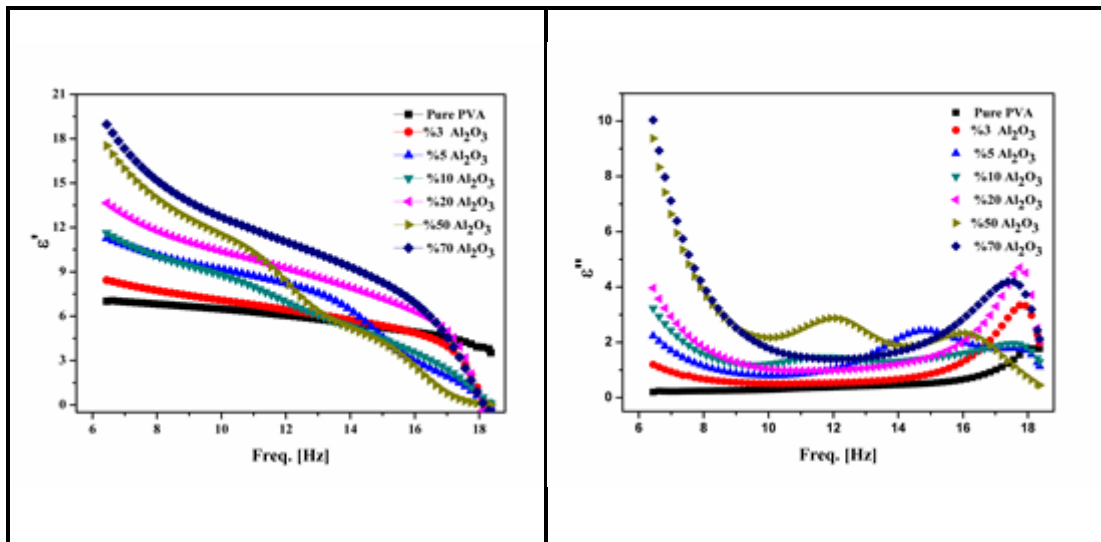


Figure 6.1: Variation of a) real and b) imaginary parts of dielectric constant with frequency for Al₂O₃:PVA nanocomposites with different wt % of Al₂O₃.

The resulting dielectric relaxations are explained by the movement of dipoles (dielectric relaxation) and the existence of free electrical charges (ionic relaxation) due to the presence of electric field. Debye relaxation model is applied to characterize the response of molecules to an applied field. The static dielectric constant of Pure PVA

films were found around 7.5, consistent with the previous work on dielectric measurement of PVA [142]. The increment of dielectric constant is obviously seen in Figure 6.1.a with the increment of Al₂O₃ ratio of the nanocomposite polymer films. PVA is a very stable polymer with its high relaxation frequency in the interval of 100Hz- 15MHz. Interpolation of Al₂O₃ nanoparticle into PVA matrix has modify the dielectric relaxation frequency of pure PVA. The real part of the dielectric constants decreases with increasing frequency. Moreover, some ratio of Al₂O₃ -PVA nanocomposites gives double dielectric relaxation at the same frequency range. The critical frequencies of each polymers are evaluated by getting the maximum of the peaks in dielectric loss graphs, are given in Figure 6.1.b.

The dielectric strength ($\Delta\epsilon=\epsilon_s-\epsilon_\infty$) of each nanocomposite are also given in Table 6.1. Investigated nanocomposites indicates a significant combination of relatively higher and large dielectric strength, yielding a high energy-storage capacity.

Analysis of the dielectric relaxation type of nanocomposites, relaxation time, τ , and absorption coefficient, α , were determined by the fitting dispersion curve obtained from Origin Lab. 8.0. The equation of dispersion curve is represented by Equation 6.2.

$$\epsilon'(\omega) = [\epsilon'_{high\ freq.} + (\epsilon'_{low\ freq.} - \epsilon'_{high\ freq.}) \frac{1 + (\omega\tau)^{1-\alpha} \sin \frac{1}{2}\alpha\tau}{1 + 2(\omega\tau)^{1-\alpha} \sin \frac{1}{2}\alpha\tau + (\omega\tau)^{2(1-\alpha)}}] \quad (6.2)$$

where ϵ_s is the static dielectric constant and ϵ_∞ is the infinite frequency dielectric constant at given frequency range.

The absorption coefficient, α , could take the values from zero to one ($0 < \alpha \leq 1$). When the absorption coefficient equals to zero, it represents to standard Debye type relation. If the α parameter is almost zero this behavior could be defined as nearly Debye type relation. The non-Debye type occurs when the value of absorption coefficient varies between; $0 < \alpha < 1$ region.

The absorption coefficient and the relaxation frequencies obtained by fitted curves and given in Table 6.1. It is seen that the fitting results of relaxation frequency is and the critical frequency values are almost same. The investigation of α parameters indicates non- Debye type relaxation phenomena is occurred with all weight ratios of the nanocomposite polymers.

Table 6.1: Dielectric Parameters of Al₂O₃:PVA nanocomposites.

	%3	%5	%10	%20	%50	%70
$\Delta\epsilon$	7.2365	10.0066	10.4017	11.5464	16.4663	17.2894
τ_1	9.79×10^{-7}	5.22×10^{-5}	4.82×10^{-4}	2×10^{-3}	5.84×10^{-4}	3×10^{-3}
τ_2	-	4.05×10^{-7}	7.09×10^{-7}	6.02×10^{-7}	1.76×10^{-6}	1.09×10^{-6}
f_{c1}	0.10×10^{-7}	2.35×10^{-5}	4.00×10^{-5}	-	3.50×10^{-4}	-
f_{c2}	-	1.2×10^{-7}	1.50×10^{-7}	1.20×10^{-7}	6.90×10^{-6}	1.7×10^{-6}
α_1	0.66	0.57	0.41	0.12	0.44	0.04
α_2	-	0.19	0.34	0.44	0.29	0.49

Dielectric relaxation mechanism of nanocomposite films was also investigated by Cole–Cole plots given in Figure 6.2. Cole–Cole plots are represented by plotting the real component of dielectric constant, ϵ' to the imaginary component of dielectric constant, ϵ'' for each frequency. Cole–Cole plots of all nanocomposites demonstrated depressed semi-circle which points non-Debye type behavior. Cole–Cole plots of nanocomposite polymers are well-matched with the absorption coefficient results.

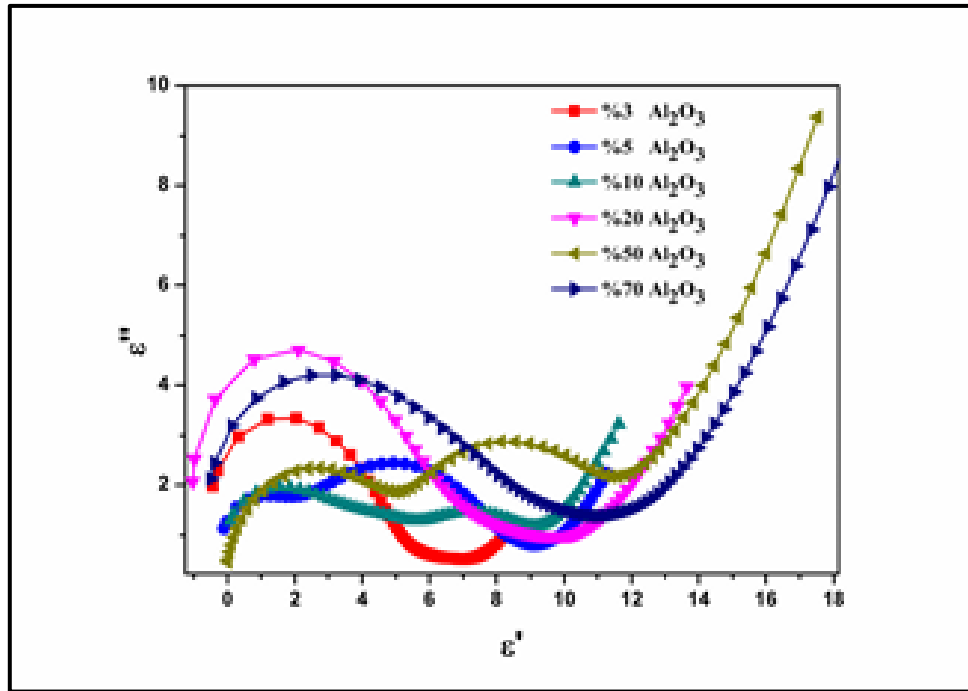


Figure 6.2: Cole-Cole plots of dielectric constants for PVA:Al₂O₃ based nanocomposite dielectric films with varying concentrations of Al₂O₃

Depressed semi-circles are indicating resistive circuit element is parallel to internal capacitor. Additionally, graphs with second circle is representing serial circuit of another R-C circuit. Last tails of the Cole-Cole plots (from the lower frequency range) are due to the serial R element of the equivalent circuit. The presence of a tail on the low frequency side (ie. increasing ϵ_r''), as shown in Figure 6.2, indicates large distribution of relaxation times and is because of the high losses in the nanocomposite. By-products of PVA synthesis are sodium acetate ions, which is the reason of ionic relaxation phenomena in lower frequency range. At the relatively larger frequencies relaxation is due to the dipolar molecules of the nanocomposite films. Almost all nanocomposite polymers are demonstrated the similar Cole- Cole plots. But the nanocomposite with the weight ratio 70% is giving only one semi-circle. This means, increasing the Al_2O_3 ratio in the composite is screening the ionic polarization at the end, where the first loop of Cole-Cole plots is giving the ionic polarization and the seconds are dipolar polarization model.

The graphical representation of AC conductivity versus $\ln(\omega)$ are given in figure 3. The AC conductivity of the Al_2O_3 -PVA films presents the Jonscher universal power-law behavior:

$$\sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s \quad (4.1)$$

where, A is a constant, ω is the angular frequency and s is the frequency exponent parameter which determines AC conduction mechanisms.

The values of parameter s (angular frequency exponent) were calculated from the slopes of $\ln |\sigma|$ versus $\ln(\omega)$ graphs. During the fit slope, linear equation $y=a+b*x$ was used, expressing $b=\ln\omega/\ln \sigma$ with R-Square: ~ 0.99 . The s parameter values can be explicated by conductivity mechanisms for frequency dependent conductivity given by $0 < s < 0.7$ for Correlated Barrier Hopping (CBH) conductivity mechanism, $0.7 \leq s < 1$ for Quantum Mechanical Tunneling (QMT) conductivity mechanism.

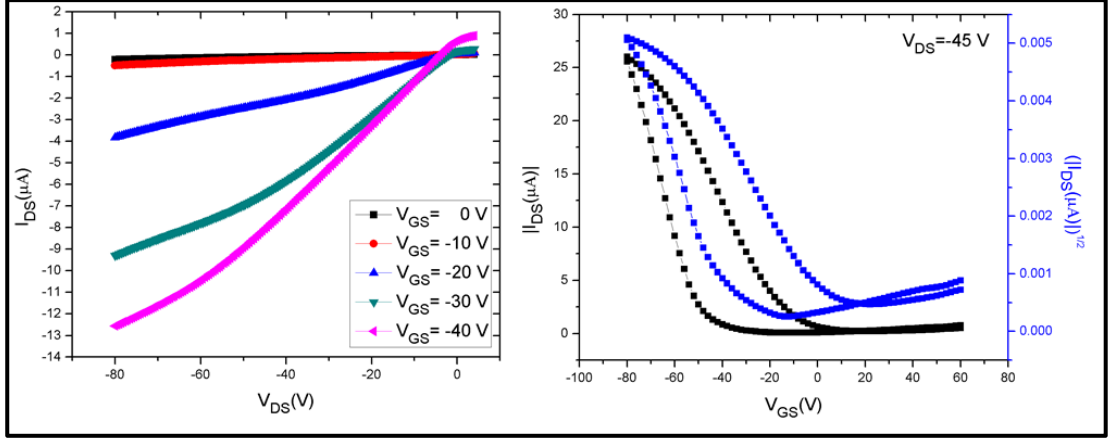


Figure 6.3: Output and transfer I-V characteristics of OFETs with PVA: Al_2O_3 based dielectric films for 0 wt% concentrations of Al_2O_3 .

Output and transfer I-V characteristics of the devices with varying wt/wt concentration of Al_2O_3 are shown in Figure 6.3 and Figure 6.4, respectively. Drain to source current (I_{DS}) of the devices was found increase with increase in drain to source voltage (V_{DS}). It was also found that source/drain current increases with increment in the concentration of Al_2O_3 .

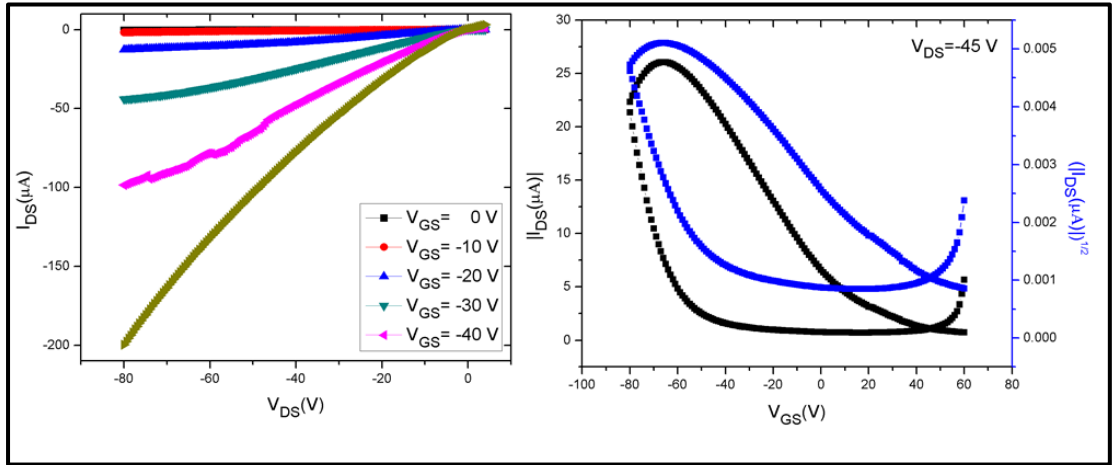


Figure 6.4: Output and transfer I-V characteristics of OFETs with PVA: Al_2O_3 based dielectric films for 50 wt% concentrations of Al_2O_3 .

