ELECTRIC FIELD EFFECT IN “METALLIC” POLYMERS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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*****

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ABSTRACT

The charge transport properties of the “metallic” polymer, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS), with a conductivity around 30 S/cm are studied in this thesis. The PEDOT:PSS is incorporated into a field effect transistor (FET) structure as an active component. Considering the screening effect of metals, it is unexpected to observe a dramatic conductance change in PEDOT:PSS under the application of a gate electric field. The conventional FET model is used to further investigate this phenomenon. Though the current-voltage (I-V) characteristics of PEDOT:PSS devices are similar to the conventional field effect transistors (FETs), the extracted field effect mobility ($\mu_{\text{FET}}$) from I-V curves is two orders of magnitude larger than that estimated from the conductivity. Further investigating the I-V curves, a hysteresis behavior is observed and varies with drain voltage sweeping rate. This hysteresis phenomenon suggests ion motion is involved in the PEDOT:PSS conductance suppression. Since the structure of the metallic polymers is viewed as metallic ordered regions embedded in poorly conducting disordered media, charge carriers conduct electricity by hopping over or resonant tunneling through the localized states in the disordered regions. Therefore, several experiments are performed to understand the origin of the electric field penetration inside the metallic polymer.
Using the transient current measurements, the relationship between inserted ion charges and PEDOT:PSS conductance variation is examined. Around 2% replacement of hole charges on the PEDOT:PSS backbone with inserted ionic charges enables the modulation of the conductance of PEDOT:PSS by three orders of magnitude. This small fraction of charge compensation of counterions by inserted ion charges suggests a percolation phenomenon for PEDOT:PSS conduction suppression.

The role of inserted ions is further investigated by measurements of the temperature dependence of this FET structure. In the presence of inserted ions, the \textit{in situ} conductivity measurements indicate that the degree of disorder in the poorly conducting regions of PEDOT:PSS increases and the observed field effect is a bulk effect, which supports the percolation phenomenon; the \textit{in situ} ESR measurements done simultaneously show no apparent change in the density of states at the Fermi level \((N(E_F))\) in the ordered regions of PEDOT:PSS.

Combining the results in the disordered regions, the ordered regions and the percolation phenomenon lead to the conclusion that the inserted ions interacting with the counterions initially present in the disordered regions increase the hole hopping distance resulting in a conductor-nonconductor transition.
To my parents,
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definitions, such as “v” or “fantasy.”
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   Electron Paramagnetic Resonance
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<td>Conducting polymer</td>
</tr>
<tr>
<td>D</td>
<td>Drain electrode</td>
</tr>
<tr>
<td>DBSA</td>
<td>Dodecylbenzensulfonic acid</td>
</tr>
<tr>
<td>ECFET</td>
<td>Electrochemical field effect transistor</td>
</tr>
<tr>
<td>EG</td>
<td>Ethyleneglycol</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>JFET</td>
<td>Junction field effect transistor</td>
</tr>
<tr>
<td>G</td>
<td>Gate electrode</td>
</tr>
<tr>
<td>G-S</td>
<td>Gate-Source</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<tr>
<td>IMT</td>
<td>Insulator-metal transition</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<td>MOSFET</td>
<td>Metal-oxide-semiconductor field effect transistor</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>OA</td>
<td>Optical adhesive</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly-3,4-ethylenedioxythiophene</td>
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<td>PEDOT-PSS</td>
<td>Poly-3,4-ethylenedioxythiophene doped with polystyrene sulfonic acid</td>
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<td>PSSA</td>
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<tr>
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<tr>
<td>PEO</td>
<td>Polyethylene oxide</td>
</tr>
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<td>S</td>
<td>Source electrode</td>
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CHAPTER 1

INTRODUCTION

The electric field effect phenomenon in semiconductors exhibits both interesting physics and practical applications. Upon applying an electrical potential to an electrode which is spatially separated from a semiconductor, the physical properties of the semiconductor become electric-field controlled. By incorporating this electric-field controlled phenomenon into a device design, numbers of high-tech products relying on microelectronics have been developed. The well known silicon (Si) technology is a typical example utilizing the benefits of the field effect phenomenon. However, the mature Si technology involves several costly process steps such as doping, oxide growing, photolithography, metal deposition and so on. Aiming to reduce the production cost and extend the technology benefits, the field effect phenomenon in organic material based devices has been considered promising to promote the current science. The practical potential of organic materials takes advantage of easy processing, large area application, and lightweight [1-5], and these advantages provide more degrees of freedom to upgrade the current technology. Therefore, organic based electronics are promising for next-generation electronics.


1.1 Application of Electric Field Effect in Organic Semiconductors

The earliest studies of electrical and optical properties of organic semiconductors on phthalocyanines [6] were carried out in 1948 by D. D. Eley [7] in England and A. T. Vartanyan [8] in Russia. It was not until the 1980s that organic semiconductors were incorporated into a thin film transistor. The initial demonstration of organic thin film transistors (OTFTs) based on small molecules (1984) [9] and conjugated polymers (1983 and 1986) [10,11] was followed by impressive improvements in performance during the past decade giving encouragement to this new direction. In 1990, Garnier et al. [12] reported the first all-polymer transistor. Four years later, Garnier et al. [13] reported the first all-polymer transistor by screen-printing technology, and by the end of 2000, large scale and all-polymer integrated circuits [14] and complementary integrated circuits [15] had been demonstrated. These demonstrations of plastic electronics illustrate the potential for inexpensive alternatives to amorphous silicon thin film transistors.

Both field effect mobility ($\mu_{FET}$) and on/off ratio are the key parameters in determining transistor performance. The $\mu_{FET}$ reveals the sensitivity of charge carriers to the electric field and the on/off ratio is important in providing the contrast for device status. Small molecules such as pentacene, $\alpha, \omega$-dihexyl-sexithiophene, and $\alpha$-sexithiophene have been used as active components in transistors. The highest $\mu_{FET}$ reported to date in this category is 1.5 cm$^2$/Vs [16] in pentacene which is comparable to that of amorphous Si-based FETs. For conjugated polymers, poly(3-sexithiophene) yield the highest $\mu_{FET}$ at 0.1 cm$^2$/Vs [17].
The $\mu_{\text{FET}}$ for an organic material can vary two orders of magnitude depending on material crystallinity, film morphology, and metal-organic interface. Generally speaking, small molecules have higher crystallinity than polymers. Thus, the electron wave functions can be delocalized along the well stacked $\pi-\pi$ orbital resulting in higher mobility. Obtaining high quality organic films is thus a top priority. The appearance of grain boundaries in the film or rough film surface generates charge traps decreasing the $\mu_{\text{FET}}$. Therefore, proper organic film deposition conditions and subsequent device process routes are keys to achieve high crystalline films and high device performance. Unfortunately, due to the internal properties of organic materials, the $\mu_{\text{FET}}$ of organic field effect transistors (OFETs) is still two to three orders of magnitude lower than that of crystalline-Si based FETs ($\mu_{\text{FET}} \sim 10^2 - 10^3 \text{cm}^2/(\text{Vs})$).

The FETs and OFETs studied belong to normally “off” devices which do not conduct current in the zero gate bias state: applying a gate voltage causes the channel conductance to increase. In 2001, researchers tried to construct OFETs working the other way round which is normally “on” devices. For normally “on” devices, the conducting form of the polymers is considered as the channel material. To obtain the conducting form of polymers, dopants are intentionally introduced. Unlike the inorganic dopants substituting the host atoms, organic dopants are interstitially doped. Since polymers are porous matrices, the anion dopants stay inside these pores and modulate the electronic potential of the polymer backbone. Mobile charge defects (solitons, polarons, and bipolarons) are generated and the Peierls gap [18] is quickly suppressed resulting in increased conductivity. A fully doped conducting polymer can hold one charge for every two ring
in the polyaniline system and every three rings for polythiophene derivatives. The resource for the broad range overview of electronic polymers and their application can be found in Ref. 19.

1.2 Application of Field Effect in Metallic Polymers

The conductivity of conjugated polymers can be altered by the reversible doping-dedoping process. By driving a conjugated polymer from oxidized state to reduced state by means of redox reactions, an apparent color change of the polymer is obtained which is known as the electrochromic effect [20,21]. The electroactive and conductive polymers with electrochromic properties have been studied for use in solid-state smart windows [22-29]. The first attempt to establish an electrochromic polymer in a window system for cars was made with polyaniline in combination with WO₃ [30, 31] by using a capacitor structure. In 1989, Scholh et al. [32] utilized the chemical response of polycrystalline WO₃ to fabricate pH-sensitive microelectrochemical transistors. For organic materials, Thackeray et al. controlled conductivity of electo-synthesized poly(3-methylthiophene) by employing transistor typed devices [33]. Both pure-chemical (by using oxidant and reductant) and electro-chemical (ion or charge transfer via aqueous electrolyte) redox processes were used in controlling the conductivity of poly(3-methylthiophene). By electrochemically oxidizing poly(3-methylthiophene), there is a clearly change in the absorption spectra in the visible range and this substantial change supports the redox process.
Three terminal fully solid-state devices using fully-doped PEDOT:PSS as active components were reported in 2001. A. G. MacDiarmid [34] reported the first studies of completely organic FETs based on fully-doped PEDOT. Lu et al. [35] and Epstein et al. [36] further investigated those normally "on" FETs made from the organic conductor, PEDOT:PSS. The change in the conductance of PEDOT:PSS channel is unexpected because of the screening effect in conductors [36]. The Debye screening length for such highly-doped organic conductors is less than 1 nm which prevents the penetration of the external electric field to deplete the carriers effectively. According to Okuzaki et al's [37] report, the field effect mobility of the charge carriers extracted from the saturation region of I-V curves is 170 cm$^2$/Vs. For the heavily doped PEDOT:PSS system with a charge carrier concentration around $10^{21}$ cm$^{-3}$ and conductivity around 30 S/cm, the mobility ($\mu$) is around 0.2 cm$^2$/Vs) from $\sigma = n e \mu$, which is much less than the value obtained by Okuzaki et al. at room temperature. In addition to the PEDOT:PSS system, this field effect phenomenon has been reported in the metallic polymers including polypyrrole [36,38,39] as well.

Nilsson et. al. [40] reported electrochemical field effect transistors (ECFETs) made from PEDOT:PSS. According to Nilsson et. al. [40], the device operation is based on reversible electrochemical switching of the conductivity in PEDOT:PSS between oxidized and reduced states as electrochromic windows [41]. However, instead of using large ion-populated electrolyte between channel and gate for electrochemical transistors, fully solid-state devices with less ion-populated insulating layer give another mechanism of device operations.
Kim [42] showed that the main process to control the conductivity of fully solid-state PEDOT:PSS field effect system is not from oxidation and reduction of PEDOT backbone. In a redox process, there is a dramatically change in optical absorption spectra in the UV-visible region. However, absorption spectra in the UV-visible range for PEDOT:PSS transistors show few percent change parallel with the a dramatic PEDOT:PSS conductance modulation. Instead of UV-visible range, dramatic changes in IR reflectance spectra indicate that the modulation of PEDOT:PSS conductance is due to charge localization-delocalization transition.

1.3 Overview of Dissertation

In this dissertation, I will present a fundamental study of the observed field effect phenomenon as well as issues for designing potential applications using a metallic polymer, PEDOT:PSS, based fully solid-state devices. To probe the observed field effect phenomenon in a hole-ion coupling system, several studies such as I-V characteristics, time dynamics transient processes, electron spin resonance (ESR) and several kinds of field-effect in situ temperature dependent measurements were performed.

The fundamental background knowledge needed for this dissertation is given in Ch. 2. Ch. 3 summarizes all nine types of devices used and the experimental circuit layouts for this study. Detailed device processing is included as well as the data acquisition. Ch. 4–Ch. 6 present the experimental results for these devices. The phenomenological examination and room temperature device characterization are discussed in Ch. 4. The discussion includes obtained I-V hysteresis characteristics, slow switching times, ion...
hopping distances, system relaxation dynamics, and the role of leakage current. A percolation phenomenon is obtained from the leakage current analysis.