SEM was used to investigate the surface morphology and micro structural features of PVA: Al_2O_3 based dielectric films at 0 wt% and 50 wt% concentrations of

Al_2O_3 . SEM images of the dielectric film surface and cross-sectional profile of the semiconductor/dielectric interface are shown in Figure 6.5 and Figure 6.6,

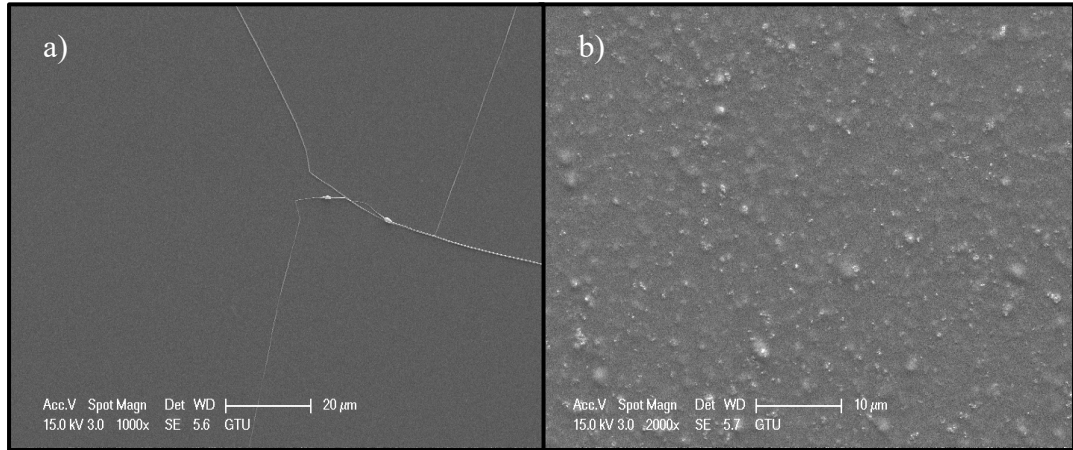


Figure 6.5: SEM images taken from the surface of PVA: Al_2O_3 based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Al_2O_3 .

respectively. As can be seen in the SEM images, agglomeration of Al_2O_3 nanoparticles is noted in PVA dielectric films with the increasing concentration of Al_2O_3 .

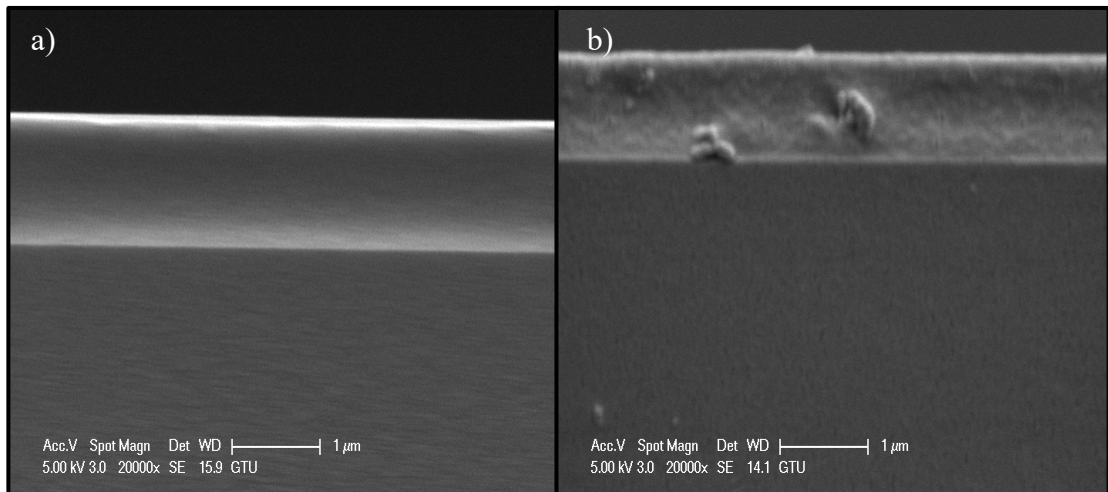


Figure 6.6: Cross-section SEM images of PVA: Al_2O_3 based dielectric films at a) 0 wt% and b) 50 wt% concentrations of Al_2O_3 .

7. EFFECT OF Ta₂O₅ INORGANIC PARTICLES ON POLYMER GEL DIELECTRIC BASED OFET PERFORMANCE³

7.1. Introduction

Organic field effect transistors (OFETs) have been used in many electronic applications such as sensors, electronic papers, radio frequency identification (RFID) tags, smart cards, skins for robotics, and organic active matrix displays due to the provided unique properties like mechanical flexibility, light weight, transparency and low cost [143-145]. Since the performance of OFETs is not enough to take the inorganic counterpart's place, the main trend is to improve the electrical properties of them. In recent years, OFETs have a promising future owing to the performance that has been shown great advance with better material performance property and different device structure studies [146, 147]. CuPc is one of the commonly used materials for OFET's because of its high carrier mobility, self-organizing tendency and large absorption coefficient in the region of visible light. It was presented that CuPc based OFETs worked under low operation voltages, and low threshold voltages [148] by using high boiling point solvent, post thermal treatment and improved gate surface properties. The gate dielectric material has a critical role on not only OFETs performance but also device stability. OFETs should have as low operating voltages as possible, as high field-effect mobility and on/off ratio as possible. Therefore, high specific capacitance of gate dielectric leads to greater induced charges in the active semiconductor layer. Thus, OFETs present high performance and long term stability at lower operating gate voltages, if tailored improvement is satisfied from material point of view. Poly (methyl methacrylate) (PMMA) is a well-known dielectric polymer with low dielectric constant, smooth and hydrophobic surface [149]. Ukah et al. presented that gate material's solvent is strongly dependent on device performance, which is correlated with solvent dipole moment. They obtained stable and low

³ This chapter has been published as Z. A. Kösemen, A. Kösemen, S. Öztürk, B. Canımkuşbey, Y. Yerli, M. Erkövan, "High Mobility and Low Operation Voltage Organic Field Effect Transistors by Using Polymer-Gel Dielectric and Molecular Doping", Solid-State Electronics, (2017).

operating voltage (-3 V) OFETs with PMMA that was dissolved in propylene carbonate (PC), which has a large dipole moment (4.9D at $20\text{ }^{\circ}\text{C}$) high dielectric constant (64.42 at $25\text{ }^{\circ}\text{C}$), low freezing point ($-49\text{ }^{\circ}\text{C}$), and high boiling point ($241\text{ }^{\circ}\text{C}$) [150]. PC has also used as a plasticizer [151], which is important to prepare gel materials. PC settles between the chains of PMMA and keeps them further apart which reduces the forces of attraction between them and makes the material more flexible. The gel has a reduced strength and stiffness compared to PMMA because of the PC.

To get high specific capacitance dielectric (over $10\text{ }\mu\text{F}/\text{cm}^2$), it is very common to use electrolyte for obtaining ion-gel gate dielectric layer for OFETs [152]. Polyelectrolyte as ion gel dielectric was used to fabricate high performance OFET, which operated under 2 V . The device performance presents high field effect mobility and on/off values $\sim 2\text{ cm}^2/(\text{Vs})$ and 10^5 respectively [153]. However, electrolyte based OFETs suffer from long term stability because of the ionic content. In this study, we have proposed to improve the operation voltage and field effect mobility. The non-ionic gel dielectric material was used to induce more charges in the active semiconductor layer near the gate dielectric. In addition to study on this article [148] PMMA dielectric layer is doped with an inorganic dielectric particle. The control device group is made from pure PMMA as dielectric layer and CuPc as active semiconductor layer.

7.2. Experimental Details

Materials were used for preparation of gel purchased commercially from Aldrich; Acetonitrile (ACN), propylene carbonates (PC) and poly (methyl methacrylate) (PMMA). The mixture is 70:20:10 in weight ratio, respectively. PMMA dissolved in ACN at $150\text{ }^{\circ}\text{C}$ and PC was added in the mixture. Mixture was stirred until becoming gel viscosity. In order to incorporate the Ta_2O_5 particles in the gel mixture before the adding PC, Ta_2O_5 particles were added in the ACN solution. Weight ratio of Ta_2O_5 particles to PMMA were arranged as 10%, 30%, 50%, 100%.

Capacitive properties of the polymer gel dielectric analyzed with MIS structure. CuPc was coated on Au coated glass substrate and gel dielectric material sandwiched between CuPc coated electrode and Platinum (Pt) coated ITO electrode. Pt was coated

on ITO from solution by brush and purchased from solaronix. Dielectric measurements of MIS structure were made by HP 4194A dielectric analyzer.

The sandwich type OFET devices were fabricated using interdigitated Au source-drain electrodes on glass and Si wafer substrates. The source-drain electrodes were photo lithographically produced. Source-drain electrodes are configured as interdigitated fingers with a channel length of 50 μm and 100 μm . Figure 7.1 shows that schematic illustration of produced OFET devices.

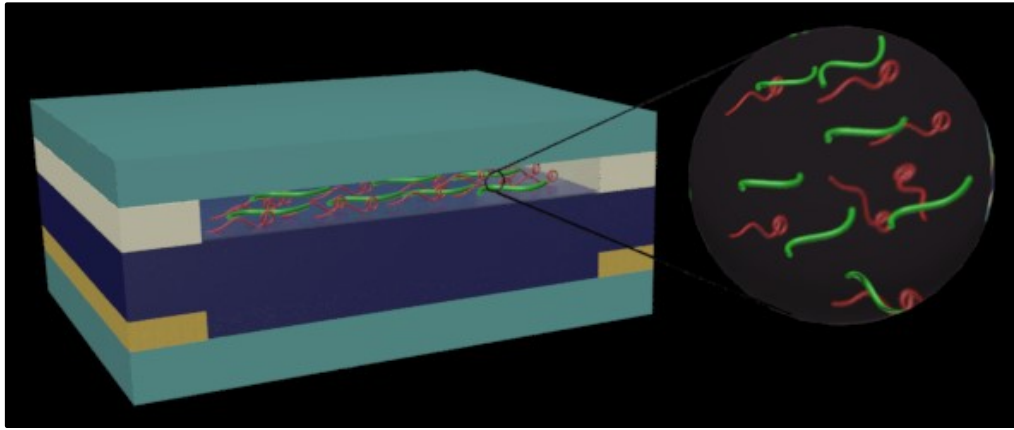


Figure 7.1: Schematic illustration of OFET device.

Cr (5nm) was coated on glass substrate and then Au (100nm) was coated on Cr layer by using thermally evaporation method. Au electrode was etched with photo lithographically method to produce interdigitated source-drain electrode. CuPc was evaporated on Au source-drain electrodes. Polymer gel dielectrics were sandwiched between CuPc coated source- drain electrodes and Pt coated ITO electrodes with 10 μm separator. Pt coated ITO electrode was used as gate electrodes. Output and transfer characteristics of designed OFET's were investigated with Keithley 4200SCS.

7.3 Results and Discussion

Capacitive properties of the PMMA thin film and gel dielectric material are given in the Figure 7.2 at different frequencies. The capacity of gel and PMMA can be extracted from the Figure 7.2 as 43 nF/cm² and 3.9 nF/cm² respectively at 100 Hz [148].

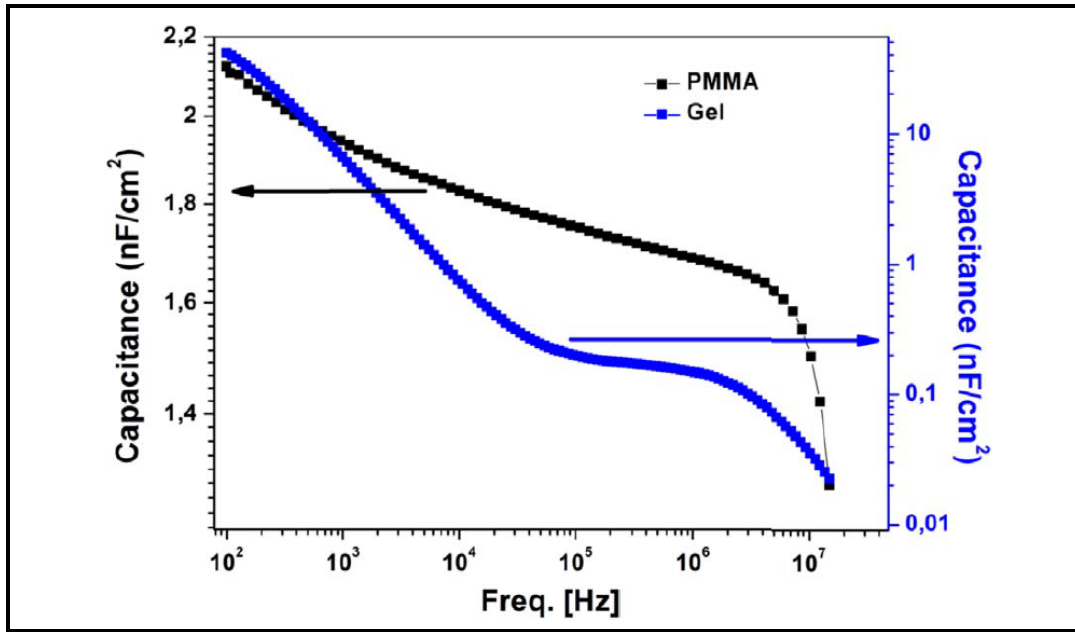


Figure 7.2: Capacitive properties of gel-dielectric material and thin film PMMA at different frequencies.

Although, the capacitance of the gel is decreasing rapidly with increasing frequency until 1000 Hz then stays constant, the capacity of the PMMA is decreasing slowly until 107 Hz. It is clearly seen from the Figure 7.2, capacitive behavior of the PMMA is changed by adding propylene carbonate (PC) into the PMMA. PC is a high- κ and aprotic plasticizer material and behaves as a normal polar liquid with a strong dipole-dipole interaction [154]. This material enters among the PMMA chains and provides gel property. Thus, significant improvement in the dielectric properties by using PC is related to the mean square end-to-end distance which is proposed by Tung et al. [155]. The mean square end-to-end distance increases with an increase in the dipole moment that mainly due to an enhanced interaction of forces between the polymer and the solvent cluster. The capacitance value of the gel dielectric decreases with an increasing frequency, as expected, because the PC polarization in polymer chain of PMMA is limited. Therefore, the total polarization response time is limited at high frequencies. Figure 7.3 a) and b) show the output characteristic of OFET having semiconducting layer of CuPc and dielectric films of gel:Ta₂O₅ with 0 wt.% and 50 wt.% concentration of Ta₂O₅, respectively.