The temperature dependence study of the field effect structure is summarized in Ch. 5. In Ch. 5, field effect in situ temperature dependent time dynamic measurements and four-probe conductivity measurements are discussed. The activation energy of ions inside the different dielectric materials is compared. The diffusion coefficient of a known ion, Li⁺, is estimated from the drain current recovering process. Further, the drain current recovery process does not follow the conventional power law diffusion. The experimental result shows a dimensionality of 1.36 for ion diffusion inside PEDT:PSS. The in situ temperature dependent four–probe conductivity measurements provide further insight into the physical mechanisms. The increase of carrier activation energy with the reduction of off-state PEDOT:PSS conductivity suggests that the observed field effect phenomenon accounts for the bulk effect as well as increasing disorder inside the PEDOT:PSS system.

ESR measurements further clarify the detail working principle which is addressed in Ch. 6. Results from comparing the polaron concentrations indicate that the charge transfer between PEDOT:PSS and inserted ions are not the dominant processes. In addition, there is almost no change in the $N(E_F)$ during gate electric field which indicates the role of inserted ions. Further, the change of ESR linewidths when the gate voltage is applied suggests the reduction of interaction paths between conduction electrons and localized spins due to the replacement of hole charges by ions in the disordered region.
Based on the physical quantities obtained in Ch. 5, design issues for practical applications of metallic polymer FETs are addressed in Ch. 7. For example, non-Volatile RAM has been demonstrated to store information up to an hour.

Ch. 8 concludes with the results obtained from various measurements. A phenomenological model for charge transport in the presence of ions inside metallic polymer is proposed. A brief summary of device design issues will be addressed following by suggestions for future work.
CHAPTER 2

THEORETICAL BACKGROUND

2.1 Effect of Electric Field in Conducting Media

2.1.1 Screening Effect

Screening is the damping of electric fields caused by the presence of mobile charge carriers. Debye and Huckel [43] first dealt with a fixed point charge embedded in a fluid of electrons. Assuming the electron fluid is in a background of heavy and positive charged-ions which can be approximated as a uniform background charges. Considering a positive charge $Q$ is introduced inside an electron fluid at a fixed position $r$. The associated charge density is $Q\delta(r)$, where $\delta(r)$ is the Dirac delta function. This positive charge will attract electrons, creating a surplus of negative charges in its neighborhood. After the system reaches thermal equilibrium, the changes in the electron density ($\Delta \rho$) and electric potential ($\Delta \phi$) satisfy Maxwell’s equation

$$-\nabla^2(\Delta \phi) = \frac{1}{\varepsilon_0}(Q\delta(r) - e\Delta \rho),$$

(2.1)

where $\varepsilon_0$ is the dielectric constant.
There are two possible approximations to obtain the induced charges, the Debye-Huckel approximation and Fermi-Thomas approximation. Debye-Huckel approximation is valid at high temperatures while the Fermi-Thomas approximation is good for low temperatures.

**Debye-Huckel approximation [43]:**

In this approximation, the system is in thermal equilibrium at temperature $T$ which the fluid particles obey Maxwell-Boltzmann statistics. At each point in space after $Q$ introduced, the density of electrons has the form

$$\rho(r) = \rho_0 \exp\left[\frac{e\phi(r)}{k_B T}\right]$$

(2.2)

where $k_B$ is the Boltzmann factor. Expanding $\exp\left[\frac{e\phi(r)}{k_B T}\right] \approx 1 + \frac{e\phi(r)}{k_B T} + \ldots$ and $\phi(r) = \phi^0(r) + \Delta\phi(r)$, where $\phi^0(r)$ is the potential at position $r$ before $Q$ is introduced, one can obtain

$$e\Delta\rho \approx \varepsilon_0 k_0^2 \Delta\phi(r)$$

(2.3)

from eq. (2-2), where $k_0 = \sqrt{\frac{e^2 \rho_0}{\varepsilon_0 k_B T}}$. The associated Debye length $\lambda_D = 1/k_0$ is the screening length of the electric field.

**Fermi-Thomas approximation [44]:**

In Fermi-Thomas approximation the system is maintained at a constant chemical potential ($\mu$) at low temperature. Thus,

$$\Delta\mu = \Delta E_k \text{ (Kinetic energy)} - e\Delta\phi = 0.$$  

(2.4)
At extremely low temperatures, $T \ll T_F$ (Fermi temperature), the behavior of the electrons comes close to that of a free electron gas. Therefore, the density of electrons and Fermi energy $(E_F)$ are

$$\rho(2\pi)^3 = \frac{4}{3}\pi k_F^3, \quad E_F = \frac{\hbar^2 k_F^2}{2m}.$$  

(2.5)

By using the perturbation method to the first order,

$$\Delta \rho \approx \frac{3\rho}{2E_F} \Delta E_F.$$  

(2.6)

Plugging Eq. (2-6) into Eq. (2-4), one can obtain

$$e\Delta \rho \approx \varepsilon_0 k_0^2 \Delta \varphi(r),$$  

(2.7)

where $k_0 = \sqrt{\frac{3e^2 \rho}{2\varepsilon_0 E_F}}$ is called the Fermi-Thomas screening wave vector. The Fermi-Thomas approximation results from free electron gas which is a model for non-interacting electrons. Therefore, this model is only valid when the electron density is high and the particle interaction are relatively weak.

By plugging Eq. (2-3) and Eq. (2-7) into Eq. (2-1), we can get the screened Poisson Equation:

$$\left[\nabla^2 - k_0^2\right] \rho(r) = -\frac{Q}{\varepsilon_0} \delta(r).$$  

(2.8)

The solution for Eq. (2-8) is

$$\varphi(r) = \frac{Q}{4\pi\varepsilon_0} \frac{1}{r} e^{-k_0 r},$$  

(2.9)
which is called screened Coulomb potential. The strength of the Coulomb potential is damped with the Debye or Fermi-Thomas wave vector.

2.1.2 Electrochemical Cell

The discussions in this section are all based on Bard and Faulkner [45]. A simple electrochemical cell can be made by placing two metallic electrodes into an electrolyte solution where either a chemical reaction uses or generates electronic current. Electrochemical cells which generate an electronic current are called voltaic cells or galvanic cells which are the types for common batteries. Other electrochemical cells that require an external driven voltage to drive the chemical reaction which does not occur spontaneously are called electrolytic cells.

When a given potential is applied to the electrochemical cell, there are two types of processes going on one after another. In the initial small voltage window, there is no charge transfer reaction that occurs between the electrode-solution interfaces. Processes such as adsorption, desorption and changing of the structure of the electrode-solution interface are called nonfaradaic processes. After the small voltage window for nonfaradaic processes, chemical reaction starts to take place. In this case, electron transfer causes reduction and oxidation to occur which are called faradaic processes.

2.1.2.1 Electrical Double Layer

When two metal electrodes are immersed inside the solution, the metal-solution interface acts as a capacitor with a positive $q^M$ on the metal and the opposite charge $q^S$ in
the solution near the vicinity of electrode surface. At all times, \( q^M = -q^S \). The whole array of charged species and oriented dipoles existing at the metal-solution interface is called the electrical double layer. The formation of the electrical double layer does not involve charge transfer across the electrode-solution interface. Thus, the double layer formation is a nonfaradaic process. The electrode-solution interface is characterized by a double layer capacitance, \( C_d \), which is a function of the potential applied.

Fig 2.1 shows the potential profile across the double-layer region in the metal-electrolyte interface. \( \phi^M \) and \( \phi^S \) stand for the potentials on metal and electrolyte, respectively. The major potential dropping occurs at the double layer.

![Diagram of potential profile across the double-layer region](image)

**Figure 2.1:** Potential profile across the double-layer region (after [45]).
2.1.2.2 Nernst Equation

A chemical reaction takes place when electrons transfer across the metal-electrolyte interface. Consider the reduction of a species O at cathode: \[ O + ne \rightarrow R. \]
The reduction rate of O associated with the applied potential \( V \) can be described by the Nernst equation for a half-reaction. The reaction rate constant \( K \) is related to the concentration of O \( (C_O) \) and R \( (C_R) \) through \( K = \frac{C_R}{C_O} \). And the potential dependent reaction rate is given by the Nernst equation [45]:

\[
V = V^{\theta} - \frac{RT}{nF} \ln \frac{1}{K},
\]

where \( F \) is the Faraday constant and \( V^{\theta} \) is the formal potential which is adjusted form of the standard potential, taking into account the chemical effects of the medium.

2.1.2.3 Metal-electrolyte Interface

The thermal equilibrium across the metal-electrolyte involves both electronic states of the metal and ion in the electrolyte. A term electrochemical potential \( (\zeta) \) which is the sum of the electrical potential \( (\phi) \) and chemical potential \( (\mu) \) is introduced to characterize the charge transport of the system. The electrochemical potential aligns throughout the system under equilibrium. Fig. 2.2 shows the band diagram of the potential alignment across the metal-electrolyte interface assuming an ideal case where no chemical potential difference occurs for either phases. Fig. 2.2 (a) shows the equilibrium condition when the metal and the electrode are brought in contact \( \zeta^M = \zeta^{el} \). By applying a bias \( V \) across the interface, the electrical potential energy is substantially reduced in the electrolyte resulting in a lowering of the electrochemical potential energy \( \zeta^{el} \) in electrolyte phase (see
Fig. 2.2 (b)). In this nonequilibrium condition, electrons will transfer from high $\zeta^M$ to low $\zeta^{el}$ phase driven by the electrical potential gradient until the electrical potential aligns on both sides. In the new equilibrium state (see Fig. 2.2 (c)), the chemical potential in the electrolyte phase increases due to electrons transferred from metal electrode and the chemical potential gradient balances out the drift current driven by electrical potential difference.

Figure 2.2 : Energy band diagram across metal – electrolyte interface. (a) equilibrium, (b) nonequilibrium with bias $V$ applied, (c) equilibrium with bias $V$ applied.
2.1.2.4 Cottrell Equation

The diffusion current generated by ion diffusing to the metal electrode can be mathematically obtained from the diffusion equation. Assuming the ion concentration profile of ions is \( C_o (x, t) \), one can write the linear diffusion equation as

\[
\frac{\partial C_o (x,t)}{\partial t} = D_o \frac{\partial^2 C_o (x,t)}{\partial x^2}
\]  

(2.11)

under the following boundary conditions

\[
C_o (x,0) = C_o^∗
\]  

(2.12)

\[
\lim_{x \to \infty} C_o (x,t) = C_o^∗
\]  

(2.13)

\[
C_o (0,t) = 0 \quad (\text{for } t > 0),
\]  

(2.14)

where \( D_o \) is the diffusion coefficient of ions. Eq. (2.12) expresses the homogeneity of the solution before the experiment starts, Eq. (2.13) is an assertion that regions distant from the electrode are unperturbed by the experiment, and Eq. (2.14) is the condition at the electrode surface, and it embodies the particular experiment here. The solution for Eq. (2.11) under the boundary conditions Eq. (2.12), (2.13) and (2.14) is [45]

\[
I(t) = nFAC_o^∗ \sqrt{\frac{D_o}{\pi t}} = K t^{-1/2},
\]  

(2.15)

where \( F \) is the Faraday constant, \( A \) is the electrode surface area and \( K \) is a constant. The power law transient current relationship is widely used in electrochemistry for a diffusion-controlled process which is the same to the conventional diffusion process except a different prefactor, \( K \).

However, the power relationship in Eq. (2.15) places a limitation on describing the atomic/ionic diffusion toward actual solid electrode surfaces which are rough, porous, or
partially blocked, etc., due to the complicated and nonuniform current density distribution on the electrode surface. In this case, the current–time (I-t) is expressed as the generalized Cottrell equation [46],

\[ I(t) \propto t^{-\alpha} \]

with \( \alpha = \frac{D_f - 1}{2} \), (2.16)

where \( D_f \) is fractal dimension of the electrode structure.