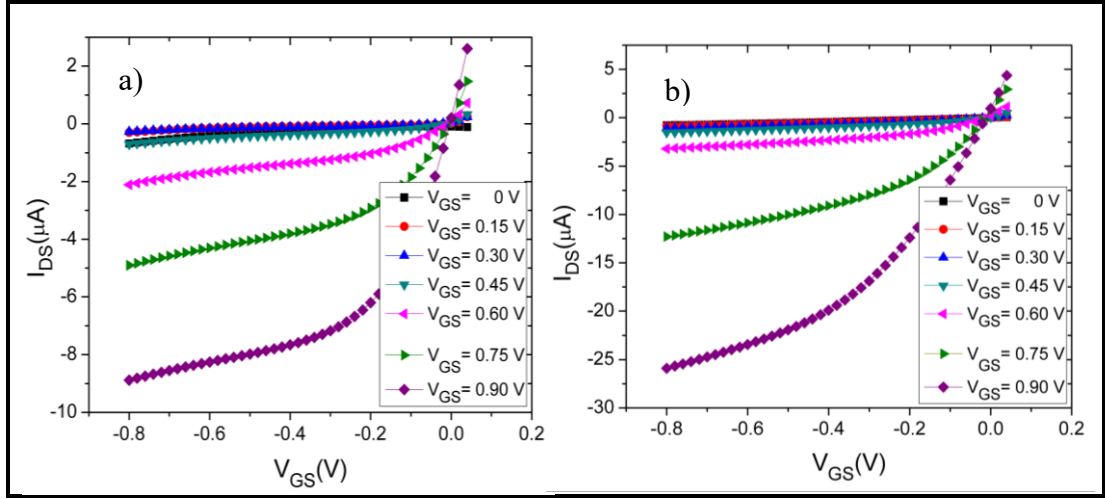


Figure 7.3: Output I-V characteristics of OFETs having semiconducting layer of CuPc and dielectric films of gel:Ta₂O₅ with (a) 0 wt.% and (b) 50 wt.% concentration of Ta₂O₅.

The I-V characteristics of the devices processed using 0 and 50 wt% concentration of Ta₂O₅ were found similar to the characteristics of typical p-type field effect transistors. But drain to source current (I_{DS}) of the devices was found increase with increase in gate to source voltage (V_{GS}), following the behavior of typical OFETs. The I-V characteristics of the devices processed using 0 and 50 wt% concentration of Ta₂O₅ were found similar to the characteristics of typical p-type field effect transistors.

8. SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF GRAPHENE OXIDE FILMS⁴

8.1 Introduction

During the past decade, materials such as fullerenes, nanotubes and graphene were demonstrated as promising candidates for potential applications in electronic industry due to superior electrical and optical properties. Graphene is a two dimensional monolayer of hexagonally arranged sp^2 hybridized carbon atoms [156]. Due to excellent physiochemical, electrical, thermal and mechanical properties, graphene is effectively used in many technological applications such as hydrogen storage, field effect transistor, ultra-capacitors and organic solar cells [157-159]. Graphene can be produced from water soluble graphene oxide using reduction process [160-162].

Graphene oxide (GO) has sp^2 and sp^3 hybridized carbon atoms and can be considered as insulating material compared to graphene. GO exhibits various carboxyl and hydroxyl functional groups and is soluble in water. The electrical properties of GO can be changed by varying the content of oxygen [163], water molecules and impurities [164]. Graphene Oxide (GO) which is reported to be highly sensitive to humidity [165], has been recently investigated/ demonstrated as dielectric & semiconducting material for Thin Film Transistors [166] and efficient hole transport material for Organic Solar Cells [167]. Due to the presence of oxygen based functional networks on the basal plane of GO, it can make bonds with variety of organic and inorganic materials [168-170]. The optical and electrical properties of GO can be enhanced using composites with conductive polymers. Solution processed semiconducting layers based microelectronic devices are preferred over conventional in-organic semiconducting materials based devices due to their low cost, room temperature fabrication and other promising features which include flexibility and potential to develop large area sensing arrays, etc. However, efficiency and response time of these devices is comparatively low. For drastic advancements in this evolving domain and to enhance the performance of

⁴ This chapter has been published as M. Yasin, T. Tauqeer, S. Zaidi, S. E.San, M. Asad, M. E. Köse, B. Canımurbey, M. Okutan, “Synthesis and electrical characterization of Graphene Oxide films”, Thin Solid Films, 590, 118-123, (2015).

devices, one way is to synthesize new materials with desired features and to develop the devices using these newly developed materials. Purpose of this work is to synthesize and investigate temperature dependent transport properties of solution processed Graphene Oxide films in order to explore the possibility of their usage for flexible organic microelectronic devices. Electrical properties of GO were studied using impedance spectroscopy, a well known technique used for similar investigations. In spite of a large number of studies on GO thin films, limited attempts have been made to investigate the effect of temperature on the dielectric properties of GO films. The underlying physical mechanism involved in the variation of dielectric/ relaxation and transport properties caused by the temperature variation in GO thin films is still not clear and thus needs to be further investigated. Temperature dependent AC conductivity analysis of the films indicated its semi-conductive behavior. Further, GO films have shown DC and CBH conductivity mechanisms at lower and higher frequency ranges, respectively.

8.2. Experimental procedure

8.2.1. Synthesis of graphene oxide

0.5 g of graphite (Aldrich) and 25 ml of sulfuric acid (98%) was mixed at room temperature for 2 hours. Then, 3 g of KMnO_4 (Aldrich) was added into this solution. The mixture was stirred at 50°C for 24 hours and left to cool down to room temperature. Distilled water of about 40 mL was gradually added to above mixture. Then, 100 mL of distilled water was added and then 3 ml of H_2O_2 (35 wt % aqueous solution, Aldrich) was added drop wise to the above solution until the reaction solution turned yellow. The yellow graphene oxide dispersion was centrifuged at 7000 rpm for 2 hours to precipitate the GO. The supernatant was removed after centrifugation. 30 mL of distilled water was further added to the dispersion. The resulting dispersion was ultrasonically treated for 15 minutes to make a uniform dispersion and remove any agglomeration. The dispersion was centrifuged again at 5,000 rpm for 30 minutes. This centrifugation process was repeated several times and supernatant was removed at each cycle until the excess of acid was removed from the GO solution. Acid removal was monitored by

measuring the changes in the pH of supernatant. The neutralized GO solution was then homogenized ultrasonically for 2 h to prepare 5mg/mL graphene oxide solution.

8.2.2. Structure fabrication

ITO coated glass substrates were ultrasonically cleaned using methanol, ethanol, isopropyl alcohol and de-ionized water, and dried using nitrogen blow. 3 μ m thick GO films were coated on the substrates using drop casting technique and samples were baked in oven at 55° C for 3 hours. Finally, around 50 nm thick conductive contacts were made on the GO films by evaporating silver in the vacuum chamber at a pressure of 10⁻⁵ mbar using Univex Leybold Vacuum Evaporator. The active area of the investigated samples was 0.06 cm². The schematic view of the fabricated parallel plate structures and, the chemical formula of graphene oxide is presented in Figure 7.1.

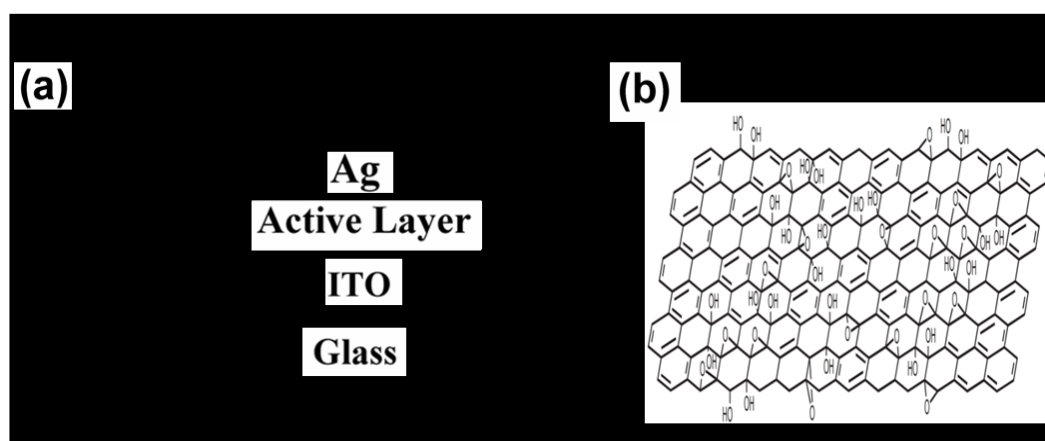


Figure 8.1: Schematic view of parallel plate structures and (b) Chemical formula of GO.

8.3. Characterization

Surface properties of the active layers (GO films) were investigated using Nanoscope Multimode Atomic Force Microscope (AFM). Absorption and transmittance spectra of the films were taken using Cary5000 UV-Vis-NIR. Electrical parameters of the samples were measured using the setup presented in Figure 7.2 [171].

This setup consists of an impedance analyzer, HP 4194A and NOVOTHERM Temperature Control System interfaced with computer.

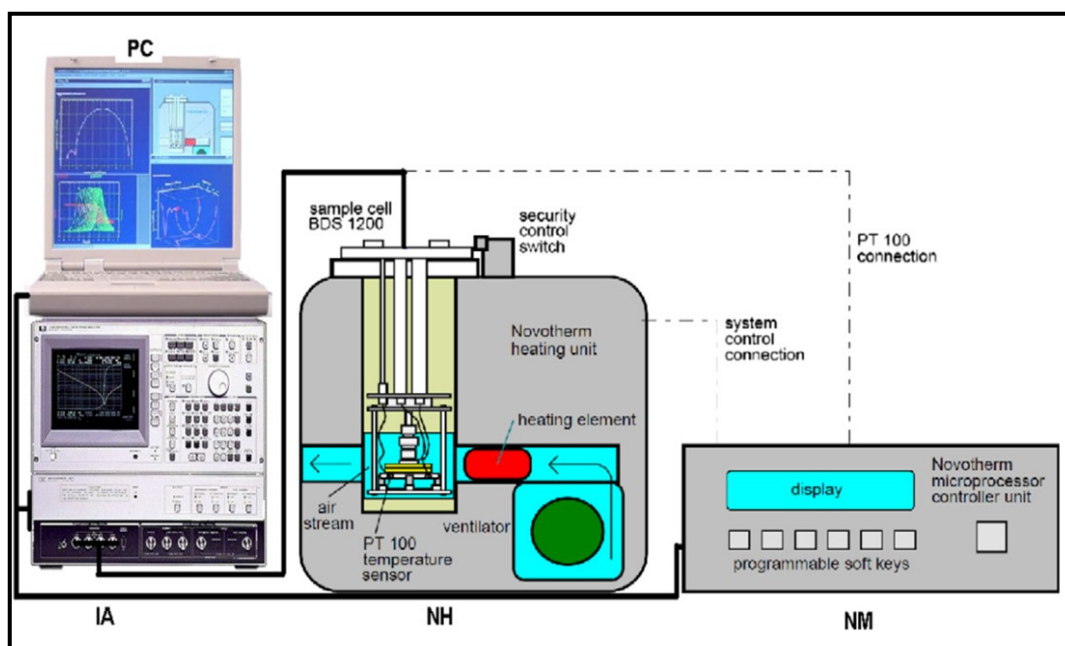


Figure 8.2: Experimental set up for temperature dependent electrical analysis of GO Films. PC: Computer Station, IA: Impedance Analyzer, NH: Novotherm Heating System, NM: Novotherm Microprocessor controller unit.

Electrical parameters such as real and imaginary dielectric constants, dielectric loss and AC conductivity of the sample were measured as a function of frequency at different temperatures. An AC signal with amplitude of 1V (RMS) was applied to the samples during these measurements. The temperature was monitored with the help of a PT 100 resistor which was in direct contact with the sample. The temperature was varied from 25 °C to 100 °C in steps, and measurements were performed with accuracy better than 0.1°C by using NOVOTHERM Temperature Control System mentioned above. Thicknesses of active layers were measured using Dektak-8 Profiler.

8.4. Results and Discussion

AFM images and absorption & transmittance spectra of GO film having 10µm×10µm dimension are shown in Figure 7.3. The Root Mean Square and Average roughness values of the film were found equal to 18.18 nm and 14.38 nm, respectively. Surface and 3D AFM profiles of the GO film present distribution of GO particles.

Agglomerations of GO particles are observable in AFM profiles, in particular in 3D AFM image shown in Figure 7.3 (b). These agglomerations and rougher surface of the glass substrate may be the reason of higher roughness values of GO film. Further, it is clear from the AFM profiles that films are free of any major structural disorder. The absorption peak found at around 220 nm, can be associated with the $\pi \rightarrow \pi^*$ transition of carbon bonds (C-C) in aromatic ring.