2.2 Operation Principle of Conventional Metal – Oxide- semiconductor Field Effect Transistors (MOSFETs)

2.2.1 Introduction to Conventional FETs

There are several architectures in the field effect transistor family such as junction field effect transistor (JFET), metal-semiconductor field effect transistor (MESFET), and metal-oxide field effect transistor (MOSFET). The structures of these three kinds of FETs are shown in Fig. 2.3. In a JFET, the resistance of a semiconductor channel is modulated between two p-n junctions where both the p+ regions are connected to a gate electrode (G), which are kept at the same voltage. When the gate voltage is 0 V, a current can flow from the source (S) to the drain (D) in the n doped region with the application of a source to drain voltage. When a negative gate voltage is applied to the gate electrode, negative charge carriers in the n doped region are repelled by the negative charge induced on the gate electrode resulting in a positive space charge region forming below the gate. At a sufficiently high gate voltage, the S/D current can be turned off [47]. MESFETs are similar devices to JFETs but replace the p-n junction with a metal-
semiconductor Schottky barrier. However, due to the limitations of fabrication techniques, both JFETs and MESFETs are less preferred architectures. The architecture with a metal gate electrode separated from the semiconductor by an insulator is preferable. The term, MOSFETs, arises from using an oxide as the gate insulator. In an ideal MOSFET, almost no current flows between S/D at $V_G = 0$ V. As a positive voltage is applied to the gate electrode, the positive charges deposited on the gate will attract electrons in the lightly p doped semiconductor to the interface. Then, a continuous carrier path is formed between the two n$^+$ doped S/D regions and the MOSFET is turned on [47].

![Figure 2.3: The cross-sectional views of (1) JFET, (b) MESFET, and (c) MOSFET.](image)

Up to now, the majority of MOSFETs are fabricated on silicon wafers. Usually the manufacturer starts with either p-doped or n-doped silicon wafers having carrier
concentration around $10^{15}$ to $10^{16}$ cm$^{-3}$. The room temperature carrier concentration for intrinsic silicon is $1.5 \times 10^{10}$ cm$^{-3}$ [47].

2.2.2 Ideal MOS Capacitor

A MOSFET can operate in depletion, accumulation or inversion mode. At the heart of the MOSFET is the metal-oxide-semiconductor (MOS) capacitor which determines MOSFET operation. Take a p-type semiconductor with doping concentration $N_a$ and dielectric constant $\epsilon_s$ for example, the energy band diagram of a MOS structure after contacting is shown as Fig. 2.4 (a) with the assumption of no work function difference between metal and p-type semiconductor. Here, the modified work functions, $q\phi_m$ and $q\phi_S$, are used to for metal and semiconductor for convenience. When $V_G < 0$, the electrons are deposited on the metal and the equal amount of net holes are expected to accumulate at the semiconductor-oxide interface which is known as accumulation mode resulting in hole conduction. Since the applied negative potential depresses the electrostatic potential of the metal relative to the semiconductor, the electron energies are raised an amount of $q|V_G|$ in the metal relative to the semiconductor. As a result, the Fermi level ($E_F$) in the metal lies above the one in the semiconductor. When $V_G > 0$, the semiconductor is in a lower potential state leading to rising the Fermi level. The positive charges on the metal tend to deplete the holes near the metal-semiconductor interface creating a space-charge region. As the gate potential is further increased, a greater voltage drop will occur at the semiconductor-oxide interface. At $V_G = V_T$ (threshold voltage), the intrinsic Fermi level ($E_i$) at the interface will lay below the Fermi level with
Figure 2.4: Band diagram for idea MOS structure
energy $2q\phi_F$ lower than that in the bulk. At this point, the charge carrier polarity of the conducting channel is strongly reverse which the inversion mode starts. If we consider the work function difference of the metal and semiconductor ($\phi_{ms}$), we can express the threshold as

$$V_T = \phi_{ms} + 2\phi_F - \frac{Q_d}{C_i},$$

(2.17)

where $Q_d$ and $C_i$ stands for the amount of fixed charges in the depletion region and capacitance of insulator, respectively. And $Q_d$ can be obtained via

$$Q_d = -q N_a W_m,$$

(2.18)

where $W_m$ is depletion width of the semiconductor. And $W_m$ can be found through

$$W_m = \sqrt{\frac{2\varepsilon_s \phi_s}{qN_a}},$$

(2.19)

where $\phi_s$ is the potential difference between the interface and bulk of the semiconductor.

### 2.2.3 Output Characteristics of MOSFETs

The applied gate voltage can be written as

$$V_G = \phi_{ms} - \frac{Q_s}{C_i} + \phi_s,$$

(2.20)

where $Q_s$ is the charges induced within the semiconductor. The induced charges $Q_d$ is composed of mobile charge $Q_n$ and fixed charge $Q_d$. Therefore, mobile charges in the channel can be found from Eq. (2.20):

$$Q_n = -C_i [V_G - (\phi_{ms} + \phi_s - \frac{Q_d}{C_i})]$$

(2.21)
with an $V_D$ applied, the voltage at a distance $x$ away from the source in the channel is $V_x$.

The fixed charge $Q_d$ is position dependent and can be written as

$$Q_d = Q_d(x) = -q N_a W_m = -\sqrt{2q \varepsilon_s N_a (2\phi_F + V_x)}.$$  \hspace{1cm} (2.22)

Thus, the mobile charge under strong inversion can be written as

$$Q_n(x) = -C_i [V_G - \phi_{ms} - 2\phi_F - V_x - \frac{Q_d(x)}{C_i}].$$ \hspace{1cm} (2.23)

Using an approximation by neglecting the variation of $Q_d(x)$ with bias $V_x$, Eq. (2.23) can be simplified as

$$Q_n(x) = -C_i [V_G - V_T - V_x].$$ \hspace{1cm} (2.24)

The drain current $I_D$ can be obtained based on the simple relation $I_D = V_G$, where $G$ is the conductance. So, we have

$$I_D = \mu |Q_n(x)| \frac{dV_x}{dx} W,$$

and $W$ and $\mu$ are the channel width and surface mobility, respectively. Integrate both sides of Eq. (2.19), we can get a complete relationship of $I_D(V_G, V_D)$ in linear regime:

$$I_D dx = (\mu |Q_n(x)| W) dV_x$$

$$\int_0^L I_D dx = \int_0^{V_D} (\mu |Q_n(x)| W) dV_x$$

$$I_D = \frac{\mu W C_i}{L} [(V_G - V_T)V_D - \frac{1}{2} V_D^2].$$ \hspace{1cm} (2.26)

The maximum $I_D$ in Eq. (2.26) can be achieved when $V_D = V_G - V_T$. In this case, one can obtain $I_D(V_G, V_D)$ in the saturation regime:
saturation regime: 
\[ I_{D(sat)} = \frac{W}{2L} \mu C_i (V_G - V_T)^2 = \frac{W}{2L} \mu C_i V_{D(sat)}^2 \] (2.27)

A typical I-V characteristic for a MOSFET includes both linear and saturation regions as in Fig. 2.5. One can extract \( \mu_{FET} \) from the I-V characteristic in both the linear and saturation regions via:

**Linear regime**
\[ \mu_{FET} = \frac{L}{WC_i} \frac{1}{V_G - V_T} \frac{\partial I_D}{\partial V_D} \] (2.28)

**Saturation regime**
\[ \mu_{FET} = \frac{L}{WC_i} \frac{1}{V_G - V_T} \frac{\partial I_{D(sat)}}{\partial V_G} \] (2.29)

Figure 2.5: Typical I-V characteristic for a MOSFET (after [48]).
2.3 Electronic State of Conducting Polymers

Polymers are plastics made of carbon, hydrogen, oxygen and/or silicon binding together into many repeat units to form a long chain. Polyethylene (see below) has the simplest polymer structure with repeat unit of -(CH$_2$)$_x$-, where the subscript $x$ denotes the repeating times. Conjugated polymer belongs to a special class of polymer which can be chemically doped to exhibit the property of electronic conduction resulting in conducting polymer. All conducting polymers are conjugated polymers. Unlike polyethylene, the conjugated polymers are built upon periodic single-double alternating carbon–carbon bondings on the backbone due to dimerization. Polyyacetylene (CH)$_x$ (see Fig. 2.7) has the simplest form among all conjugated polymers. Because of the different possible arrangements of the carbon atoms, one can obtain trans- or cis-polyacetylene.

![Chemical structure of polyethylene.](image)
2.3.1 Overview of Conducting Polymers (CPs)

Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shrikawa began their work on CPs by studying polyacetylene \((\text{CH})_x\). The conductivity of \textit{trans}-polyacetylene can be varied through a range of 11 orders by introducing a small amount of dopants such as chlorine, bromine, iodine, arsenic pentafluoride, or \(\text{NH}_3\) to the polymer \([49]\). Due to synthesis flexibility, various kinds of organic groups can replace the hydrogen atoms in \((\text{CH})_x\) \([50]\). Thus, a number of CP families in the pristine forms have been created (see Fig. 2.8) \([51]\).

As seen in Fig. 2.8, these polymers all have in common a conjugated backbone with \(P_Z\) orbitals overlapping throughout the chain which is called a \(\pi\)-conjugated network. From the possible bonding structures, the ground state of the conjugated polymers can be degenerate such as \textit{trans}-polyacetylene. Because there is no electronic energy differences between two dimerized bonding structure \(1\text{=}2\text{=}3\text{=}4\text{=}5\text{=}6\text{=}7\) (A phase) and \(1\text{=}2\text{=}3\text{=}4\text{=}5\text{=}6\text{=}7\) (B phase), where \(1,2,\ldots,7\) denote carbon atoms and \(-\text{/}=-\) stands for single/double bonds. But for \textit{cis}-polyacetylene, the ground state energies are different for A and B phases. The wave function overlapping feature of the unhybridized \(P_Z\)
Figure 2.8: Chemical structures of several conjugated polymers (adapted from [51]).
the chain axis. However, CPs in the pristine forms are either insulators or semiconductors due to Peierls instability [52] in one-dimensional systems. According to Bloch Theory, the conduction band is partially filled in a periodic lattice in the case of one free electron per atom. However, in one-dimensional CP systems, when the band is half-filled, the tendency toward spontaneous symmetry breaking is particularly strong and the lattice distortion leads to pairing the successive sites along the chain called dimerization. The distortion of lattice opens up an energy gap at the Fermi surface resulting in a lowering of the electronic energy of the occupied states and stabilizing the distortion. Therefore, the Peierls instability changes the periodicity of the lattice resulting in splitting one metallic band into two subbands, a filled valence band and an empty conduction band. Thus, there is no intrinsic one-dimensional metal in a CP family.

By introducing dopants into a CP system, the conductivity of the pristine electronic polymers can be modified from insulating regime ($\sim 10^{-10}$ S/cm) to metal regime ($4 \times 10^4$ S/cm [53,54,58]), comparable to the conductivity of good metals (e.g., $5.95 \times 10^5$ S/cm for copper at room temperature [55]). The conductivity of electronic polymers increases as the doping level increases [56-60]. The doping processes in polymers are very different from the substitutional doping process in inorganic semiconductors. In polymers, the doping atomic or molecular ions are positioned interstitially between polymer chains to donate charges or accept charges from the polymer backbone. In this case, the dopants are not bound but coulombically attracted to the polymer backbone. In some cases, the dopants are covalently bound to the polymer [61] to form copolymer which is called self-doping. Therefore, by using different doping techniques, new electronic structures are
formed depending on various dopants, doping level, process routes, and degree of disorder [62,63].

The detail in chemically doping the polymer systems is very different from that of traditional diffusion doping in semiconductors. Atoms in inorganic semiconductors are covalently bonded together by sharing their outer shell electrons (four electrons) in $sp^3$ hybridized orbital format with their neighboring atoms to form a periodic rigid lattice structure. All available charges fill up the valence band after hybridization and leave the conduction band empty. By replacing the host atoms with III/V group elements, vacancies/electrons are introduced to host lattice. Those vacancies/charges are loosely coulombically bound to the dopants which introduce the acceptor/donor levels close to valence/conduction band. Mobile charges are supplied through the thermal excitation of these artificial defects. For a soft polymer system, adding positive or negative charges into a polymer chain does not simply begin to fill the conduction band (Lowest Unoccupied Molecular Orbital or LUMO) or valence band (Highest Occupied Molecular Orbital or HOMO) causing metallic behavior immediately. The strong electron (hole)-phonon interaction causes distortions of bond length nearby the doped charged [50]. The electronic structure of the local bond length distortion can not be understood as introducing a defect level inside the forbidden bandgap. For a polymer with a degenerate ground state, charges added to the polymer backbone at low doping levels are stored in charged soliton and polaron states [64,65,66] while charged polarons or bipolarons for nondegenerate systems [67]. At high doping levels for degenerate polymers, the soliton energy level will overlap with the filled valence band and empty conduction band,
leading to conducting polymers [68,69]. In the case of nondegenerate polymers, high
doping results in the formation of a polaron lattice or electrically conducting, partially
filled energy band due to the polarons mutual interaction [70,71] which is different from
the traditional semiconductor doping results. Therefore, polarons are important at low
doping levels and for doping into a highly conducting state (a polaron lattice with partial
filled band forms). Bipolarons or paired polarons are formed in less-ordered regions of
doped polymers [72].

By the improvement of polymer conductivity through chemical doping, many
traditional signatures of an intrinsic metallic nature have become apparent such as
negative dielectric constant, a Drude metal response, temperature-independent Pauli-
susceptibility, and a linear dependence of thermoelectric power on temperature. The
conductivities of highly conducting polymers comparable to traditional metals generally
decrease as the temperature decrease. Some highly conducting polymers still maintain a
finite conductivity even at millikelvin range. Comparing the temperature behavior of the
conductivity with traditional metals, one can expect a very different transport mechanism
in this class of material.

In highly doped conducting polymers, though there is a finite density of states of
conduction electrons around the Fermi level, the carriers may be spatially localized due to
the structural disorder in the polymers [62]. In this case, the conduction can not
participate in transport except through hopping [58,60]. X-ray diffraction studies of these
polymers show that there is modest crystallinity existing which can be pictured as
ordered regions distributing among disordered regions as shown in Fig. 2.9.
As can be seen in Fig. 2.9, each individual polymer chain passes through both ordered and disordered regions. The polymer chains in the ordered regions are well packed with chains parallel to each other. The conduction electrons are three-dimensionally delocalized within these crystallites. Typical size of those crystallites is about 3-10 nm across. For carriers to conduct electricity, the electrons have to diffuse through the disordered regions before reaching the other crystalline regions. In the disordered regions, the polymer chains can be straight, tightly coiled or intermediate disorder which limits the overlapping of wave functions. Therefore, charges in the amorphous regions are more localized. The localization length of charges depends on the details of the disorder. And the percentage of crystallinity varies from near zero to 50%-60% for polypyrrole and polyaniline and >80% for polyacetylene.

Figure 2.9: Schematic view of inhomogeneous disorder in doped polymer. The circled regions are ordered regions and the rest are disordered area.
When impurities and defects are introduced to a periodic crystal, the mobile electrons suffer backscattering from those imperfections with resulting in a “Anderson localization” [73], potential energy fluctuation smearing out the conduction band edge. The electronic structure of the system is discussed by Neville Mott [74]. The electronic structure of the impurity and defect presenting system strongly depends on the degree of disorder. Both defects and impurities generate energy states within the forbidden bandgap and create band tail states to broaden the bandwidth. The Mott variable-range-hopping (VRH) model is proposed to describe the strong disorder system under the assumption of homogeneous substantial disorder through the three-dimensional sample, even when the energy disorder is greater than bandwidth. The VRH model has received more experimental attention for doped and ion-implanted polymers [57,58,60] in describing temperature dependent conductivity. The conductivity is enhanced at high temperature due to phonon-assist hopping.

However, the X-ray diffraction results show partial crystallinity of the doped polymers, the detailed morphology of these doped polymers is not homogeneously disordered throughout the whole sample. Considering an isolated polymer chain, the quantum interference due to the static backscattering of electrons [74] (weak disorder) will cause charge localization which is in contrast to the strong disorder required for localization in three-dimensional structure. Therefore, the localization effect in partially crystalline (inhomogeneously disordered) conducting polymers is proposed to originate from a one-dimensional localization in the disordered regions. Wang et al. [75] and Kohlman et al. [76] proposed the inhomogeneous disorder model based on experimental results to
describe the conducting polymers. In this model, charges travel between ordered regions by resonance tunneling through the resonance states in disordered regions. The small concentration of electrons participating in transport was assigned to the low density of the resonance states and the long relaxation times were related to the narrow width of resonance levels [77]. The localization length of carriers decreases as the degree of disorder increases. This inhomogeneous disorder model accounts for the localized behavior at low temperature in spite of the excess of Mott’s minimum conductivity at room temperature [80].

Polymer conduction properties strongly depend on the dopants, different solvents and synthesis routes. According to Joo et al. [78, 79], the temperature dependence on the dc conductivity is very different for polypyrrole (PPy) doped with different dopants in m-cresol. When PPy doped with larger dopants, dodecylbenzenesulfonic acid (DBSA) or naphthalenesulfonic acid (NSA), both PPy-DBSA and PPy-NSA reside in an insulator regime. While PPy is doped with hexafluorophosphate (PF₆⁻), the material is in the metallic or critical regime. This is because the percentage of interchainlinks or sidechains reduces in the sample with large dopant size. Thus, the available doping centers decreases compared to PPy-PF₆⁻. Therefore, the electric field due to counterions with large size is relatively weak which leads to weak interchain interactions, low dc conductivity and strong charge localization (localization length decrease). Further, Joo et al. [78] also demonstrated different charge transport properties in doped polyaniline (PAN) with different solvents used. According to Joo et al, solvents affect the
crystallinity of samples. High crystallinity yields high room temperature dc conductivity. And different processing routes result in different morphology as well.

To understand the charge transport inside conducting polymers, it is necessary to have background knowledge of electronic states in polymers. The fundamental theory for the electronic structure of undoped conjugated polymers, using polyacetylene as an example, is given in Sect. 2.3.2. The physics for charge storage in a conjugated polymer system will be addressed in Sect. 2.3.3. The discussion of electron-electron interaction in polymer systems is given in Sect. 2.3.4.

### 2.3.2 Polyacetylene: The Su-Schrieffer-Heeger Model (SSH model)

The discussion in this section is from Refs. 51, 80, and 79. The SSH model, theoretical model, has successfully explained one-dimensional electronic structure in polyacetylene [51, 80, 81]. The SSH model assumes: (1) the existence of bond alternation (alternating single and double bonds) and (2) relative weak interchain coupling (quasi-one-dimensional behavior). Figure 2.10 shows the perfect dimerized trans-polyacetylene with the dimerization coordinate $u_d$ for degenerate ground states as well as the $\pi$-band structure of a perfect dimerized chain. As can been seen in Fig. 2.10 (c), a Peierls gap occurs at the Fermi surface at $k = \pm \frac{\pi}{2a}$ after dimerization.

The Hamiltonian of a trans-polyacetylene can be described by the following form:

$$H_{SSH} = H_\pi + H_{\pi-ph} + H_{ph},$$

(2.30)
Figure 2.10  Perfect dimerized trans- polyacetylene with dimerization coordinate $u_n$.
(a) A phase  (b) B phase [82]  (c) $\pi$-band structure of a perfect dimerized chain [81].
where
\[
H_\pi = -t_0 \sum_{n,s} (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}^+) \tag{2.31}
\]
describing the \(\pi\) electrons hopping along the chain without spin flip by a hopping integral \(t_0\) for the undimerized chain. The \(C_{n,s}^+\) and \(C_{n,s}\) stand for create and destroy \(\pi\) electrons of \(s = \pm 1/2\) on the \(n\)th (CH) group. The electron-phonon interaction is related by the electron-phonon constant (lattice displacement), \(\alpha\), to the linear term (dominated) of displacement after dimerization:
\[
H_{e-ph} = \alpha \sum_{n,s} (u_{n+1} - u_n)(c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}^+). \tag{2.32}
\]
Finally, the phonon Hamiltonian is considered through the mass \((M)\) of (CH), effective spring constant \((K)\) and momentum conjugated to displacement \(u_n\) in the following form:
\[
H_{ph} = \frac{P_n^2}{2M} + \frac{K}{2} \sum (u_{n+1} - u_n)^2. \tag{2.33}
\]
So, Eq. (2.30) can be rewritten as
\[
H_{SSH} = H_\pi + H_{\pi-ph} + H_{ph}
\]
\[
= \sum_{n,s} (t_0 - \alpha (u_{n+1} - u_n))(c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}^+) + \frac{K}{2} \sum (u_{n+1} - u_n)^2 + \sum \frac{P_n^2}{2M}
\]
\[
= \sum_{n,s} t_{n+1,n} (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}^+) + \frac{K}{2} \sum (u_{n+1} - u_n)^2 + \sum \frac{P_n^2}{2M}, \tag{2.34}
\]
where \(t_{n+1,n}\) is the hopping integral. For a perfect chain, these hopping integrals are
\[
t_{n+1,n} = t_0 - t_1 \quad \text{single bond}
\]
\[
= t_0 + t_1 \quad \text{double bond}. \tag{2.35}
\]
For a perfectly dimerized chain, the configuration coordinates are constrained to be

\[ u_n = (-1)^n u, \quad (2.36) \]

where \( u \) is a fixed value. Therefore, Eq. (2.34) can be rewritten in terms of the parameter \( u \) without considering the kinetic energy term:

\[
H_{SSH}(u) = -\sum_{n,s} t_{n+l,s} (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}) + \frac{K}{2} \sum (u_{n+1} - u_n)^2 \\
= -\sum_{n,s} [t_0 + (-1)^n 2\alpha u] (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}) + 2NKu^2, \quad (2.37)
\]

where \( N \) is number of (CH) group in a chain. The diagonalized Hamiltonian of Eq. (2.37) can be written as

\[
H = \sum_{k,s} E_k (a_{k,s}^c a_{k,s}^c - a_{k,s}^v a_{k,s}^v) + 2NKu^2, \quad (2.38)
\]

where \( E_k = (\varepsilon_k^2 + \Delta_k^2)^{1/2} \) with \( \varepsilon_k = 2t_0 \cos (ka) \), the gap parameter defined by \( \Delta_k = 4\alpha u \sin(ka) \) and \( a_{k,s}^c a_{k,s}^c \) (or \( a_{k,s}^v a_{k,s}^v \)) is the number operator which creates or annihilates charge carriers in the conduction (c) or valence (v) band. Therefore, the ground state energy per (CH) group can be calculated from Eq. (2.38) by integrating over the first Brillouin zone (-\( \pi \) / (2a) < \( k \) < \( \pi \) / (2a)):

\[
\frac{E_0(u)}{N} = -\frac{4t_0}{\pi} E(1-z^2) + 2Ku^2, \quad (2.39)
\]

where \( E(1-z^2) \) is the elliptic integral and \( z = t_1 / t_0 = 2au / t_0 \). For small \( z \), we have

\[ E(1-z^2) = 1 + \frac{1}{2} \left( \frac{\ln 4}{|z|} - \frac{1}{2} \right) z^2 + \ldots \]

\[ 
\]

to be plugged into Eq. (2-39) which gives

\[
\frac{E_0(u)}{N} = -\frac{4t_0}{\pi} \left[ 1 + \frac{1}{2} \left( \frac{4}{z} - \frac{1}{2} \right) z^2 \right] + 2Ku^2 = -\frac{4t_0}{\pi} \left( \frac{2t_0}{\pi} (\ln \frac{4}{z} - \frac{1}{2}) z^2 + 2Ku^2. \quad (2.40)
\]

\[ 
\]
One can plot \( E_0(u) / N \) versus \( u \) in Fig. 2.11 and there are two energy minima which come from the spontaneous symmetry breaking due to the Pierels instability resulting in twofold degeneracy of the ground state. By assumed parameters of polyacetylene \( \alpha = 4.1 \) eV/Å, \( K = 21 \) ev/Å\(^2\), and \( t_0 = 2.5 \) eV, the SSH model gives a minimum-energy with distortion \( u_0 \approx 0.04 \) Å which is in good agreement with the structural studies \[83\] and NMR results \[84\]. And the condensation energy per site in eV can be estimated:

\[
\frac{-E_C}{N} = \frac{1}{N} [E_0(u_0) - E_0(0)] = -0.015. \tag{2.41}
\]

The density of states per site can be obtained from the first derivative of \( E_k \):

![Figure 2.11: The total energy per (CH) group site (electronic plus lattice distortion) as a function of \( u \). Note that the double minimum associated with the spontaneous symmetry breaking and the twofold-degenerate ground state \[82\].](image)
where $\Delta = 4au_0 = 2t_f$ and the graphical relation is plotted in Fig. 2.12.