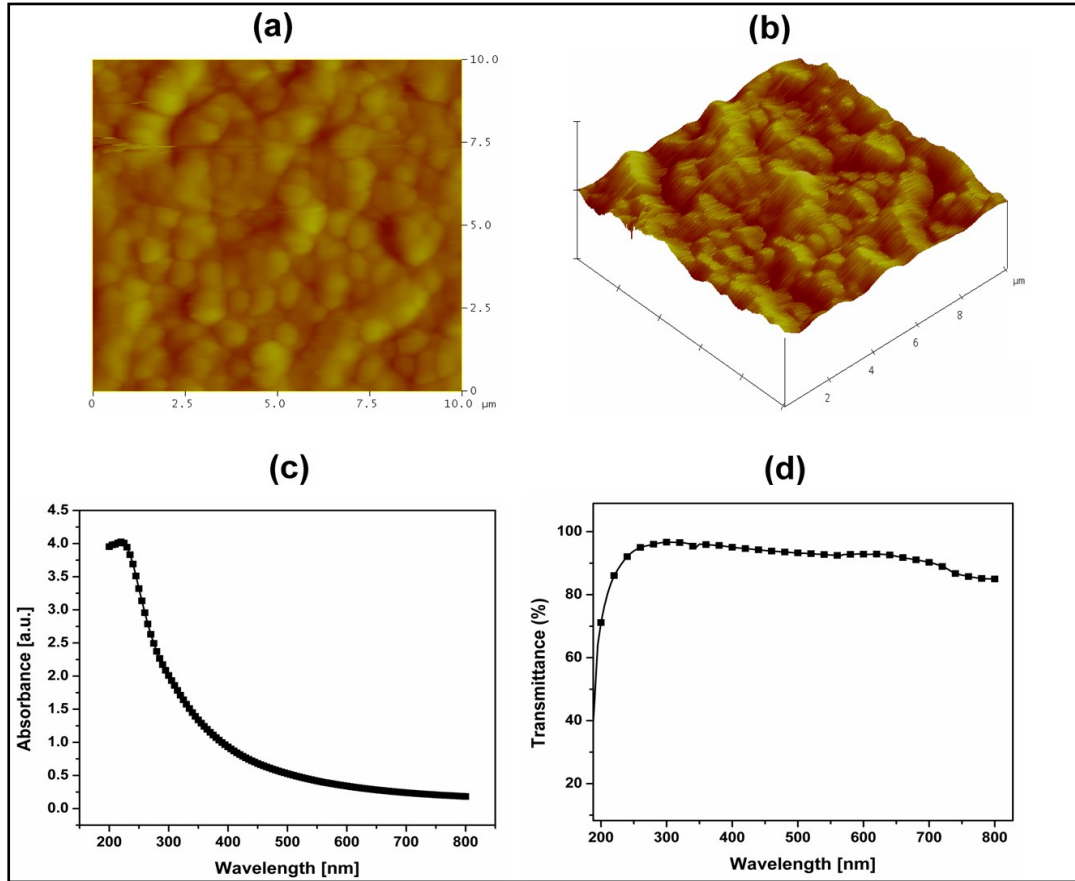


Figure 8.3: a) Surface and b) 3D AFM profiles, c) Absorption and d) Transmittance Spectra of GO Films.

The absorption peak of the investigated GO film is in accordance with the literature [172, 173]. Further, GO film showed excellent transmittance characteristics, in agreement with earlier investigations [174], over the investigated wavelength range. The variation in real & imaginary dielectric constants (ϵ' and ϵ'') and dielectric loss of GO film as a function of frequency at different temperatures is shown in Figure 7.4. The frequency of the applied AC signal was varied from 100 Hz to 10 MHz. Figure 7.4 (a) shows the real dielectric constant - frequency plots of the films in the frequency range of 100 Hz to 10 MHz. At 100 Hz, the magnitude of ϵ' was observed to decrease

from 2.81 at 30 °C to 1.12 at 100 °C. Furthermore, magnitude of ϵ' was found to decrease with increase in frequency from 100 Hz to 2 KHz.

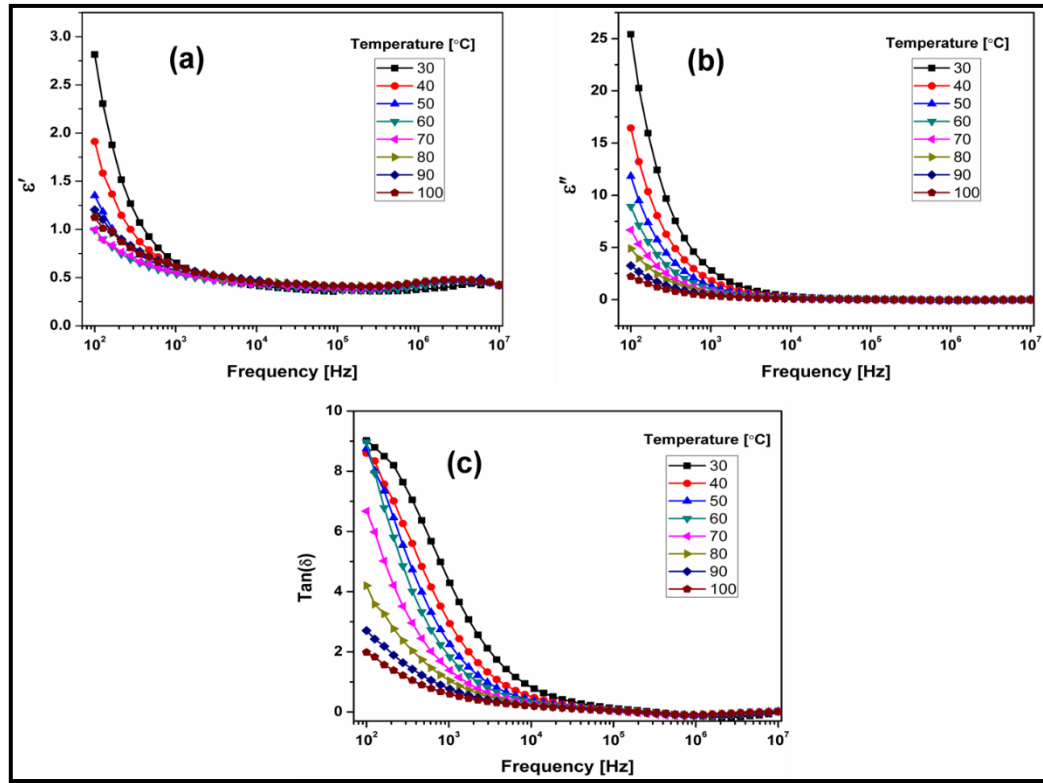


Figure 8.4: a) Real and b) Imaginary Dielectric Constants, and c) Loss Tangent Plots of GO film as a function of frequency at given temperatures.

However, no significant effect of frequency and temperature variation was observed as frequency becomes higher than 2 KHz. The magnitude of ϵ' was found to be equal to around 0.5 within the frequency range of 2 KHz to 10 MHz at all the investigated temperature values. Capacitance (C) of the film can be calculated using the following equation [175]:

$$C = \epsilon_0 \epsilon' A/d \quad (8.1)$$

Where ϵ_0 is the dielectric constant of free space, A is the surface area and d is the thickness of active layer. Figure 7.4 (b) presents the ϵ'' - frequency plots of the films in the frequency range of 100 Hz to 10 MHz at selected temperatures (30, 40, 50, 60, 70, 80, 90 and 100°C). The behavior of ϵ'' as a function of frequency at different

temperatures was found similar to ϵ' - frequency trend. The magnitude of ϵ'' is given as [175]:

$$\epsilon'' = \epsilon' \tan \delta \quad (8.2)$$

Where $\tan \delta$, is called as loss tangent or dielectric loss. Thus ϵ'' is measurement of the $\tan \delta$ of the investigated films. The variation of the $\tan \delta$ as a function of frequency and temperature is shown in Figure 7.4 (c). The magnitude of $\tan \delta$ was observed to decrease with an increase in both frequency and temperature. Further, at higher frequencies $\tan \delta$ showed insensitive behavior similar to the behavior of dielectric constants. The insensitive behavior of real & imaginary dielectric constants and dielectric loss, at high frequency range can be explained with the help of molecule dielectric physics. At high frequencies, applied electrical field changes at a rate higher than the relaxation time of the ions of adsorbed water molecules [176].

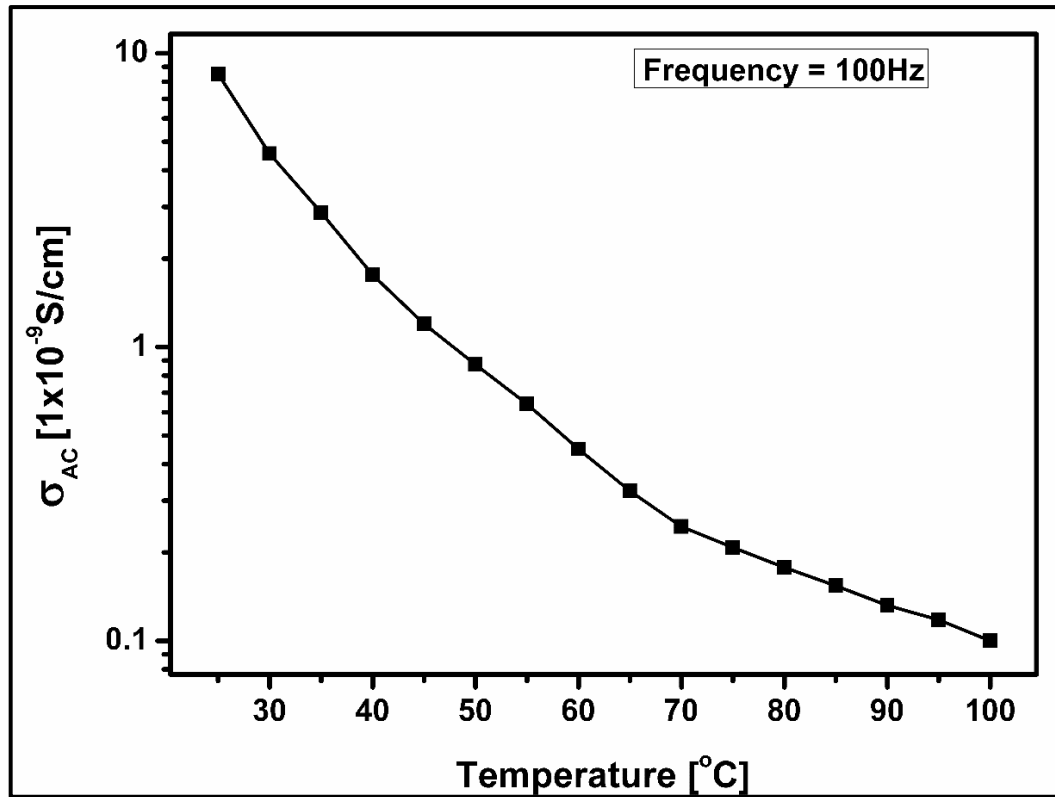


Figure 8.5: Plot of AC conductivity of GO film as a function of temperature at 100 Hz.

Variation in the electrical conductivity of GO film as a function of temperature at 100 Hz is shown in Figure 7.5. As can be seen, proportional decrease in conductivity of the film with increase in temperature was observed. The conductivity of film decreases 85 times with the increase of temperature from 25 °C to 100 °C at a fixed frequency of 100 Hz. This behavior of the sample is similar to earlier investigations [164] where it was concluded that the dissipation of water molecules and impurities, out from GO sample, with increase in temperature at low frequency might be the reason of decrease in conductivity of the sample.

Thus, conductivity of the investigated GO film can be tuned to a specific value by controlling the amount of water molecules, as already known [177, 178], with temperature. Yao et al. [179] have investigated the effect of ambient humidity on the electrical properties of GO film and AC impedance was reported to increase significantly with decrease in ambient humidity level in particular at low frequency ranges. Investigations of Yao et al. [179] also support our findings. The temperature sensitive behavior of GO film highlights the potential of investigated sample for the realization of low cost disposable temperature sensors.

The plots of $\ln\sigma_{AC} - \ln\omega$ of the GO film at different temperatures is shown in Figure 7.6, inset presents comparison of Go film conductivity at room temperature and 100°C as a function of frequency. These plots show strong dependency of AC conductivity (σ_{AC}) on temperature, in particular at low frequencies.

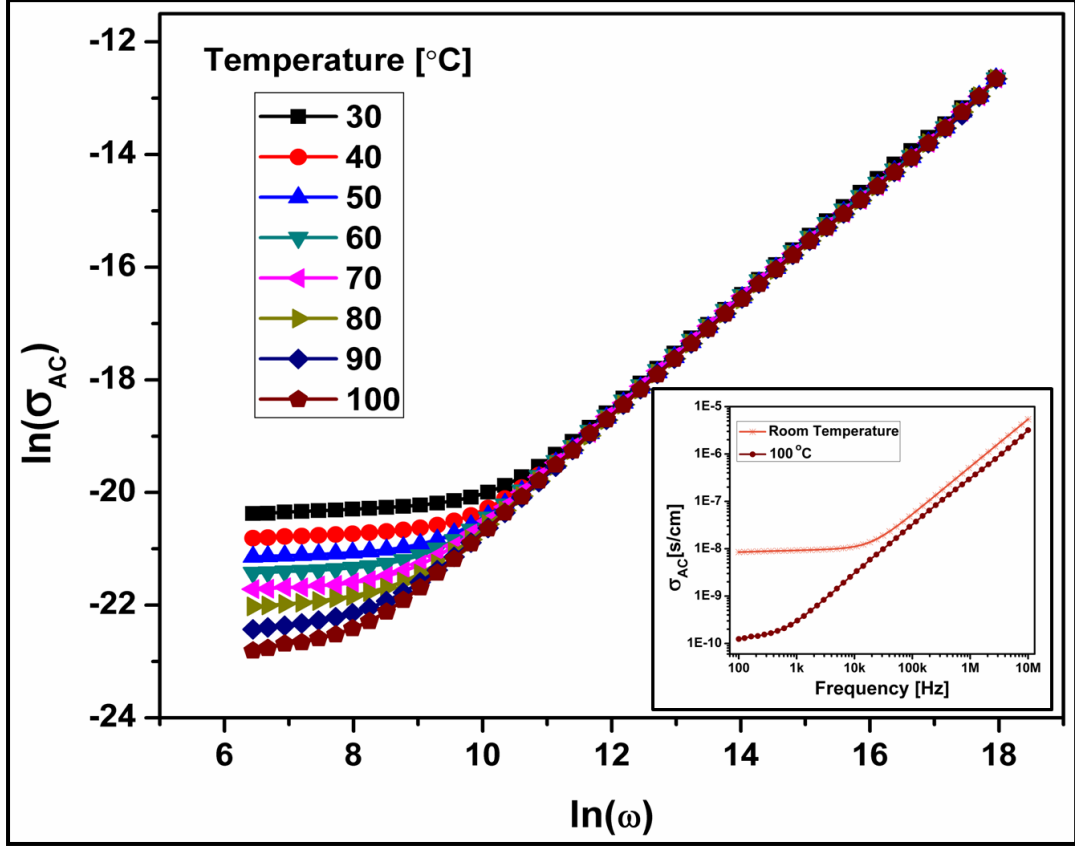


Figure 8.6: AC Conductivity of GO film as a function of frequency at given temperature values, inset: Comparison of GO film AC conductivity at room temperature and 100°C as a function of frequency.