By introducing dopants into a undoped polyacetylene system, charge carriers are introduced to the polymer backbone depending on either n-doping or p-doping process. The formation of charge species is discussed in the following section.
\[ \varphi_n = (-1)^n u_n. \]  

(2.43)

Then, we can denote the A and B phase as

\[ \varphi_{0n} = -u_0, \quad \text{A phase} \]
\[ = u_0, \quad \text{B phase}. \]

(2.44)

For a long chain, the polymer tends to approach the B phase as \( N \to -\infty \) but the A phase as \( N \to \infty \), to minimize the energy. There is a transition region for the A phase which gradually emerges into the B phase; this transition region (or domain wall) corresponds to the delocalization length of a soliton to minimize its energy in the configuration shown in Fig. 2.13. In Fig. 2.13 (a), the bond alternation is different beyond the domain wall and the order parameter gradually changes from \(-u_0\) to \(u_0\) (a kink) within the domain wall about 15 repeat units of (CH) group (see Fig. 2.13(b)). The soliton state exists in the gap center which can accommodate at most 2 electrons due to spin degeneracy. A neutral soliton has spin \( \frac{1}{2} \) which is analogous to a neutral free radical and charged solitons are spinless as shown in Fig. 2.14. In addition, the SSH model predicts that the energy to create a soliton at rest is 0.42 eV which is less than half of the single particle gap, \( \Delta \). Therefore, solitons are spontaneously generated when electrons and or holes are injected by doping, by photoexcitation, by thermal generation.
Figure 2.13: Solitons (or bond alternation domain wall in trans-polyacetylene) and order parameter for soliton [52].

Figure 2.14: Electronic structure of various charge and spin state of a soliton. The middle band structure shows a neutral soliton with two possible spin states. And other band structures present a positive charged soliton (left) and a negative charged soliton (right) and both are spinless [52].
For a nondegenerate ground state polymer, the energies are different for the A phase and the B phase. In this case, a domain wall can not balance the energy difference between two phases. Instead of a kink alone on the polymer chain, another charged antikink will be created to minimize the energy of the system. This kink-antikink bounded pair (or bound soliton-antisoliton pair) (see Fig. 2.15 (a)) makes up a polaron, having two energy levels close to the conduction and the valence bands; in effect, the lower energy state is split off from the top of the valence band while it is separated from the bottom of the conduction band for the upper energy state. Each of these states can accommodate one electron of each spin. A neutral soliton bounded with a negative charged soliton forms a negative charged polaron with the lower energy state filled and the upper state is half-filled with spin = 1/2 (see Fig. 2.15 (b)). A positive polaron can be generated by having a neutral and a positive charged soliton as a pair as shown in Fig. 2.15(c).

![Figure 2.15](image)

Figure 2.15: The order parameter (a) and possible polaron configurations (b) and (c) [52].
If one adds a second electron into a negative polaron, the polymer does not simply put the second electron in the top half-filled polaron state, instead, the system will try to generate another free kink-antikink pair to bind with the negative polaron resulting in a negative bipolaron structure. Generally speaking, a bipolaron can be thought of as two charged polarons binding together with four energy states split from the interaction of the individual upper two and lower two polaron states. Two of the bipolaron states reside in the valence and conduction bands, respectively; the rest of the two bipolaron states are close to the midgap. Bringing two positive polarons together results in the formation of a spinless positive bipolaron with the lowest energy state filled and binding two negative polarons forms a spinless negative bipolaron with an empty state in the conduction band.

The solitons, polarons, bipolarons are carrier species conducting electricity in a conducting polymer system. These carrier species transport charges by the movement of domain walls plus a lattice distortion. A graphical summary of solitons, polarons, and bipolarons is shown in Fig. 2.16. And the physical quantities of solitons, polarons and bipolarons are summarized in Table 2.1.
Table 2.1: Summary of physical quantities for solitons, polarons and bipolarons.

<table>
<thead>
<tr>
<th>Species</th>
<th>Q</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>solitons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>neutral</td>
<td>0</td>
<td>½</td>
</tr>
<tr>
<td>positive</td>
<td>+e</td>
<td>0</td>
</tr>
<tr>
<td>negative</td>
<td>-e</td>
<td>0</td>
</tr>
</tbody>
</table>

| polaron     |    |     |
| positive    | +e | ½   |
| negative    | -e | ½   |

| bipolaron   |    |     |
| positive    | +2e| 0   |
| negative    | -2e| 0   |
Figure 2.16: Schematic structure of solitons, polarons, and bipolarons in conjugated polyacetylene (from [86]).
2.3.4 Electron-electron Interaction in SSH model

The SSH model is a purely one-dimensional model and does not take into account the Coulomb interaction between $\pi$ electrons. However, electron-electron interaction (Coulomb interaction) is a long-range effective interaction which yields a significant contribution to a system. For example, the ground state energy for a $\text{H}^+$ atom (-0.6 eV) is much less than that for a neutral H atom (-13.6 eV). The net energy originates from the Coulomb interaction between original and added electrons. Therefore, in this section, the effect of Coulomb interaction on the zeroth-order approximation of SSH model will be discussed.

The Hamiltonian considering Coulomb interaction is

$$ H = H_{\text{SSH}} + H_{\text{int}}, $$

(2.45)

where $H_{\text{SSH}}$ is the SSH Hamiltonian defined in Eq. (2-34), and $H_{\text{int}}$ is the electron-electron interaction, which can be written in its most general forms as

$$ H_{\text{int}} = \delta \mu \sum_{n,s} C_{ns}^{\dagger} C_{ns} + \sum_{n,m,l,p,n,s'} V(n,m,l,p) C_{ns}^{\dagger} C_{ms'}^{\dagger} C_{ln} C_{ps}, $$

(2.46)

where $C_{ns}^{\dagger}$ creates an electron of spin $s$ on site $n$, $V(n, m, l, p)$ is the appropriate matrix element of electron-electron interaction potential $V(r)$ and $\delta \mu$ is an appropriate shift in the chemical potential so that the Fermi energy remains. The first term in Eq. (2.46) stands for the on-site repulsion and the second term is the off-site repulsion. It is called Hubbard Hamiltonian, if only on-site repulsion is considered. In addition to on-site repulsion term, when the nearest neighbor interaction is considered, it is called the extended Hubbard model by physicists and Pariser-Parr-Pople (PPP) model by chemists.
Coulomb Effect on Dimerization

Based on the results of first-order approximation on Coulomb potential terms, the ground-state energy changes as

\[ \Delta E(z) = \frac{2}{\pi^2 (3W - V) z^2 \ln^2 \left(\frac{4}{ez}\right)}, \]  

(2.47)

where \( W \) is the bandwidth of \( \pi \) band, and \( z = \Delta/(2t_0) \). The change in the ground-state energy results in a change in the magnitude of the dimerization. For \( 3W - V > 0 \), the short-range interactions oppose dimerization. This is because the Coulomb repulsion between electrons provides additional stiffness against distortion away from the uniform structure and thereby opposes the dimerization induced by electron-phonon interaction. By including the interaction on bonds between sites, the dimerization monotonically decreases with increasing Coulomb interaction strength [87,88]. For longer-range interactions, there is an initial rise in dimerization before it begins to fall for large interactions [89]. The effect of electron-electron repulsion would be to reduce the single-particle gap for a fixed amount of dimerization.

Coulomb Effect on Solitons

The Coulomb interaction on solitons type excitations will be discussed here. In the absence of Coulomb repulsion, the relationship \( 2\hbar \omega_s = E_g \) holds. \( \hbar \omega_s \) is the energy required to photogenerate solitons in the midgap. However, this energy is shifted,

\[ 2\hbar \omega_s^{ph} = 2\Delta - U_S, \]  

(2.48)
where $U_s$ is an effective interaction describing the difference in Coulomb energy between initial state (charged soliton) and final state (neutral soliton plus band excitation). For doping-induced solitons,

$$2\hbar \omega_s^{\text{dop}} = 2\Delta - (U_s - E_B), \quad (2.49)$$

where $E_B$ is the Coulomb binding energy of charged soliton to the dopant counter ions. The contribution from $U_s$ and $E_B$ approximately cancel because they both depend on the spatial extent of the soliton.

Although SSH model ignores the contribution from Coulomb interaction, this noninteracting model yields a good explanation of the experimental observations. This successful explanation suggests that the effective electron-electron interactions in the conducting polymers are indeed weak; i.e. $U/W << 1$, where $U$ is the on-site Coulomb repulsion energy. Adding an additional charge in a polymer backbone causes either changing in bond alternation to generate an opposite charge-type or moving of mobile carriers to screen the electric field. Thus, the Coulomb interaction is weak in polymers.

### 2.4 Charge Transport in Disordered Polymer Matrix

#### 2.4.1 Introduction

Unlike the band transport in crystal materials, charge must hop among localized states to conduct electricity in a disordered system. The thermally activated-type hopping has a very different temperature behavior compared to band transport. The room-temperature conductivities of conjugated polymers dramatically increase upon doping. However, in spite of a large value for room temperature conductivity and a finite residual conductivity
the transport of these highly conducting polymers is still far from being
typical of traditional metals, conductivity increases as temperature decreases. The
conductivity of heavily doped polymers decreases as temperature decrease and follows
either an activation-type or a weak logarithmic behavior [90,93]. In addition, the thermal
power [94] and Pauli susceptibility [95] suggest a finite density of states at the Fermi
level.

Based on the above observations, it was suggested [96, 97, 98] that the last generation
of conducting polymers is close to the insulator-metal transition (IMT). The general
consensus for IMT is an Anderson disorder-driven localization-delocalization transition
[44, 90, 99-102]. However, the Anderson model does not fulfill the dielectric response
behavior of a metallic polymer system. Therefore, a resonance quantum tunneling model
for the inhomogeneous polymer system is proposed [103].

In this section, a brief summary of the variable range hopping model (VRH) [104] for
charge transport used in a disordered system will be provided. After that, the charge
localized-delocalized Anderson model [89, 98-102] for homogeneous system will be
addressed. Finally, the resonance quantum tunneling model [103] for inhomogeneous
system will be given.

2.4.2  Hopping and Mott Variable Range Hopping Model (VRH)

In disordered system, electrons conduct electricity through phonon-activated hopping
among the energy states in the amorphous regions.
**Electron Hopping**

Fig. 2.17 shows the schematic view of Mott’s hopping model. There are two factors which determine an electron hopping from site $i$ (below Fermi level) to site $j$ (above Fermi level). One is the tunneling factor and the other is the Boltzmann factor. The tunneling factor is of the form of $e^{-2\alpha R}$, where $\alpha^{-1} = \xi$ (localization length) and $R$ is the hopping distance. The form of the tunneling factor implies electrons hop as short a distance as possible. The Boltzmann factor is known as $\exp[-\frac{\Delta E}{k_BT}]$, where $\Delta E = E_j - E_i$ is the energy difference for an electron to overcome without considering the electron-electron interaction. And this Boltzmann factor suggests the hopping preference of an electron, i.e., choosing a site with energy difference as small as possible. Therefore, the hopping probability for an electron to hop among sites is

$$P_j \propto \exp(-2\alpha R - \frac{\Delta E}{k_BT}).$$  \hspace{1cm} (2.50)

An optimum hop for an electron is the competition result of $R$ and $\Delta E$. 
Mott Variable Range Hopping

Mott variable range hopping (VRH) model is applicable to a system with strong disorder (disorder potential energy $\gg$ energy bandwidth $[75]$). By neglecting the electron correlations, the general form of the temperature-dependent conductivity ($\sigma$) of Mott’s model $[104]$ is

$$
\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{d+1}} \right],
$$

(2.51)

where $d$ is the dimensionality and $T_0$ is the activation energy. The activation energy is related to the localization length ($\xi$) through

$$
T_0 = \frac{c}{k_B N(E_F) \xi^d},
$$

(2.52)

where $c$ is the proportionality constant, $k_B$ the Boltzmann constant, and $N(E_F)$ density of states at the Fermi level. $T_0$ can be interpreted as an effective energy barrier between
localized states which can also be understood as a measurement of the degree of disorder in disordered regions. Polymer chains without crosslinks are quasi-one-dimensional ($d=1$) system regarding to the charge transfer and vibrational energy. In quasi-one-dimension transport, a charge hops mainly along the polymer chain but hops to the neighboring chain for a lower energy barrier state when it encounters a high energy barrier. Efros and Shklovskii [105,106] pointed out that at low temperature the interactions between localized electrons and holes become important in the hopping transport. Therefore, the expected temperature dependent conductivity involving Coulomb interaction becomes

\begin{equation}
\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{2}} \right], \tag{2.53}
\end{equation}

where $T_0 = \frac{e^2}{\varepsilon L}$ ($e$ is the electron charge and $\varepsilon$ is the dielectric constant). For materials close to IMT, a conductivity with a power law temperature dependence is predicted [107].

To distinguish the transport of a material, one can tell from the logarithmic derivative of $\sigma (T)$ by $T$

\begin{equation}
W = \Delta \ln \sigma / \Delta \ln T, \tag{2.54}
\end{equation}

where $W > 0$ for metal side, $W < 0$ for insulating side and $W = 0$ for critical region of IMT.
2.4.3 Polaron Hopping

The discussion in this section is based on D. Emin’s [108, 109] theories. As a charged particle is placed inside a solid its neighboring atoms interact with it and alter their equilibrium positions. If these atomic displacements produce a sufficiently deep potential well, the charged particle is trapped inside a bound state which is called self-trapped. This charged particle can not move without altering the positions of atoms surrounding it. Thus, a polaron results from coupling of a charge with the lattice relaxation associated with this charge. When the lattice deformation is localized in an individual molecule, i.e. strongly localized states, the polaron is termed a small polaron or a radical cation. When the lattice deformation extends over a few molecular repeat units, the charge particle associated with it is called large polaron (a shallow trap).

Polaron motion occurs through a succession of random jumps of electrons hopping from site to site. A charge moves among spatially localized states accompanied by a change of atomic vibration states. Thus, the hopping rate for polarons depends on the electron-lattice coupling [110-112]. The electron-lattice coupling is weak in the case of charge hopping among shallow impurity states due to large spatial extent of donor/acceptor wave functions. For an electronic state of radius r, the maximum energy for an acoustic phonon is \( \sim \omega_D (a/r) \), where \( \omega_D \) is the Debye frequency and a is the lattice constant. Thus, the temperature regime for acoustic phonon-assisted hopping between large-radius states \( (a/r < 1) \) is less than 10 K and the required activation energies are \( \sim 10^{-3} \) eV. At high temperature, \( k_B T > \hbar \omega \), the hopping rate (R) for charge jumping among weak electron-lattice coupling states is not a thermal activated behavior, but follows a
power law, $R \sim T^n$. For charge hopping among strongly localized states, multiphonon absorption and emission processes are involved and phonons of relatively low energies are favored [110]. In addition, the magnitude of energy differences ($\Delta$) between initial and final states contributes to the charge hopping rate via $\exp[-\Delta/(k_B T)]$. The thermally activated charge hopping rate is found above the Debye temperature.

The origin of thermal activated hopping rate can be understood as supplying a minimum energy (or activation energy) to the system’s ground state to distort the atomic displacement and create an equal potential well configuration (coincident configuration) of initial and final hopping states. In this case, the carrier can tunnel to an adjacent site and then the atomic displacement pattern subsequently relaxes. The same process repeats to pass down a charge. If the lattice relaxation does not occur before a subsequent hop, the charge has time to follow the lattice deformations and this is an adiabatic process [113]. In this case, the consecutive hops of a carrier are “correlated” and the activation energy for a hopping motion is reduced or activationless hopping. The carrier mobility shows a weak temperature dependence and has a magnitude on the order of $ea^2/\hbar$, where $a$ is the typical hop distance and $\hbar$ is Planck’s constant. Typically, the value of this mobility is comparable to 1 cm$^2$/Vs. For thermal activated hops, the residual vibrational energy remaining at coincident sites is $\sim E_a/(\delta \nu \tau)^{d/2}$, where $E_a$ is the activation energy, $\delta \nu$ is the bandwidth of vibrational frequencies associated with the coincident deformation and $d$ is the dimensionality of the vibration system [114-116]. Generally, optical phonons are responsible for intramolecular deformation in a molecular solid. The corresponding relaxation time $\tau$ [108].
\[ \tau = \delta \nu^{-1} \left( \frac{E_a}{k_B T} \right)^{\frac{2}{d}}, \quad (2.55) \]

and the mean time between hops is related to carrier mobility \( \mu \) [108]

\[ t_{\text{hop}} = \frac{e a^2}{\mu k_B T}. \quad (2.56) \]

Correlation effect plays a role when lattice relaxation time exceeds the mean time between hops. Thus, the mobility

\[ \mu > \frac{e a^2 \nu \left( \frac{\delta \nu}{\nu} \right) \left( \frac{k_B T}{E_a} \right)^{\frac{d}{2}}}{k_B T}. \quad (2.57) \]

From Eq. (2-55), in molecular solids, the hopping mobilities in excess of \( 10^{-2} \text{ cm}^2/(\text{Vs}) \) are attributed to correlated hopping. In the high temperature limit, the mobility of a adiabatic small polaron is given as [113]

\[ \mu = \frac{e a^2 \nu}{k_B T} \exp\left[ - \frac{E_a}{k_B T} \right]. \quad (2.58) \]

At low temperatures, variation of the mobility is found to deviate from the thermal activated law.

### 2.4.4 Localization-delocalization

#### 2.4.4.1 Anderson Localization

The Anderson localization model assumes the materials are isotropic (electrically the same in all direction) and homogeneously disordered. The electron wave functions form Bloch waves [44] delocalized over the whole solid in a perfect crystal with periodic
potential (see Fig. 2-18 (a)). The electrons lie in a band of width $B = 2zI$, where $z$ is the coordinate number and $I$ is the transfer integral

$$I = \int \psi(|r-a_n|)H\psi(|r-a_{n+1}|)d^3r$$  \hspace{1cm} (2.59)

$H$ is Hamiltonian here, $\psi (|r-a_n|)$ is the electron wave function for potential well at location $a_n$. Systems with defects, disorder, and impurities introduce substantial scattering of the electron wave function which may lead to localization. Anderson showed [73] that the electronic wave function can be localized if the random component of the disordered potential ($W$) is large enough compared with the electronic bandwidth ($B$) (see Fig. 2.18). The localized wave function has the form of

$$\psi(r) \propto \exp(-r/\xi) \text{Re}(\psi_0)$$ \hspace{1cm} (2.60)

where $\xi$ is the localization length of the state. Later, Mott showed that band tail states are more easily localized than the states in the center of the band [75]. Therefore, a mobility edge ($E_c$) is introduced to separate localized states in the band tail from extended states in the center of the band (see Fig. 2-18). The resulting electronic properties of materials depends on the location of the Fermi level ($E_F$). The material shows a metallic behavior; i.e. $\sigma_{dc}(T)$ has a finite value as $T \rightarrow 0$, if the $E_F$ lies in the range of extended states. It $E_F$ lies in the range of localized states due to strong potential disorder, the material is nonmetallic even though there is a finite density of states at the Fermi level. When $E_F$ is close to $E_C$ on the insulating side of the insulator-metal transition, $\xi$ will diverge as the electronic wave function becomes delocalized through the material. This disordered-induced I-M transition is called the “Anderson transition” [117,118]. The localization
length increase as Fermi energy approaches $E_C$, $\xi \sim a \left[ \frac{E_0}{E_C - E} \right]^{\nu}$, where $\nu \approx 1$ and $E_0$ is a constant.
Figure 2.18: (a) The Anderson transition and (b) the form of wave function in an Anderson metal-insulator transition. (c) The Fermi gas state where the Fermi level lies in the region of localized states [73,74,119].
2.4.5  Resonance Quantum Tunneling

Conducting polymers have a rich variety in their morphology [62], partially crystalline and partially disordered as shown in Fig. 2.9. If the localization length in the more disordered regions of the electrons (ξ) is comparable to or smaller than the crystalline coherence length (~10Å) in the polymer, the disorder present in the conducting polymer is viewed as inhomogeneous [54, 58, 120, 122]. The localized effects in the inhomogeneously disordered (partially crystalline) conducting polymers are proposed to originate from quasi-one-dimensional localization in the disordered regions [58, 120, 121, 125] surrounding the ordered regions.

Based on the puzzles revealed in the frequency dependence of conductivity of highly doped conducting polymers [120-125], Prigodin et al. [103] proposed that highly doped conducting polymers demonstrate a new mechanism of charge transport and a new type of IMT.

According to Prigodin et al. [103], the doped conducting polymer systems can be treated as metallic islands coupled into a network with twisted and tangled polymer chains as shown in Fig. 2.19. The metallic islands, crystalline regions (or ordered regions), are composed of chains that are regularly and densely packed. The sizes of these metallic grains are essentially quantum sized such that the energy levels inside these grains are appreciably quantized. In addition, there is no single geometric form that can be used to describe the shape of the metallic grains. As a result, the energy spectra as well as eigenfunctions obey chaotic statistics [126]. Outside these regions the chains are poorly ordered and can be viewed as amorphous media. Also, single chains provide the
coupling between metallic dots as well as the remote ones. Various shapes and sizes of grains as well as intergrain coupling fluctuate strongly over the entire system.

Figure 2.19: Schematic view on the structure of polymers. The lines represent polymer chains and the dashed squares mark the region where the polymer chains demonstrate the crystalline order [103].

In this granular model for polymers, the mean energy level spacing ($\Delta E$) of the metallic grain is estimated to be [126]

$$\Delta E = \frac{1}{N(E_F)N_\perp N_\parallel} ,$$  \hspace{1cm} (2.61)

where $N_\perp$ chains are densely packed over the length $N_\parallel$ in cell units and $N(E_F)$ is the density of states per unit cell. The level broadening, $\delta E$, can be estimated to as

$$\delta E = 2N_\perp g\Delta E ,$$  \hspace{1cm} (2.62)

where $g$ is the transmission coefficient [127] or dimensionless conductance (in units of $2e^2/\hbar$) of chain-link between the grains. The IMT in electronic disordered systems happens as noted by Thouless [128] when the level broadening $\delta E$ is of the order of level
spacing $\Delta E$ (see Fig. 2-19). The critical coupling in terms of transmission coefficient $g_c$ is $2N_g g_c = 1$. For PANI-CSA, $g_c \approx 10^{-2}$ [62,127,129]. When $g < g_c$, the material is a dielectric. Thus, the electrical phase of a material depends on the intergrain coupling. The system is an insulator in the limit of weak intergrain coupling.

![Figure 2.20: Electronic conduction between metallic grains (well-packed and well overlapping chain regions) embedded in amorphous media.](image)

(a)

(b)

Figure 2.20: Electronic conduction between metallic grains (well-packed and well overlapping chain regions) embedded in amorphous media. (a) the localization radius of electronic states in metallic grain is of the grain size and is of scale of the polymer unit in the amorphous media; (b) intergrain charge transfer effectively is provided by tunneling through resonance states in the amorphous regions. (from [103])

At critical intergrain coupling, the system undergoes the transition into a metallic state. Unlike the mechanical contacts between grains assumed in the standard granular metals, direct tunneling is suppressed due to spatial separation of the crystalline domains in polymers. The electronic states in the disordered regions are strongly localized and there

60
is no interaction between chains in the disordered regions. Therefore, the probability of finding a resonance state located in the center of a chain is proportional to its width $\gamma$, and $\gamma = \frac{1}{T} e^{\frac{-L}{T}}$ (L is the length of the chain and T is the temperature). When near IMT, intergrain coupling in polymers occurs through single resonance chains out of the whole bundle of chains connecting grains. Although the probability of finding a resonance state in $\sim 10^{-2}$, the resonance is realized as least for one chain, and this resonance tunneling dominates the entire transport through a grain.

### 2.5 Percolation Theory – An Introduction

Percolation [130] is a random process. When a system undergoes an imposed random process, transition can occur in the system. Statistics method is employed to describe the average properties of the system undergoing transition. The concept of percolation has been applied in several systems or phenomena such as the glass transition, mobility edge in amorphous semiconductor, variable-range hopping in amorphous semiconductors and so on.

Consider a two-dimensional conducting network composed of square-lattice interconnection shown in Fig. 2.21. This communication network conducts current by a bias applied to it. If one starts to cut the connecting links randomly, the conductance of the network start to drop as the red arrow shown in Fig. 2.21. As the fraction of cut links reaches to a critical value $P_c$, the conducting network undergoes conducting–nonconducting transition. The action of cutting connecting links introduces structure
disorder into an ordered system resulting in phase transition in the system. For a network with infinite size, a sharp transition is expected (see Fig 2.21). The critical threshold ($P_C$) leads to phase transition called the \textit{percolation threshold}. For systems which undergo a phase transition involving only statistically disorder is called lattice percolation.