At low frequencies, a plateau was observed which characterizes the direct current conductivity (DC), while at high frequency; the conductivity was observed to increase gradually with an increase in frequency. AC conductivity was observed to decrease with an increase in temperature. The sample has demonstrated semi-conductive behavior within the investigated temperature range similar to earlier investigations [180] for the case of GO paper. The AC conductivity dependence of the angular frequency can be expressed by the following relation, as the empirical Jonscher's universal law [181, 182]:

$$\sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s \quad (4.1)$$

Where, A is a constant, ω is the angular frequency and s is the frequency exponent parameter which identifies AC conduction mechanisms. The magnitude of exponent s, which represents main body interactions of electrons and impurities, is usually less

than unity [183]. The magnitude of parameter s (angular frequency exponent) was calculated from the slopes of Figure 8.6.

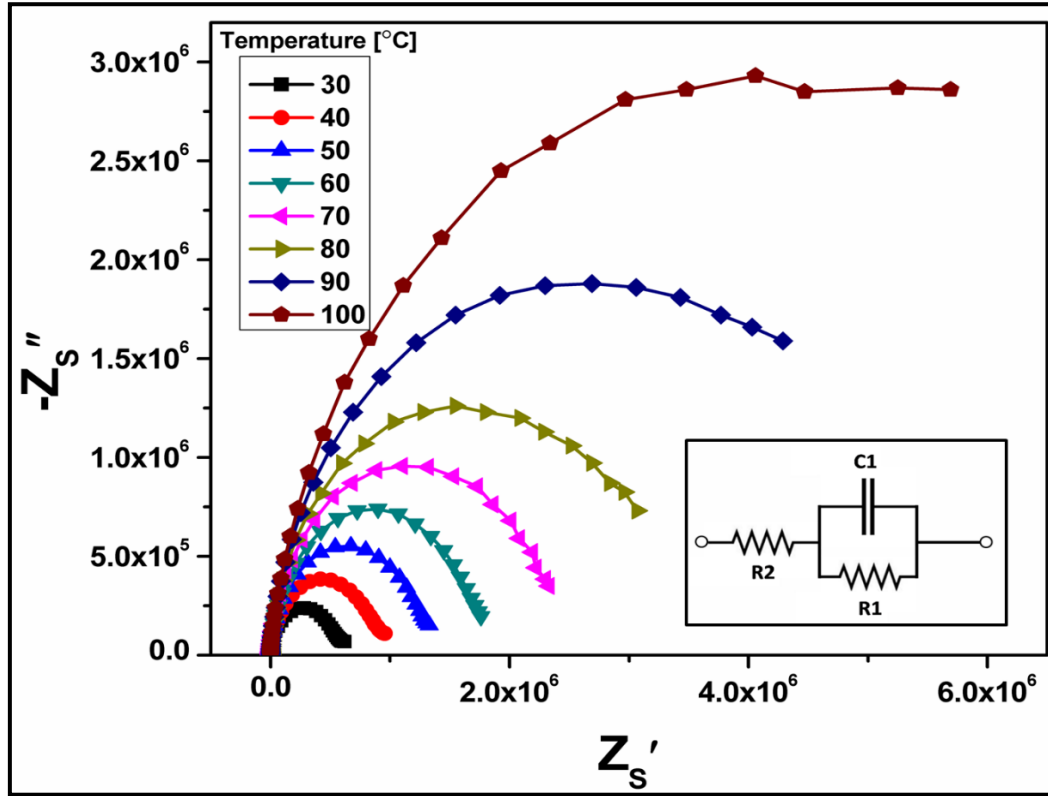


Figure 8.7: Complex impedance spectra/ Nyquist Plots of GO film at various temperatures, inset: Equivalent RC network.

In this work, the value of parameter s was found equal to 0 at low frequency region, showing DC conductivity behavior [182] of GO film and very close to unity at high frequency region. Furthermore, its magnitude was found to vary slightly with increase in temperature. So, based on the magnitude of parameter s (which is close to unity at high frequency region) and its temperature dependent behavior, it can be concluded that the results are consistent with the correlated barrier hopping (CBH) model [184-186] at high frequency regimes. This model proposes temperature activated hopping of charge carriers between localized sites [187]. Thus, GO film contains DC and CBH conductivity mechanisms at low and high frequency regimes, respectively. The transition region from DC to CBH conductivity shifted to low frequency with increase in temperature.

The complex impedance spectra of Graphene Oxide (GO), obtained by plotting Z_s' vs. Z_s'' at different temperatures is shown in Figure 7.7. This pattern not only

informs about the electrical processes occurring within the sample but also presents their correlation with the microstructure of the sample when modeled in terms of an electrical equivalent circuit [188] as presented in the inset of the Figure 7.7 R2 in the equivalent circuit represents contact resistance whereas R_1 in parallel with Z_{C1} (impedance of C_1) represents polarization resistance. The impedance spectrum of the GO is based on semicircular arcs whose pattern is found to change with increase in temperature. As can be seen, in the Nyquist plots of GO sample, complete semicircles do not form at higher temperatures. This is due to very high impedance of GO sample at higher temperatures.

It is pertinent to mention that variation in the dielectric and electrical parameters of GO film as a function of frequency and temperature is in good agreement with the literature [164, 179, 180, 189-191]. Detailed investigation of the effect of surface roughness in addition to temperature and frequency on the dielectric and electrical properties of GO film is in process and expected to be published in near future.

8.5. Conclusion

In this work, we have synthesized Graphene Oxide using modified Hummers Method and investigated the effect of temperature and frequency variation on its dielectric and transport properties using impedance spectroscopic technique. Graphene Oxide films were prepared using drop casting method on Indium Tin Oxide (ITO) coated glass substrate. Atomic force microscopy was used to characterize the films microstructure and surface topography. Electrical characterization was carried out using LCR meter in frequency regime (100 Hz to 10 MHz) at different temperatures. Results showed that AC conductivity σ_{ac} of the films varied with angular frequency, ω as ω^S , with $S < 1$. Temperature and frequency variation has significantly influenced on the electrical properties of GO film, in particular at low frequency regions. Analysis showed that film contains DC and CBH conductivity mechanisms at low and high frequency ranges, respectively. Realization and understanding the transport properties of similar solution processed films will provide potential and foundation for the development of advanced microelectronic devices in future.

9. CONCLUSION

In recent years, organic semiconductors have attracted considerable attention for application in electronic devices such as solar cells, photodetectors, light-emitting diodes and field-effect transistors. This thesis discusses the application of solution-processed composite dielectric and low voltage organic field-effect transistors. A great deal of effort for the device engineering has been given to the control and modification of the interfaces directly in contact with the semiconductor layer, which are between the semiconductor and dielectric. We investigated a series of outstanding problems related to charge injection and transport in organic field-effect transistors. This is a more work needs to be done in way of understanding the nature of charge transport in these devices.

In chapter 4, poly(3-hexylthiophene) (P3HT): [6,6]-phenyl C61-butyric acid methyl ester (PCBM) blend with 1:1 wt/wt ratio was used as a semiconducting layer, and poly (methyl methacrylate) (PMMA): Ta₂O₅ blends with varying concentration of Ta₂O₅ were used as dielectric layers of OFETs. Dielectric layers were used as the blends of PMMA: Ta₂O₅ with different Ta₂O₅ concentration. Once concentration of Ta₂O₅ were increased, dielectric constant of PMMA: Ta₂O₅ nanocomposites were found to increase. Additionally, devices with 7 wt% and higher concentration of Ta₂O₅ showed electron mobility in addition to hole mobility indicating ambipolar behavior of the devices. Based on excellent saturation behavior and promising mobility values of the investigated solution processed devices, it is expected that the investigated devices can possibly be utilized in some practical application such as low-cost large area sensing arrays in future.

In chapter 5, present a novel ambipolar OFET composed of a hybrid dielectric thin film of Ta₂O₅: PMMA nanocomposite material, and solution processed poly (selenophene, benzotriazole and dialkoxy substituted [1,2-b:4, 5-b'] dithiophene (P-SBTBDT)-based organic semiconducting material as the active layer of the device. It has been observed that activation energy value decreases with increasing the Ta₂O₅ concentration. The addition of Ta₂O₅ inorganic particle to PMMA matrix enhances the electrical conduction of PMMA due to the electronic and impurity contributions arising from the Ta₂O₅ particle.

Frequency dependent dielectric constant was increased due to the increment of filler ratio. This behavior can be explained with the presence of higher permittivity metal oxide nanoparticle and the interfacial Maxwell-Wagner polarization with the polymer matrix and filler. Additionally, shift in Cole-Cole plots of nanocomposites with different percentage of Ta₂O₅ points out the increment of dielectric constant with the increasing filler ratio. Increasing filler ratio is a source of rise in oxygen vacancies. Each oxygen vacancy, which is the most dominant type of defect in Ta₂O₅, offers dangling bonds and donates two electrons close to the vacancy location. The dangling bonds result in electronic states within the band gap. These electronic states may trap excited electrons, creating many trap levels within the band gap of Ta₂O₅. Consequently, the presence of oxygen vacancies is expected to make Ta₂O₅ an n-type semiconductor. It was also seen that electron mobility increases with increase in the concentration of Ta₂O₅ from output and transfer curves.

In chapter 6, widely used small molecule CuPc in the production of OFET is preferred. Solution processed Al₂O₃: PVA composite layer was used as the dielectric layer. It has been observed dielectric constant is obviously increased with the increment of Al₂O₃ ratio of the nanocomposite polymer films. Interpolation of Al₂O₃ nanoparticle into PVA matrix has modified the dielectric relaxation frequency of pure PVA. The real part of the dielectric constants has decreased with increasing frequency. Moreover, some ratio of Al₂O₃: PVA nanocomposites has given double dielectric relaxation at the same frequency range.

In chapter 7, we present a method to increase the performance in organic field effect transistors (OFET) by using gel as dielectric. In order to compare the performance improvement, Poly (methylmethacrylate) (PMMA) and CuPc material system were used as a reference. Propylene carbonate (PC) is introduced into PMMA to form the gel for using as gate dielectric. The mobility values are increased and operation voltage decreases from -80 to -0.8 with gel dielectric. The increase in performance is discussed in terms of better charge inducing by high dielectric properties of gel.

In chapter 8, we have synthesized Graphene Oxide (GO) using modified Hummers method and investigated its electrical properties using parallel plate impedance spectroscopic technique. Graphene Oxide films were prepared using drop casting method on Indium Tin Oxide (ITO) coated glass substrate. Atomic force

microscopy was used to characterize the films' microstructure and surface topography. Electrical characterization was carried out using LCR meter in frequency regime (100 Hz to 10 MHz) at different temperatures. AC conductivity σ_{ac} of the films was observed to be varied with angular frequency, ω as ω^S , with $S < 1$. The electrical properties of GO were found to be both frequency and temperature dependent. Analysis showed that GO film contains direct current (DC) and Correlated Barrier Hopping (CBH) conductivity mechanisms at low and high frequency ranges, respectively. Photon absorption and transmittance capability in the visible range and excellent electrical parameters of solution processed graphene oxide suggest its suitability for the realization of low cost flexible organic solar cells and organic thin film transistors, respectively.

REFERENCES

- [1] Rogers J. A., Someya T., Huang Y., (2010), "Materials and mechanics for stretchable electronics", *Science*, 327 (5973), 1603-1607.
- [2] Forrest S. R., (2004), "The path to ubiquitous and low-cost organic electronic appliances on plastic", *Nature*, 428 (6986), 911-918.
- [3] Segev-Bar M., Landman A., Nir-Shapira M., Shuster G., Haick H., (2013), "Tunable touch sensor and combined sensing platform: Toward nanoparticle-based electronic skin".
- [4] Shortliffe E. H., Cimino J. J., (2013), "Biomedical informatics: computer applications in health care and biomedicine", Edition, Springer Science & Business Media.
- [5] Orilall M. C., Wiesner U., (2011), "Block copolymer based composition and morphology control in nanostructured hybrid materials for energy conversion and storage: solar cells, batteries, and fuel cells", *Chemical Society Reviews*, 40 (2), 520-535.
- [6] Forrest S. R., Thompson M. E., (2007), "Introduction: organic electronics and optoelectronics", *Chemical Reviews*, 107 (4), 923-925.
- [7] Sirringhaus H., (2005), "Device physics of solution-processed organic field-effect transistors", *Advanced Materials*, 17 (20), 2411-2425.
- [8] Osaka I., Abe T., Shinamura S., Miyazaki E., Takimiya K., (2010), "High-mobility semiconducting naphthodithiophene copolymers", *Journal of the American Chemical Society*, 132 (14), 5000-5001.
- [9] Kyriasis I., (2008), "Organic Field Effect Transistors: Theory, Fabrication and Characterization", Edition, Springer Science & Business Media.
- [10] Kudo K., Yamashina M., Moriizumi T., (1984), "Field effect measurement of organic dye films", *Japanese Journal of Applied Physics*, 23 (1R), 130.
- [11] Tsumura A., Koezuka H., Ando T., (1986), "Macromolecular electronic device: Field-effect transistor with a polythiophene thin film", *Applied Physics Letters*, 49 (18), 1210-1212.

- [12] Facchetti A., Yoon M. H., Marks T. J., (2005), "Gate Dielectrics for Organic Field-Effect Transistors: New Opportunities for Organic Electronics", *Advanced Materials*, 17 (14), 1705-1725.
- [13] Gutman F., Lyons L. E., (1967), "Organic semiconductors", Wiley, New York.
- [14] Itaka K., Yamashiro M., Yamaguchi J., Haemori M., Yaginuma S., Matsumoto Y., Kondo M., Koinuma H., (2006), "High-Mobility C60 Field-Effect Transistors Fabricated on Molecular- Wetting Controlled Substrates", *Advanced Materials*, 18 (13), 1713-1716.
- [15] Ortiz R. P., Facchetti A., Marks T. J., (2009), "High-k organic, inorganic, and hybrid dielectrics for low-voltage organic field-effect transistors", *Chemical Reviews*, 110 (1), 205-239.
- [16] Maliakal A., Katz H., Cotts P. M., Subramoney S., Mirau P., (2005), "Inorganic oxide core, polymer shell nanocomposite as a high K gate dielectric for flexible electronics applications", *Journal of the American Chemical Society*, 127 (42), 14655-14662.
- [17] Wang L., Myung-Han Y., Lu G., Yang Y., Facchetti A., Marks T. J., (2006), "High-performance transparent inorganic-organic hybrid thin-film n-type transistors", *Nature materials*, 5 (11), 893.
- [18] Dimitrakopoulos C. D., Malenfant P. R., (2002), "Organic thin film transistors for large area electronics", *Advanced Materials*, 14 (2), 99-117.
- [19] Facchetti A., Yoon M. H., Marks T. J., (2005), "Gate dielectrics for organic field-effect transistors: New opportunities for organic electronics", *Advanced Materials*, 17 (14), 1705-1725.
- [20] Veres J., Ogier S., Lloyd G., De Leeuw D., (2004), "Gate insulators in organic field-effect transistors", *Chemistry of Materials*, 16 (23), 4543-4555.
- [21] Cai X., Burand M. W., Newman C. R., da Silva Filho D. A., Pappenfus T. M., Bader M. M., Brédas J.-L., Mann K. R., Frisbie C. D., (2006), "N-and P-channel transport behavior in thin film transistors based on tricyanovinyl-capped oligothiophenes", *The Journal of Physical Chemistry B*, 110 (30), 14590-14597.
- [22] Majewski L., Schroeder R., Grell M., (2004), "Organic field-effect transistors with electroplated platinum contacts", *Applied Physics Letters*, 85 (16), 3620-3622.

- [23] Tate J., Rogers J. A., Jones C. D., Vyas B., Murphy D. W., Li W., Bao Z., Slusher R. E., Dodabalapur A., Katz H. E., (2000), "Anodization and microcontact printing on electroless silver: Solution-based fabrication procedures for low-voltage electronic systems with organic active components", *Langmuir*, 16 (14), 6054-6060.
- [24] Zaumseil J., Sirringhaus H., (2007), "Electron and ambipolar transport in organic field-effect transistors", *Chemical Reviews*, 107 (4), 1296-1323.
- [25] Kobayashi S., Nishikawa T., Takenobu T., Mori S., Shimoda T., Mitani T., Shimotani H., Yoshimoto N., Ogawa S., Iwasa Y., (2004), "Control of carrier density by self-assembled monolayers in organic field-effect transistors", *Nature materials*, 3 (5), 317-322.
- [26] Pernstich K., Haas S., Oberhoff D., Goldmann C., Gundlach D., Batlogg B., Rashid A., Schitter G., (2004), "Threshold voltage shift in organic field effect transistors by dipole monolayers on the gate insulator", *Journal of Applied Physics*, 96 (11), 6431-6438.
- [27] Brondijk J. J., (2012), "Device physics of organic field-effect transistors".
- [28] Xie H., (2010), "Charge transport at organic/dielectric and organic/organic interfaces".
- [29] Gundlach D., Zhou L., Nichols J., Jackson T., Necliudov P., Shur M., (2006), "An experimental study of contact effects in organic thin film transistors", *Journal of Applied Physics*, 100 (2), 024509.
- [30] Hill I., (2005), "Numerical simulations of contact resistance in organic thin-film transistors", *Applied Physics Letters*, 87 (16), 163505.
- [31] Street R., Salleo A., (2002), "Contact effects in polymer transistors", *Applied Physics Letters*, 81 (15), 2887-2889.
- [32] Lei C., Das A., Elliott M., Macdonald J. E., Turner M., (2004), "Au-poly (3-hexylthiophene) contact behaviour at high resolution", *Synthetic metals*, 145 (2), 217-220.
- [33] Newman C. R., Chesterfield R. J., Panzer M. J., Frisbie C. D., (2005), "High mobility top-gated pentacene thin-film transistors", *Journal of Applied Physics*, 98 (8), 084506.

- [34] Roichman Y., Tessler N., (2002), "Structures of polymer field-effect transistor: Experimental and numerical analyses", *Applied Physics Letters*, 80 (1), 151-153.
- [35] DiBenedetto S. A., (2009), "Theory aided design and analysis of dielectric and semiconductor components for organic field-effect transistors", Northwestern University.
- [36] Ortiz R. P., Facchetti A., Marks T. J., (2010), "High-k Organic, Inorganic, and Hybrid Dielectrics for Low-Voltage Organic Field-Effect Transistors", *Chemical reviews*, 110 (1), 205-239.
- [37] Kanbur, (2011), "Conductive Polymer Nanocomposites Of Polypropylene And Organic Field Effect Transistors With Polyethylene Gate Dielectric", Middle East Technical University
- [38] Singh T. B., Meghdadi F., Günes S., Marjanovic N., Horowitz G., Lang P., Bauer S., Sariciftci N. S., (2005), "High-Performance Ambipolar Pentacene Organic Field-Effect Transistors on Poly (vinyl alcohol) Organic Gate Dielectric", *Advanced Materials*, 17 (19), 2315-2320.
- [39] Bartic C., Jansen H., Campitelli A., Borghs S., (2002), "Ta₂O₅ as gate dielectric material for low-voltage organic thin-film transistors", *Organic Electronics*, 3 (2), 65-72.
- [40] Lee J., Kim J., Im S., (2003), "Pentacene thin-film transistors with Al₂O₃+x gate dielectric films deposited on indium-tin-oxide glass", *Applied Physics Letters*, 83 (13), 2689-2691.
- [41] Majewski L., Grell M., Ogier S., Veres J., (2003), "A novel gate insulator for flexible electronics", *Organic Electronics*, 4 (1), 27-32.
- [42] Shi M. Y., (2012), "Organic Logic Circuits: Fabrication Process and Device Optimisation", University of Manchester.
- [43] Matthews F. L., Rawlings R. D., (1999), "Composite materials: engineering and science", Edition, Elsevier.
- [44] Almadhoun M. N., (2011), "Process Optimization of P (VDF-TrFE)-BaTiO₃ Nanocomposites for Storage Capacitor Applications".
- [45] Nakayama K.-i., Umehara M., Yokoyama M., (2006), "Electron injection layers consisting of naphthalene tetracarboxylic dianhydride and indium in n-

type organic field-effect transistors”, Japanese Journal of Applied Physics, 45 (2R), 974.

- [46] Schroeder R., Majewski L. A., Grell M., (2004), “Improving organic transistor performance with Schottky contacts”, Applied Physics Letters, 84 (6), 1004-1006.
- [47] Tsukagoshi K., Shigeto K., Yagi I., Aoyagi Y., (2006), “Interface modification of a pentacene field-effect transistor with a submicron channel”, Applied Physics Letters, 89 (11), 113507.
- [48] Ishii H., Sugiyama K., Ito E., Seki K., (1999), “Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces”, Advanced Materials, 11 (8), 605-625.
- [49] Anthopoulos T. D., de Leeuw D. M., Cantatore E., van’t Hof P., Alma J., Hummelen J. C., (2005), “Solution processible organic transistors and circuits based on a C 70 methanofullerene”, Journal of Applied Physics, 98 (5), 054503.
- [50] Hamadani B., Natelson D., (2004), “Temperature-dependent contact resistances in high-quality polymer field-effect transistors”, Applied Physics Letters, 84 (3), 443-445.
- [51] Bürgi L., Richards T., Friend R., Sirringhaus H., (2003), “Close look at charge carrier injection in polymer field-effect transistors”, Journal of Applied Physics, 94 (9), 6129-6137.
- [52] Bässler H., Köhler A. (2011), "Charge transport in organic semiconductors". "Unimolecular and supramolecular electronics I", Springer.
- [53] Podzorov V., Menard E., Borissov A., Kiryukhin V., Rogers J., Gershenson M., (2004), “Intrinsic charge transport on the surface of organic semiconductors”, Physical review letters, 93 (8), 086602.
- [54] Coropceanu V., Cornil J., da Silva Filho D. A., Olivier Y., Silbey R., Brédas J.-L., (2007), “Charge transport in organic semiconductors”, Chemical Reviews, 107 (4), 926-952.
- [55] Hamadani B. H., (2007), “Electronic charge injection and transport in organic field-effect transistors”, Rice University.
- [56] Schwoerer M., Wolf H., (2005), “Bucher und Software-Organische Molekulare Festkörper”, Physik Journal, 4 (8-9), 109.

- [57] Unay H., Unlu N. A., Hizalan G., Hacıoglu S. O., Yildiz D. E., Toppare L., Cirpan A., (2015), "Benzotriazole and benzodithiophene containing medium band gap polymer for bulk heterojunction polymer solar cell applications", *Journal of Polymer Science Part A: Polymer Chemistry*, 53 (4), 528-535.
- [58] Sariciftci N. S., Smilowitz L., Heeger A. J., Wudl F., (1992), "Photoinduced electron transfer from a conducting polymer to buckminsterfullerene", *Science*, 1474-1476.
- [59] von Hauff E., Dyakonov V., Parisi J., (2005), "Study of field effect mobility in PCBM films and P3HT: PCBM blends", *Solar energy materials and solar cells*, 87 (1), 149-156.
- [60] Deman A.-L., Tardy J., (2005), "PMMA-Ta₂O₅ bilayer gate dielectric for low operating voltage organic FETs", *Organic Electronics*, 6 (2), 78-84.
- [61] Horowitz G., (1998), "Organic field-effect transistors", *Advanced Materials*, 10 (5), 365-377.
- [62] Gu G., Kane M. G., Mau S.-C., (2007), "Reversible memory effects and acceptor states in pentacene-based organic thin-film transistors", *Journal of Applied Physics*, 101 (1), 014504.
- [63] Katz H. E., Hong X. M., Dodabalapur A., Sarpeshkar R., (2002), "Organic field-effect transistors with polarizable gate insulators", *Journal of Applied Physics*, 91 (3), 1572-1576.
- [64] Jung T., Dodabalapur A., Wenz R., Mohapatra S., (2005), "Moisture induced surface polarization in a poly (4-vinyl phenol) dielectric in an organic thin-film transistor", *Applied Physics Letters*, 87 (18), 182109.
- [65] Miller E., Dang X., Yu E., (2000), "Gate leakage current mechanisms in AlGaIn/GaN heterostructure field-effect transistors", *Journal of Applied Physics*, 88 (10), 5951-5958.
- [66] Khatami Y., Banerjee K., (2009), "Steep subthreshold slope n-and p-type tunnel-FET devices for low-power and energy-efficient digital circuits", *IEEE Transactions on Electron Devices*, 56 (11), 2752-2761.
- [67] Kunugi Y., Takimiya K., Negishi N., Otsubo T., Aso Y., (2004), "An ambipolar organic field-effect transistor using oligothiophene incorporated with two [60] fullerenes", *Journal of Materials Chemistry*, 14 (19), 2840-2841.

- [68] Singh T. B., Günes S., Marjanović N., Sariciftci N., Menon R., (2005), "Correlation between morphology and ambipolar transport in organic field-effect transistors", *Journal of Applied Physics*, 97 (11), 114508.
- [69] Lehar O. P., Sagan J. P., Zhang L., Dammel R. R., (2000). "Solvent content of thick photoresist films", *Microlithography 2000*, 442-451.
- [70] Horowitz G., (1999), "Field-effect transistors based on short organic molecules", *Journal of materials chemistry*, 9 (9), 2021-2026.
- [71] Gerhardt R., (1994), "Impedance and dielectric spectroscopy revisited: distinguishing localized relaxation from long-range conductivity", *Journal of Physics and Chemistry of Solids*, 55 (12), 1491-1506.
- [72] Jonscher A. K., (1977), "The 'universal' dielectric response", *Nature*, 267 (5613), 673-679.
- [73] Holmegaard L., Hansen J. L., Kalhøj L., Kragh S. L., Stapelfeldt H., Filsinger F., Küpper J., Meijer G., Dimitrovski D., Abu-Samha M., (2010), "Photoelectron angular distributions from strong-field ionization of oriented molecules", *Nature Physics*, 6 (6), 428-432.
- [74] Block H. (1979), "The nature and application of electrical phenomena in polymers". "Electric Phenomena in Polymer Science", Springer Berlin Heidelberg.
- [75] Gallone G., Levita J., Mijovic S., Andjelic S., Rolla P., (1998), "Anomalous trends in conductivity during epoxy—amine reactions", *Polymer*, 39 (11), 2095-2102.
- [76] Gray F. M., (1991), "Solid polymer electrolytes", Edition, VCH New York etc.
- [77] Seanor D. A., (2013), "Electrical properties of polymers", Edition, Elsevier.
- [78] Prodromakis T., Papavassiliou C., (2009), "Engineering the Maxwell–Wagner polarization effect", *Applied Surface Science*, 255 (15), 6989-6994.
- [79] Macdonald J. R., (1992), "Impedance spectroscopy", *Annals of biomedical engineering*, 20 (3), 289-305.
- [80] Ukah N. B., Granstrom J., Gari R. R. S., King G. M., Guha S., (2011), "Low-operating voltage and stable organic field-effect transistors with poly (methyl

methacrylate) gate dielectric solution deposited from a high dipole moment solvent”, *Applied Physics Letters*, 99 (24), 243302.