![Diagram of percolation process](image)

Figure 2.21: Randomly cut network as an example of Percolation and the current as a function of fraction of uncut bonds. (after [128])

There are many percolation processes that can occur in a medium. Two basic types of percolation, bond percolation and site percolation, have been studied mathematically in different lattice structures in terms of cluster size, correlation function, etc. For experimentalists, what researchers are concerned with is using the percolation theory to relate the physical quantities with a universal rule.

The dc conductivity ($\sigma$) of the system near the percolation threshold can be described as
\[ \sigma \sim (p - p_c)^t, \quad (2.63) \]

where the critical exponent \( t \) is the dimensionality of the system. The percolation threshold \( p_c \) depends on lattice structure and the type of percolation. The critical exponents are dimensional invariants. Other physical quantities can be expressed as Eq. (2-47) with different values of exponents. Based on the relation between physical quantities, the universal relaxation between critical exponents can be obtained.

The charge transport in a polymer matrix can be interpreted as a percolation phenomenon. By substantially increasing dopant concentration in a dielectric, the conductivity of the dielectric raises as the concentrations increases. Or by blending doped polymer with various concentration of dielectric, the conductivity of the medium drops and the system becomes insulating at a critical blending ratio [131]. For the system with dimension \( 1+\varepsilon \) where \( \varepsilon < 1 \), the theoretical calculation value for \( t \) is

\[ \frac{1+\varepsilon}{\varepsilon^2} \exp\left(1 - \frac{1+\varepsilon}{\varepsilon}\right) \] [132].

2.6 Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) also named electron spin resonance (ESR) is one of the most sensitive tools to detect unpaired electrons.

2.6.1 Fundamental Knowledge

2.6.1.1 Spin Transition

Zavoisky was the [133-135] first scientist to report the technique of EPR in U.S.S.R. in 1945. The working principle of EPR is based on the theories and observations of
Gorter and coworkers [136-139] a decade earlier. EPR utilizes the fact that energy levels of electrons split (Zeeman Splitting) in the presence of a static magnetic field. The transition between two levels occurs as a microwave field applied perpendicular to the static field (see Fig. 2.22 [140]).

In the EPR measurement, the sample is centered within the cavity tuned to the frequency of the microwave field. Because of this constraint, the magnetic field sweeping is employed instead of frequency sweeping as in optical absorption measurements. The static magnetic field is swept through the resonance region and a detector is used to measure the reflected microwaves from the cavity in comparison to those incidents upon it. The first derivative of the absorption signal is collected. By analyzing the linewidth, lineshape, and intensity of the collected spectrum, magnetic paramagnetic susceptibility and spin motion can be further understood.

The Hamiltonian of a material in the magnetic field under an undamped condition is described by

\[ H = -\mu \cdot H = g_e \mu_B H_0 S_Z, \]

(2.64)

where \( g_e \) is the electronic g-factor (2.002319 for a free electron), \( \mu_B \) is the Bohr magneton (= \( \frac{e\hbar}{2mc} = 9.274096 \times 10^{-21} \) erg/Gauss), \( H_0 \) is the magnetic field in resonance (in Gauss) and \( S_Z \) is z component of the spin quantum number. For electrons, \( S = \frac{1}{2} \) and \( S_z = \frac{1}{2} \), it is required for the incident microwave with frequency, \( \nu \) (Hz), supplying the energy

\[ \Delta E = \hbar \nu = \hbar \omega = g_e \mu_B H_0 \]

(2.65)

to initiate the electron transition.
2.6.1.2 Spin Relaxation

The relaxation phenomena determine the shape of the absorption lines and from analysis of the lineshapes we are able to determine the rates of a variety of kinetic processes. Considering a collection of non-interacting spins in a static magnetic field, $H_z$, the relative population of two levels is given by Boltzmann distribution at thermal equilibrium,

$$
\frac{n^0_H}{n^0_L} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{2\beta H_z}{k_B T}\right)
$$

(2.66)

where $n^0_H$ and $n^0_L$ are the number of spins in the upper and lower levels, respectively.

When an additional field $H_1$ is provided by the microwave radiation, three processes occur: (1) absorption, (2) induced emission and (3) spontaneous emission. The rate of (1) depends on $n^0_L$ and the intensity of microwave radiation at the appropriate frequencies.

Figure. 2.22: Diagram of energy states as a function of magnetic field, after Bruker Instruments, Inc. [138]
The rate of (2) is slower than (1) by a factor of $n_{h}^{0}/n_{l}^{0}$. Process (3) does not make an appreciable contribution to the transition rate from upper level to lower level at microwave frequency. And process (3) will eventually equalize the population of the two levels. Equal population would be a condition of complete saturation and no ESR signal can be detected. ESR detects signals when there is a population difference. In a real system the spin interacts with their environment, lattice, and most of the excess energy is carried off. Thus, the population difference is maintained in the spin system. We can regard the lattice as having an infinite specific heat such that it is always in thermal equilibrium.

A spin is a radical can be subject to a constantly fluctuating magnetic field arising from its environment. The randomly fluctuating field at a particular electron spin will contain a component at the Larmor frequency which will be able to induce transitions between the levels. The efficiency of this transition depends on the molecular nature of the environment of the spin and on its physics state. One can specify the efficiency of the spin-lattice interaction by the \textit{spin-lattice relaxation time}, $T_{1}$. $T_{1}$ called the longitudinal relaxation time can be understood as the rate in which bulk magnetization approaches its thermal equilibrium value when the magnetic field is on. In another words, it relates to the rate of change of the magnetization parallel to the applied field. Thus, the spin-lattice interaction can be reduced by lowering the temperature.

In addition to spin – lattice interaction, the other energy consuming process with an origin of interaction between localized spin and conduction electrons [141] is called The Korringa relaxation rate. The Korringa relaxation processes also contribute to $T_{1}$. The
Korringa relaxation mechanism is obtained via a spin-exchange interaction between localized electrons \( l \) and free carriers \( d \). For a well-isolated or weakly correlated spin, the rate for the local-moment spin flips due to the exchange coupling energy between localized-free electrons is

\[
\frac{1}{T_{ld}} = \pi [N(E_F)J]^2 k_B T ,
\]  

(2.67)

where \( N(E_F) \) is the density of states at the Fermi level, \( J \) is the free carrier to localized spin exchange parameter \( H_{exchange} = -J\vec{S} \cdot \vec{s} \), and \( T \) is the temperature.

The other category of spin relaxation process which does not involve the exchange of energy between the spin and the lattice is called spin-spin interaction (an adiabatic process) and is characterized by \( T_2 \). \( T_2 \) (transverse relaxation time) can be understood as the rate of decay of the magnetization concomitant with loss of phase. The spin-spin interaction is not temperature dependent. Therefore, the relaxation time of the system, \( T \), is the combination of both spin-lattice and spin-spin relaxation time:

\[
\frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} .
\]  

(2.68)

The resonant spins spend a finite time in the higher energy level which gives a line width of \( \delta \omega = \frac{1}{T} \).
2.6.1.3 Lineshape

The spin relaxation $T$ is defined by

$$T = \pi g(\omega - \omega_0)_{\text{max}}$$  \hspace{2cm} (2.69)

in which $g(\omega - \omega_0)$ is the line shape function. There are two types of fundamental lineshapes, Gaussian and Lorentzian. Table 2-2 summarizes the absorption lines of both Gaussian and Lorentzian lineshapes. The calculated line widths for different absorption lines are summarized in Table 2.3.

![Table 2.2: Summary of EPR absorption functions for Gaussian and Lorentzian line shapes. (x = T(\omega - \omega_0)) [142]](image)

![Table 2.3: The calculated line widths for Gaussian and Lorentzian absorption lines. [142]](image)
2.6.1.4 Line Width Broadening/Narrowing

Consider the Heisenberg uncertainty principle

\[ \Delta E \Delta t \geq \hbar. \]  

(2.70)

The spin relaxation time \( T \) gives the linewidth of ESR lineshape. In this case, the linewidth for a system with spin relaxation time \( T \) is

\[ \Delta E \geq \frac{\hbar}{T}. \]  

(2.71)

and gives

\[ \Delta E = g \mu_B \Delta H \geq \frac{\hbar}{T}, \]

\[ \Rightarrow \Delta H \geq \frac{\hbar}{g \mu_B T}. \]  

(2.72)

Therefore, the shorter the mean life time of a spin state, the broader the linewidth one can expect.

2.6.1.4 (a) Source of Broadening

There are many other sources which can cause the line broadening. The broadening reason mainly can be divided into two groups, inhomogeneous broadening and homogeneous broadening. The following information is based on Ref. [143].

**Inhomogeneous Broadening:** The unpaired electrons in various free radicals in the sample are subjected to slightly different effective magnetic field. The reasons for inhomogeneous broadening are: (1) inhomogeneous magnetic field, and (2) anisotropic interactions in a randomly oriented system in the solid state. The distribution of local
magnetic field resulting from anisotropic \( g \) and hyperfine interaction gives rise to the inhomogeneity. The lineshape in this case may be highly unsymmetrical. And (3) unresolved hyperfine structure. Therefore, only a small fraction of the spins are in resonance as the external field is swept. The observed line is then a superposition of a large number of individual components (referred to as spin pocket), each slightly shifted from each other. The resultant envelope is approximately a Gaussian shape.

**Homogeneous Broadening:** The static and the time-average magnetic fields can be considered to be the same at each dipole, but the instantaneous magnetic field is not. This means that the line shape is the same for each dipole and the resulting line usually has a Lorentzian shape. The width of this line is usually greater than one’s expectation from \( T_1 \). For stable free radicals, \( T_1 \gg T_2 \). And \( T_2=1/(k\gamma_e \Gamma) \) where \( \Gamma \) is the half the line width at half-height, \( \gamma_e \) is the electronic magnetogyric ratio and \( k \) is the constant depending on the line shape. \( k = 1 \) for Lorentzian lines and \( k = (\pi \ln 2)^{1/2} \) for Gaussian lines.

### 2.6.1.4 (b) Mechanisms of Broadening

The mechanisms contribute to the line broadening, electron spin–electron-spin dipolar interaction and electron spin–nuclear spin interaction.

**Electron spin–electron spin dipolar interaction:** Spin-spin interaction is probably the most important single contribution to \( T_2 \). Spin-Spin interaction happens in all but the most dilute samples. There is a magnetic field associated with a magnetic moment. If another unpaired electron is at a distance \( r \) away, the magnitude of the magnetic field at
the electron can take the values between $\pm 2\mu_e/r^3$, depending on the orientation. For 0.1 mole paramagnetic species in a host material with 0.2 nm lattice spacing, at one electron the average dipolar field arising from another electron will be $\pm 2$ G. Thus, the deviations in the electron energy levels will result in a line width of $\sim 4$ G. In liquid, a solution of low viscosity, the spin-spin interaction is rather small and is masked by electron-exchange effects.

**Electron spin – nuclear spin interaction:** The electron spin-nuclear spin interactions are analogous to the electron spin-electron spin interactions but the random local magnetic fields are produced by magnetic nuclei in the vicinity of a radical. For example, the protons at an average distance 0.3 nm away will cause $\pm 1$ G variation of magnetic field at an unpaired electron. The anisotropic interaction with magnetic nuclei within the radical are averaged to zero in a liquid of low viscosity. When the radical is tumbling slowly in a viscous liquid, the anisotropy of $g$ and hyperfine interaction can contribute to $T_2$.

### 2.6.1.4 (c) Mechanisms of Narrowing

There are three basic types of narrowing: exchange interaction, spin diffusion and molecular motional narrowing.

**Exchange interaction:** A bimolecular reaction in which the unpaired electrons of two free radicals exchange their spin states. Electron spin exchange is a dynamic effect which in liquid produces a much greater broadening than the dipole-dipole effect. The spin exchange rate is twice as indicated in the broadened spectra. Besides, the exchange
rate, it also depends on the concentration of the radicals. Thus, the overall spin exchange rate can be written as \( k_s = \frac{1}{2\tau[R]} \), where \( 1/(2\tau) \) is the electron spin exchange rate for a given molecular and \([R]\) is the concentration of the free radicals. As the concentration of free radicals increases, the ESR line will coalesce to a single line, which becomes narrower at even higher concentration. The strong exchange arises from the overlap of molecular wave functions.