- [81] Singh T. B., Günes S., Marjanović N., Sariciftci N. S., Menon R., (2005), “Correlation between morphology and ambipolar transport in organic field-effect transistors”, *Journal of Applied Physics*, 97 (11), 114508.
- [82] Dodabalapur A., Katz H. E., Torsi L., Haddon R. C., (1995), “Organic Heterostructure Field-Effect Transistors”, *Science*, 269 (5230), 1560-1562.
- [83] Yasuda T., Goto T., Fujita K., Tsutsui T., (2004), “Ambipolar pentacene field-effect transistors with calcium source-drain electrodes”, *Applied Physics Letters*, 85 (11), 2098-2100.
- [84] Singh T. B., Meghdadi F., Günes S., Marjanovic N., Horowitz G., Lang P., Bauer S., Sariciftci N. S., (2005), “High-Performance Ambipolar Pentacene Organic Field-Effect Transistors on Poly(vinyl alcohol) Organic Gate Dielectric”, *Advanced Materials*, 17 (19), 2315-2320.
- [85] Singh T. B., Senkarabacak P., Sariciftci N. S., Tanda A., Lackner C., Hagelauer R., Horowitz G., (2006), “Organic inverter circuits employing ambipolar pentacene field-effect transistors”, *Applied Physics Letters*, 89 (3), 033512.
- [86] Takebayashi S., Abe S., Saiki K., Ueno K., (2009), “Origin of the ambipolar operation of a pentacene field-effect transistor fabricated on a poly(vinyl alcohol)-coated Ta₂O₅ gate dielectric with Au source/drain electrodes”, *Applied Physics Letters*, 94 (8).
- [87] Bartic C., Jansen H., Campitelli A., Borghs S., (2002), “Ta₂O₅ as gate dielectric material for low-voltage organic thin-film transistors”, *Organic Electronics*, 3 (2), 65-72.
- [88] Navan R. R., Prashanthi K., Shojaei Baghini M., Ramgopal Rao V., (2012), “Solution processed photopatternable high-k nanocomposite gate dielectric for low voltage organic field effect transistors”, *Microelectronic Engineering*, 96, 92-95.
- [89] Cai Q. J., Gan Y., Chan-Park M. B., Yang H. B., Lu Z. S., Li C. M., Guo J., Dong Z. L., (2009), “Solution-Processable Barium Titanate and Strontium Titanate Nanoparticle Dielectrics for Low-Voltage Organic Thin-Film Transistors”, *Chemistry of Materials*, 21 (14), 3153-3161.

- [90] Halik M., Klauk H., Zschieschang U., Kriem T., Schmid G., Radlik W., Wussow K., (2002), "Fully patterned all-organic thin film transistors", *Applied Physics Letters*, 81 (2), 289-291.
- [91] Parashkov R., Becker E., Ginev G., Riedl T., Johannes H. H., Kowalsky W., (2004), "All-organic thin-film transistors made of poly(3-butylthiophene) semiconducting and various polymeric insulating layers", *Journal of Applied Physics*, 95 (3), 1594-1596.
- [92] Uemura S., Yoshida M., Hoshino S., Kodzasa T., Kamata T., (2003), "Investigation for surface modification of polymer as an insulator layer of organic FET", *Thin Solid Films*, 438, 378-381.
- [93] Tanaka T., Montanari G. C., Mulhaupt R., (2004), "Polymer nanocomposites as dielectrics and electrical insulation-perspectives for processing technologies, material characterization and future applications", *IEEE Transactions on Dielectrics and Electrical Insulation*, 11 (5), 763-784.
- [94] deLeeuw D. M., Simenon M. M. J., Brown A. R., Einerhand R. E. F., (1997), "Stability of n-type doped conducting polymers and consequences for polymeric microelectronic devices", *Synthetic Metals*, 87 (1), 53-59.
- [95] Sakanoue T., Yahiro M., Adachi C., Takimiya K., Toshimitsu A., (2008), "Electrical characteristics of single-component ambipolar organic field-effect transistors and effects of air exposure on them", *Journal of Applied Physics*, 103 (9).
- [96] M.Kang, K.-J. B., D., Khim Y.-Y. N., D.-Y. Kim, (2013), "Printed, Flexible, Organic Nano-Floating-Gate Memory: Effects of Metal Nanoparticles and Blocking Dielectrics on Memory Characteristics", *Advanced Functional Materials*, 23 (28), 3503-3512.
- [97] Wu Y.-L., Lin J.-J., Ma C.-M., (2008), "Fabrication of an organic thin-film transistor by direct deposit of a pentacene layer onto a silicon substrate", *Journal of Physics and Chemistry of Solids*, 69 (2-3), 730-733.
- [98] Chang S. C., Hsiao Y. J., Li T. S., (2015), "Selecting annealing temperature of P3HT/PCBM incorporated with nano-diamonds using thermal desorption spectroscopy", *International Journal of Electrochemical Science*, 10 (2), 1658-1668.
- [99] Liu C., Minari T., Lu X., Kumatani A., Takimiya K., Tsukagoshi K., (2011), "Solution-Processable Organic Single Crystals with Bandlike Transport in Field-Effect Transistors", *Advanced Materials*, 23 (4), 523-526.

- [100] Kang-Jun Baeg , Dongyoon Khim, Soon-Won Jung, Minji Kang , In-Kyu You, Dong-Yu Kim, Antonio Facchetti , Noh Y.-Y., (2012), “Remarkable Enhancement of Hole Transport in Top-Gated N-Type Polymer Field-Effect Transistors by a High-k Dielectric for Ambipolar Electronic Circuits”, *Advanced Materials*, 24, 5433-5439.
- [101] Singha S., Thomas M. J., (2008), “Permittivity and tan delta characteristics of epoxy nanocomposites in the frequency range of 1 MHz-1 GHz”, *IEEE Transactions on Dielectrics and Electrical Insulation*, 15 (1), 2-11.
- [102] Singha S., Thomas M. J., (2008), “Dielectric properties of epoxy nanocomposites”, *IEEE Transactions on Dielectrics and Electrical Insulation*, 15 (1), 12-23.
- [103] Thakur O. P., Agrawal N., (2014), “Effect of Fillers on Electromechanical Properties of Composites for Potential Sensing Applications”, *IEEE Sensors Journal*, 14 (8), 2665-2671.
- [104] Yildiz A., Canli N. Y., Özdemir Z. G., Ocak H., Eran B. B., Okutan M., (2016), “The role of temperature on dielectric relaxation and conductivity mechanism of dark conglomerate liquid crystal phase”, *Physica B: Condensed Matter*, 485, 21-28.
- [105] Perevalov T. V., Shaposhnikov A. V., (2013), “Ab initio simulation of the electronic structure of Ta₂O₅ crystal modifications”, *Journal of Experimental and Theoretical Physics*, 116 (6), 995-1001.
- [106] Zhuiykov S., (2014), “Nanostructured semiconductor oxides for the next generation of electronics and functional devices: properties and applications“, Edition.
- [107] Nam S., Hwang H., Kim H., Kim Y., (2010), “Effect of Gate Voltage in Organic Phototransistors Based on Polythiophene/Fullerene Bulk Heterojunction Nanolayers”, *Molecular Crystals and Liquid Crystals*, 519 (1), 260-265.
- [108] Szendrei K., Jarzab D., Chen Z., Facchetti A., Loi M. A., (2010), “Ambipolar all-polymer bulk heterojunction field-effect transistors”, *Journal of Materials Chemistry*, 20 (7), 1317.
- [109] Głowacki E. D., Leonat L., Voss G., Bodea M.-A., Bozkurt Z., Ramil A. M., Irimia-Vladu M., Bauer S., Sariciftci N. S., (2011), “Ambipolar organic field effect transistors and inverters with the natural material Tyrian Purple”, *AIP Advances*, 1 (4), 042132.

- [110] Meric I., Han M. Y., Young A. F., Ozyilmaz B., Kim P., Shepard K. L., (2008), "Current saturation in zero-bandgap, top-gated graphene field-effect transistors", *Nat Nano*, 3 (11), 654-659.
- [111] Yasin M., Tauqeer T., Karimov K. S., San S. E., Kösemen A., Yerli Y., Tunc A. V., (2014), "P3HT:PCBM blend based photo organic field effect transistor", *Microelectronic Engineering*, 130 (0), 13-17.
- [112] Rost-Bietsch C., (2005), "Ambipolar and Light-Emitting Organic Field-Effect Transistors", Edition, Cuvillier Verlag.
- [113] Veres J., Ogier S. D., Leeming S. W., Cupertino D. C., Mohialdin Khaffaf S., (2003), "Low-k Insulators as the Choice of Dielectrics in Organic Field-Effect Transistors", *Advanced Functional Materials*, 13 (3), 199-204.
- [114] Wen Y., Liu Y., Guo Y., Yu G., Hu W., (2011), "Experimental Techniques for the Fabrication and Characterization of Organic Thin Films for Field-Effect Transistors", *Chemical Reviews*, 111 (5), 3358-3406.
- [115] (2009), "Origin of the ambipolar operation of a pentacene field-effect transistor fabricated on a poly(vinyl alcohol)-coated Ta₂O₅ gate dielectric with Au source/drain electrodes", *Applied Physics Letters*, 94 (8), 083305.
- [116] Zhang X.-H., Domercq B., Wang X., Yoo S., Kondo T., Wang Z. L., Kippelen B., (2007), "High-performance pentacene field-effect transistors using Al₂O₃ gate dielectrics prepared by atomic layer deposition (ALD)", *Organic Electronics*, 8 (6), 718-726.
- [117] Klauk H., Halik M., Zschieschang U., Schmid G., Radlik W., Weber W., (2002), "High-mobility polymer gate dielectric pentacene thin film transistors", *Journal of Applied Physics*, 92 (9), 5259-5263.
- [118] Parashkov R., Becker E., Ginev G., Riedl T., Johannes H.-H., Kowalsky W., (2004), "All-organic thin-film transistors made of poly(3-butylthiophene) semiconducting and various polymeric insulating layers", *Journal of Applied Physics*, 95 (3), 1594-1596.
- [119] Uemura S., Yoshida M., Hoshino S., Kodzasa T., Kamata T., (2003), "Investigation for surface modification of polymer as an insulator layer of organic FET", *Thin Solid Films*, 438-439, 378-381.
- [120] Milanov A. P., Xu K., Laha A., Bugiel E., Ranjith R., Schwendt D., Osten H. J., Parala H., Fischer R. A., Devi A., (2010), "Growth of Crystalline Gd₂O₃

Thin Films with a High-Quality Interface on Si(100) by Low-Temperature H₂O-Assisted Atomic Layer Deposition”, *Journal of the American Chemical Society*, 132 (1), 36-37.

- [121] Lee J., Kim J. H., Im S., (2003), “Pentacene thin-film transistors with Al₂O₃+x gate dielectric films deposited on indium-tin-oxide glass”, *Applied Physics Letters*, 83 (13), 2689-2691.
- [122] Yoshiki I., Youji I., Yoshihide F., Hideo F., Hiroto S., Masahiro K., Shizuo T., Hiroshi K., (2003), “Organic Thin-Film Transistors on a Plastic Substrate with Anodically Oxidized High-Dielectric-Constant Insulators”, *Japanese Journal of Applied Physics*, 42 (1R), 299.
- [123] Rasul A., Zhang J., Gamota D., Singh M., Takoudis C., (2010), “Flexible high capacitance nanocomposite gate insulator for printed organic field-effect transistors”, *Thin Solid Films*, 518 (23), 7024-7028.
- [124] Chen F.-C., Chu C.-W., He J., Yang Y., Lin J.-L., (2004), “Organic thin-film transistors with nanocomposite dielectric gate insulator”, *Applied Physics Letters*, 85 (15), 3295-3297.
- [125] Chen F.-C., Chuang C.-S., Lin Y.-S., Kung L.-J., Chen T.-H., Shieh H.-P. D., (2006), “Low-voltage organic thin-film transistors with polymeric nanocomposite dielectrics”, *Organic Electronics*, 7 (5), 435-439.
- [126] Jung C., Maliakal A., Sidorenko A., Siegrist T., (2007), “Pentacene-based thin film transistors with titanium oxide-polystyrene/polystyrene insulator blends: High mobility on high K dielectric films”, *Applied Physics Letters*, 90 (6), 062111.
- [127] Schroeder R., Majewski L. A., Grell M., (2005), “High-Performance Organic Transistors Using Solution-Processed Nanoparticle-Filled High-k Polymer Gate Insulators”, *Advanced Materials*, 17 (12), 1535-1539.
- [128] Kim P., Zhang X. H., Domercq B., Jones S. C., Hotchkiss P. J., Marder S. R., Kippelen B., Perry J. W., (2008), “Solution-processible high-permittivity nanocomposite gate insulators for organic field-effect transistors”, *Applied Physics Letters*, 93 (1).
- [129] Yang F.-Y., Hsu M.-Y., Hwang G.-W., Chang K.-J., (2010), “High-performance poly(3-hexylthiophene) top-gate transistors incorporating TiO₂ nanocomposite dielectrics”, *Organic Electronics*, 11 (1), 81-88.

- [130] Shim H., Kumar A., Cho H., Yang D., Palai A. K., Pyo S., (2014), “Laterally-Stacked, Solution-Processed Organic Microcrystal With Ambipolar Charge Transport Behavior”, *ACS Applied Materials & Interfaces*, 6 (20), 17804-17814.
- [131] Baeg K.-J., Khim D., Jung S.-W., Kang M., You I.-K., Kim D.-Y., Facchetti A., Noh Y.-Y., (2012), “Remarkable Enhancement of Hole Transport in Top-Gated N-Type Polymer Field-Effect Transistors by a High-k Dielectric for Ambipolar Electronic Circuits”, *Advanced Materials*, 24 (40), 5433-5439.
- [132] Sharma M., Yashonath S., (2008), “Correlation between conductivity or diffusivity and activation energy in amorphous solids”, *The Journal of Chemical Physics*, 129 (14), 144103.
- [133] Sudha L., Sukumar R., Uma Rao K., (2014), “Evaluation of Activation Energy (E_a) profiles of nanostructured alumina polycarbonate composite insulation materials”, *International Journal of Materials. Mechanics and Manufacturing*, 2 (1), 96-100.
- [134] Saq'an S. A., Ayesh A. S., Zihlif A. M., Martuscelli E., Ragosta G., (2004), “Physical properties of polystyrene/alum composites”, *Polymer Testing*, 23 (7), 739-745.
- [135] Ali M., Hirai T., (2012), “Relationship between electrode polarization and electrical actuation of dielectric PVC gel actuators”, *Soft Matter*, 8 (13), 3694-3699.
- [136] Hemalatha K. S., Sriprakash G., Prasad M. V. N. A., Damle R., Rukmani K., (2015), “Temperature dependent dielectric and conductivity studies of polyvinyl alcohol-ZnO nanocomposite films by impedance spectroscopy”, *Journal of Applied Physics*, 118 (15), 154103.
- [137] Minji Kang, Kang-Jun Baeg, Dongyoon Khim, Yong-Young Noh, Kim D.-Y., (2013), “Printed, Flexible, Organic Nano-Floating-Gate Memory: Effects of Metal Nanoparticles and Blocking Dielectrics on Memory Characteristics”, *Adv. Funct. Mater.*, 23, 3503-3512.
- [138] Tanaka T., (2005), “Dielectric nanocomposites with insulating properties”, *IEEE Transactions on Dielectrics and Electrical Insulation*, 12 (5), 914-928.
- [139] Zhang C. H., Chi Q. G., Dong J. F., Cui Y., Wang X., Liu L. Z., Lei Q. Q., (2016), “Enhanced dielectric properties of poly(vinylidene fluoride) composites filled with nano iron oxide-deposited barium titanate hybrid particles”, *Scientific Reports*, 6.

- [140] Canimkurbey B., Kösemen Z. A., Çakırlar Ç., San S. E., Yasin M., Berber S., Kösemen A., (2017), “Fabrication and investigation of P3HT: PCBM bulk heterojunction based organic field effect transistors using dielectric layers of PMMA: Ta₂O₅ nanocomposites”, *Microelectronic Engineering*.
- [141] Yasin M., Tauqeer T., Karimov K. S., San S. E., Kosemen A., Yerli Y., Tunc A. V., (2014), “P3HT:PCBM blend based photo organic field effect transistor”, *Microelectronic Engineering*, 130, 13-17.
- [142] Ortiz-Serna P., Díaz-Calleja R., Sanchis M., Riande E., Nunes R., Martins A., Visconte L., (2011), “Dielectric spectroscopy of natural rubber-cellulose II nanocomposites”, *Journal of Non-Crystalline Solids*, 357 (2), 598-604.
- [143] Di C.-a., Liu Y., Yu G., Zhu D., (2009), “Interface engineering: an effective approach toward high-performance organic field-effect transistors”, *Accounts of chemical research*, 42 (10), 1573-1583.
- [144] Scheinert S., Paasch G., Hörselmann I., Herasimovich A. (2009), "Low-cost submicrometer organic field-effect transistors". "Organic Electronics", Springer.
- [145] Liao C., Yan F., (2013), “Organic semiconductors in organic thin-film transistor-based chemical and biological sensors”, *Polymer Reviews*, 53 (3), 352-406.
- [146] Torsi L., Magliulo M., Manoli K., Palazzo G., (2013), “Organic field-effect transistor sensors: a tutorial review”, *Chemical Society Reviews*, 42 (22), 8612-8628.
- [147] Chortos A., Lim J., To J. W., Vosgueritchian M., Dussault T. J., Kim T. H., Hwang S., Bao Z., (2014), “Highly stretchable transistors using a microcracked organic semiconductor”, *Advanced Materials*, 26 (25), 4253-4259.
- [148] Kösemen Z. A., Kösemen A., Öztürk S., Canimkurbey B., Yerli Y., (2017), “High mobility and low operation voltage organic field effect transistors by using polymer-gel dielectric and molecular doping”, *Materials Science in Semiconductor Processing*, 66, 207-211.
- [149] Le N. C. H., Gubala V., Clancy E., Barry T., Smith T. J., Williams D. E., (2012), “Ultrathin and smooth poly (methyl methacrylate)(PMMA) films for label-free biomolecule detection with total internal reflection ellipsometry (TIRE)”, *Biosensors and Bioelectronics*, 36 (1), 250-256.

- [150] Ukah N., Granstrom J., Sanganna Gari R., King G., Guha S., (2011), “Low-operating voltage and stable organic field-effect transistors with poly (methyl methacrylate) gate dielectric solution deposited from a high dipole moment solvent”, *Applied Physics Letters*, 99 (24), 273.
- [151] Hou X., Siow K. S., (2000), “Mechanical properties and ionic conductivities of plasticized polymer electrolytes based on ABS/PMMA blends”, *Polymer*, 41 (24), 8689-8696.
- [152] Mitra S., Shukla A., Sampath S., (2001), “Electrochemical capacitors with plasticized gel-polymer electrolytes”, *Journal of power sources*, 101 (2), 213-218.
- [153] Lee J., Kaake L. G., Cho J. H., Zhu X.-Y., Lodge T. P., Frisbie C. D., (2009), “Ion gel-gated polymer thin-film transistors: Operating mechanism and characterization of gate dielectric capacitance, switching speed, and stability”, *The Journal of Physical Chemistry C*, 113 (20), 8972-8981.
- [154] Chandra S., Sekhon S., Arora N., (2000), “PMMA based protonic polymer gel electrolytes”, *Ionics*, 6 (1), 112-118.
- [155] Tung K.-L., Lu K.-T., Ruaan R.-C., Lai J.-Y., (2006), “Molecular dynamics study of the effect of solvent types on the dynamic properties of polymer chains in solution”, *Desalination*, 192 (1-3), 380-390.
- [156] Geim A. K., Novoselov K. S., (2007), “The rise of graphene”, *Nat Mater*, 6 (3), 183-191.
- [157] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A., (2004), “Electric Field Effect in Atomically Thin Carbon Films”, *Science*, 306 (5696), 666-669.
- [158] Zhu Y., Murali S., Cai W., Li X., Suk J. W., Potts J. R., Ruoff R. S., (2010), “Graphene and graphene oxide: synthesis, properties, and applications”, *Adv Mater*, 22 (35), 3906-3924.
- [159] Balandin A. A., Ghosh S., Bao W., Calizo I., Teweldebrhan D., Miao F., Lau C. N., (2008), “Superior Thermal Conductivity of Single-Layer Graphene”, *Nano Letters*, 8 (3), 902-907.
- [160] Frank I. W., Tanenbaum D. M., van der Zande A. M., McEuen P. L., (2007), “Mechanical properties of suspended graphene sheets”, *Journal of Vacuum Science & Technology B*, 25 (6), 2558-2561.

- [161] Avouris P., Chen Z., Perebeinos V., (2007), "Carbon-based electronics", *Nat Nano*, 2 (10), 605-615.
- [162] Wei Z., Wang D., Kim S., Kim S.-Y., Hu Y., Yakes M. K., Laracuenta A. R., Dai Z., Marder S. R., Berger C., King W. P., Heer W. A. d., Sheehan P. E., Riedo E., (2010), "Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics", *Science*, 328 (5984), 1373-1376.
- [163] Jeong H. K., Jin M. H., So K. P., Lim S. C., Lee Y. H., (2009), "Tailoring the characteristics of graphite oxides by different oxidation times", *Journal of Physics D: Applied Physics*, 42 (6), 065418.
- [164] Xingyi H., Fei L., Pingkai J., Tanaka T., (2013). "Is graphene oxide an insulating material?", *Solid Dielectrics (ICSD)*, 2013 IEEE International Conference on, 904-907, June 30 2013-July 4 2013.
- [165] Borini S., White R., Wei D., Astley M., Haque S., Spigone E., Harris N., Kivioja J., Ryhänen T., (2013), "Ultrafast Graphene Oxide Humidity Sensors", *ACS Nano*, 7 (12), 11166-11173.
- [166] Eda G., Nathan A., Wöbkenberg P., Colleaux F., Ghaffarzadeh K., Anthopoulos T. D., Chhowalla M., (2013), "Graphene oxide gate dielectric for graphene-based monolithic field effect transistors", *Applied Physics Letters*, 102 (13), 133108.
- [167] Li S.-S., Tu K.-H., Lin C.-C., Chen C.-W., Chhowalla M., (2010), "Solution-Processable Graphene Oxide as an Efficient Hole Transport Layer in Polymer Solar Cells", *ACS Nano*, 4 (6), 3169-3174.
- [168] Park S., Ruoff R. S., (2009), "Chemical methods for the production of graphenes", *Nat Nano*, 4 (4), 217-224.
- [169] Dreyer D. R., Park S., Bielawski C. W., Ruoff R. S., (2010), "The chemistry of graphene oxide", *Chemical Society Reviews*, 39 (1), 228-240.
- [170] Loh K. P., Bao Q., Ang P. K., Yang J., (2010), "The chemistry of graphene", *Journal of Materials Chemistry*, 20 (12), 2277-2289.
- [171] San S. E., Okutan M., Nyokong T., Durmuş M., Ozturk B., (2011), "Temperature activated ionic conductivity in gallium and indium phthalocyanines", *Polyhedron*, 30 (6), 1023-1026.

- [172] Li D., Muller M. B., Gilje S., Kaner R. B., Wallace G. G., (2008), “Processable aqueous dispersions of graphene nanosheets”, *Nat Nano*, 3 (2), 101-105.
- [173] Xu C., Wang X., Zhu J., (2008), “Graphene–Metal Particle Nanocomposites”, *The Journal of Physical Chemistry C*, 112 (50), 19841-19845.
- [174] Chang C. W., Hon M. H., Leu I. C., (2012), “Patterns of Solution-Processed Graphene Oxide Produced by a Transfer Printing Method”, *Journal of The Electrochemical Society*, 159 (6), H605-H609.
- [175] Okutan M., Yerli Y., San S. E., Yılmaz F., Günaydın O., Durak M., (2007), “Dielectric properties of thiophene based conducting polymers”, *Synthetic Metals*, 157 (8–9), 368-373.
- [176] Wang J., Shi K., Chen L., Zhang X., (2004), “Study of polymer humidity sensor array on silicon wafer”, *Journal of Materials Science*, 39 (9), 3155-3157.
- [177] Shulga Y. M., Baskakov S. A., Smirnov V. A., Shulga N. Y., Belay K. G., Gutsev G. L., (2014), “Graphene oxide films as separators of polyaniline-based supercapacitors”, *Journal of Power Sources*, 245 (0), 33-36.
- [178] Smirnov V. A., Denisov N. N., Dremova N. N., Vol’fkovich Y. M., Rychagov A. Y., Sosenkin V. E., Belay K. G., Gutsev G. L., Shulga N. Y., Shulga Y. M., (2014), “A comparative analysis of graphene oxide films as proton conductors”, *Applied Physics A*, 117 (4), 1859-1863.
- [179] Yao Y., Chen X., Zhu J., Zeng B., Wu Z., Li X., (2012), “The effect of ambient humidity on the electrical properties of graphene oxide films”, *Nanoscale Research Letters*, 7 (1), 363.
- [180] Huang X., Zhi C., Jiang P., Golberg D., Bando Y., Tanaka T., (2012), “Temperature-dependent electrical property transition of graphene oxide paper”, *Nanotechnology*, 23 (45), 455705.
- [181] Song C. H., Kim M., Choi H. W., Kim H. J., Yang Y. S., (2007), “Conductivity Analysis of Dielectric Response in Ionic Conducting $2(K_x \cdot Li_{1-x})NbO_3 \cdot SiO_2$ Glasses”, *Journal of the Korean Physical*, 51, S71-S74.
- [182] Atyia H. E., Farid A. M., Hegab N. A., (2008), “AC conductivity and dielectric properties of amorphous $GexSb_{40-x}Se_{60}$ thin films”, *Physica B: Condensed Matter*, 403 (21–22), 3980-3984.

- [183] Okutan M., Köysal O., San S. E., Şentürk E., (2009), “Temperature dependency of impedance spectroscopy behaviors in side-chain liquid crystalline polymer”, *Journal of Non-Crystalline Solids*, 355 (52–54), 2674-2677.
- [184] Shaaban M. H., Ali A. A., El-Nimr M. K., (2006), “The AC conductivity of tellurite glasses doped with Ho_2O_3 ”, *Materials Chemistry and Physics*, 96 (2–3), 433-438.
- [185] Özer M., Altındal A., Özkaya A. R., Bulut M., Bekaroğlu Ö., (2005), “Synthesis, characterization, and electrical, electrochemical and gas sensing properties of a novel cyclic borazine derivative containing three phthalocyaninato zinc(II) macrocycles”, *Synthetic Metals*, 155 (1), 222-231.
- [186] El-Barry A. M. A., Atyia H. E., (2005), “Dielectric relaxation and AC conductivity of XS ($\text{X}=\text{Cd}, \text{Zn}$) compounds”, *Physica B: Condensed Matter*, 368 (1–4), 1-7.
- [187] Şentürk E., Okutan M., San S. E., Köysal O., (2008), “Debye type dielectric relaxation in carbon nano-balls’ and 4-DMAABCA acid doped E7 coded nematic liquid crystal”, *Journal of Non-Crystalline Solids*, 354 (30), 3525-3528.
- [188] Ben Rhaïem A., Hlel F., Guidara K., Gargouri M., (2009), “Electrical conductivity and dielectric analysis of $\text{AgNaZnP}_2\text{O}_7$ compound”, *Journal of Alloys and Compounds*, 485 (1–2), 718-723.
- [189] Bi H., Yin K., Xie X., Ji J., Wan S., Sun L., Terrones M., Dresselhaus M. S., (2013), “Ultrahigh humidity sensitivity of graphene oxide”, *Sci. Rep.*, 3.
- [190] Jin M., Jeong H.-K., Yu W. J., Bae D. J., Kang B. R., Lee Y. H., (2009), “Graphene oxide thin film field effect transistors without reduction”, *Journal of Physics D: Applied Physics*, 42 (13), 135109.
- [191] Venugopal G., Krishnamoorthy K., Mohan R., Kim S.-J., (2012), “An investigation of the electrical transport properties of graphene-oxide thin films”, *Materials Chemistry and Physics*, 132 (1), 29-33.

BIOGRAPHY

Betül CANIMKURBEY was born in Erzurum, 1987. She had lived in Bursa, till 2006. She started Physics Department in 2006 and Civil Engineering Department in 2007 at Atatürk University. She has taken her bachelor degree in 2010 with high honor degree and she graduated 2013 from Civil Engineering. Right after bachelor degree she has started to study in Physics Department as master student in Atatürk University. She was awarded with TUBITAK 2211/A National Scholarship for PhD Student by TUBITAK. She has worked as a research assistant at Gebze Technical University Graduate School of Natural and Applied Sciences Department of Physics in 2012-2017. Now, she is a research assistant at Amasya University.