In a liquid, the spin exchange is more pronounced than dipole–dipole interaction. For example, a solution having a radical concentration \( 10^{-3} \text{ M} \) and spin exchange rate \( 10^{10} \text{ mole e}^{-1}\text{s}^{-1} \), the spin exchange mechanism contribute 0.57 G to the linewidth while only 0.01 G by dipolar interaction.

**Spin diffusion:** During sweeping of the magnetic field, different spin environments are sampled through physical movements of the charge carriers. For delocalized electrons, the effective local field they experience is averaged by their own motion within the spin environment. This is also referred to as motional narrowing.

**Molecular motional narrowing:** Motional narrowing comes from the intrachain spin delocalization among the molecular axis and interaction hopping of charge carriers between molecules. The narrowing effect is seen in media allowing for movements of constituents of charge-containing matrix. This is almost exclusively a solution effect.
2.6.2 Further Analysis

2.6.2.1 Spin Concentration

In a doped polymer system, charges can be stored in the form of solitons, polarons and bipolarons. For the species to be able to carry spin or unpaired electrons (paramagnetic centers) it is detectable by ESR measurements. The distribution of those paramagnetic centers can be obtained by integrating the first derivative of ESR spectrum. Thus, the area under the integrated ESR spectrum is the relative total concentration of unpaired electrons.

2.6.2.2 Magnetic Susceptibility

The linear relationship between M and H exists in a large class of materials. For isotropic materials, the relationship is described through

\[ M = \chi H, \] (2.73)

where \( \chi \) is called the magnetic susceptibility. \( \chi \) is positive for paramagnetic material while negative for diamagnetic substance. The magnetic field is strengthened in the present of paramagnetic materials but weakened in the other. Paramagnetic behavior usually causes more attentions than the other.

There are two models for spin behavior in the paramagnetic substance, Curie and Pauli spins. Curie paramagnetism originates from the localized charges which can be described by Boltzmann statistics and follows the Curie law [144]

\[ \chi_c = \frac{N g_s \mu_B^2 S(S + 1)}{3k_B T}, \] (2.74)
where $\chi_C$ is the Curie susceptibility, $N_A$ is Avogadro’s number (6.02 $\times$ 10$^{23}$ particles), $T$ is the temperature in Kelvin, $k_B$ is the Boltzmann constant (1.38 $\times$ 10$^{-16}$ erg/K), and $S$ is the value of spin quantum number. As can be seen in Eq. (2-54), the Curie paramagnetic susceptibility is temperature dependent.

**Pauli paramagnetism** originates from the delocalized carriers which obey Fermi-Dirac statistics as shown in the Pauli law [44]:

$$N(E_F) = \frac{\chi_p}{2\mu_B^2},$$  \hspace{1cm} (2.75)

where $\chi_p$ is Pauli paramagnetic susceptibility and $N(E_F)$ is the density of states. Pauli susceptibility does not show any temperature dependency.

Generally, the nature of carriers in a material can have both Curie and Pauli components. In this case, the obtained susceptibility can be written as

$$\chi = \chi_C + \chi_p$$  \hspace{1cm} (2.76)

$$\Rightarrow \quad \frac{C}{T} + \chi_p$$  \hspace{1cm} (2.77)

$$\Rightarrow \quad \chi T = C + \chi_p,$$  \hspace{1cm} (2.78)

where $C$ is the Curie constant. By plotting the measured susceptibility vs. 1/T, both Curie and Pauli components can be extracted.
CHAPTER 3

EXPERIMENTAL METHODS

There are two parts to the experimental details highlighted in chapter 3. The detail for the devices used in this study including material structures, a brief material introduction, and device fabrication procedures will be described in the first part of this chapter. Various sample characterization circuits, methods and data acquisition will be addressed in the second part of this chapter.

3.1 Sample Preparation

3.1.1 Device Building Block

The samples were either made on a transparency or a piece of glass depending on the material properties and experimental designs. All samples are made using the fundamental building block shown in Fig. 3.1. Two electrodes (source (S) and drain (D)) were thermally deposited on the substrates to define the channel dimensions followed by spin coating poly-3,4-ethylenedioxythiophene doped with polystyrenesulfonic acid (PEDOT:PSS) as the active component. A dielectric layer is served as a spacer to
separate the conducting channel and the gate (G) electrode. The detail of sample fabrication procedures will be addressed later.

Figure 3.1: The building block of sample studied in this thesis.

3.1.2 Materials

The materials used in device fabrication are listed in Table 3-1 as well as their corresponding chemical structures.

The active component, PEDOT:PSS (purchased from Aldrich), is PEDOT heavily doped with PSS⁻ which is an organic conductor with conductivity ~ 1 Scm⁻¹. Fig. 3.2 shows the UV-Vis-NIR of PEDOT:PSS. Delocalization of the polarons (weakly localized carriers) is evident from the free carrier tail (λ>1500 nm). The observed peak around 800 nm (1.5 eV) is contributed from the localized polaron. For fully doped PEDOT:PSS system, every three PEDOT repeat units carries one hole charge and the estimated volume per charge is around 1000 Å³.
<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical structure</th>
</tr>
</thead>
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<td></td>
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<td><img src="image" alt="PEO" /></td>
</tr>
<tr>
<td>Polyethylene oxide (PEO) - LiClO₄</td>
<td><img src="image" alt="PEO-LiClO₄" /></td>
</tr>
<tr>
<td>Pentacene</td>
<td><img src="image" alt="Pentacene" /></td>
</tr>
<tr>
<td>Polymethyl-methacrylate (PMMA)</td>
<td><img src="image" alt="PMMA" /></td>
</tr>
</tbody>
</table>

Table 3.1 Materials used in the field effect devices.
The formula for the active material is the mixture of 80 wt% PEDOT:PSS (Aldrich), 20 wt% EG (Aldrich) and < 0.05% DBSA (Acros). A magnetic stirring bar is used to mix the solution before passing through a 5 µm filter. The conductivity for this formula is ~30 Scm\(^{-1}\) by standard four-probe method. The purpose for adding EG is to enhance the conductivity [145] while small amounts of DBSA are needed to increase the adhesion between the PEDOT:PSS and the substrate. Figure 3.3 shows the x-ray diffraction pattern for a free standing PEDOT:PSS film. Two intense broad bands centered at \(2\theta \approx 17^\circ\) and \(\approx 25.5^\circ\) show that the PEDOT:PSS is partially crystalline. According to Bragg formula

\[
\lambda = 2d \sin \theta ,
\]

where \(\lambda\) is the x-ray wavelength used and \(d\) is the lattice plane spacing. The values for \(d\)

![Absorption spectrum of PEDOT:PSS](image)

**Figure 3.2:** UV-Vis –NIR absorption of PEDOT:PSS.
are ~ 3.5 Å and ~ 5.2 Å at angular positions $2\theta$ ~ 25.5° and ~17°, respectively. The crystalline domain size, or the extend of order, $L$, can be estimated from the ring’s angular width ($\Delta 2\theta$) (full width at half maximum) using Scherrer formula [146]

$$L = \frac{0.9\lambda}{\Delta(2\theta)\cos \theta}. \quad (3.2)$$

The estimated domain sizes, $L$, for ordered regions are ~ 16Å in the PEDOT:PSS film. And this XRD result supports the morphology of conducting polymers, chain-link granular model [103].

![Figure 3.3: Densitometer tracing as a function of the Bragg angle $\theta$ of PEDOT:PSS film diffraction patterns taking at $\lambda=1.54056\text{Å}$.](image)

Various insulating polymers were used as dielectric layer such as OA, PVP, PEO, PEO-LiClO$_4$, pentacene, PMMA and Al$_2$O$_3$. OA purchased from Norland Product Inc. is a kind of optical binder and needed to be cured with 366 nm UV light. Al$_2$O$_3$ was
deposited by ion sputtering method. Chemical materials such as PVP, PEO, PEO-LiClO₄, PMMA, and pentacene were purchased from Sigma-Aldrich and used directly without further purification steps.

Silver (Ag) was selected for S/D electrodes and Al or PEDOT:PSS was used as the G electrode.

### 3.1.3 Device Fabrication

In this thesis study, both 2-probe and 4-probe devices were fabricated according to the designed experiments. The fabrication procedures for 4-probe devices are addressed following the fabrication processes of 2-probe devices. All types of 2-probe devices made for this study using the building block in Fig. 3.1 are summarized in Table 3-2. There is no overlapping between gate electrode and source/drain electrodes for all devices.

<table>
<thead>
<tr>
<th>Type</th>
<th>Substrate</th>
<th>PEDOT:PSS</th>
<th>Dielectric material</th>
<th>Gate material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Transparency</td>
<td>150 nm</td>
<td>OA (4 μm)</td>
<td>PEDOT:PSS (150 nm)</td>
</tr>
<tr>
<td>2</td>
<td>Transparency</td>
<td>150 nm</td>
<td>PVP (10 μm)</td>
<td>PEDOT:PSS</td>
</tr>
<tr>
<td>3</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>PVP (30 nm – 50 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>4</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>PMMA (50 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>5</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>PEO (50 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>6</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>PEO-LiClO₄ (50 nm – 80 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>7</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>Al₂O₃ (14 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>8</td>
<td>Glass</td>
<td>50 nm – 80 nm</td>
<td>Pentacene (50 nm)</td>
<td>Al (30 nm)</td>
</tr>
<tr>
<td>9</td>
<td>Glass</td>
<td>0.7 μm – 4 μm</td>
<td>PEO-LiClO₄ (1 μm – 2 μm)</td>
<td>Al (25 nm)</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of different kinds of devices for 2-probe measurements.
Type 2 and 2 devices utilized line patterning techniques [147-150] to shape the channel dimension and the rest of them were defined by thermal deposited S/D electrodes. Materials in solution forms were handled by spin coating to form thin films.

Processing for type 1 devices:

A few drops of PEDOT:PSS mixture were placed on the side of transparency then rolled over the drawn pattern with a glass tube and air gun blow dry (see Fig. 3.4). The black ink pattern can be washed away by sonification in acetone. The remaining blue parts can be cut off by scissors for S/D and G elements. Applying a drop of the mixture of OA with 6 mg of 3 µm polystyrene microspheres on the middle of H shaped element then covered this structure with another T shape gate electrode. The structure was then clamped between a micrometer and 366 nm UV light was shined on it for 5 minutes to solidify the OA. The finished device is mechanically flexible.

![Figure 3.4: The fabrication procedure for type 1 devices.](image-url)
Processing for type 2 devices:

A mixture of PEDOT:PSS solution was drop coated onto the drawn pattern and then spin coating at 3000 rpm. This film was dried in air for a day before spin coating 10 wt% PVP solution on top of it. The PVP solution was made by dissolving PVP in isopropanol. Finally, Teflon tape was used to define gate dimension and spin coated the PEDOT:PSS again to accomplish the device fabrication (see Fig. 3.5 for the whole process).

Processing for type 3, 4, 5, and 6 devices:

Figure 3.6 shows the procedures for making type 3, 4, 5, and 6 devices. There are two methods to define the channel dimensions in this group of devices. One is using scotch

Figure 3.5: The fabrication procedure for type 2 devices.
tape and Teflon tape to mask the channel dimensions and the other is using photolithography to define the channel dimensions. The photolithography method gives well controllable channel dimensions. After defining dimensions and separation of S/D electrodes, Cr (5 nm) and Ag (450 nm) were thermally deposited consecutively. PEDOT:PSS was spin coated on the glass to cover the S/D metal electrodes after removing the scotch tape or lifting off the photoresist. After one day of air drying, a drop of 0.5 % or 1 % PVP (or PMMA, PEO and PEO-LiClO₄) solution was spin coated on top of PEDOT:PSS at 2000 rpm as a dielectric layer. Another one day of drying, Al (25 nm) was evaporated on top of the dielectric layer as the gate electrode patterned by Teflon tape.

Figure 3.6: The fabrication procedure for type 3, 4, 5, and 6 devices.
Processing for type 7 and 8 devices:

The process and method for making type 7 and 8 devices is the same as configuration (3) – (6) except the dielectric layers, pentacene and Al$_2$O$_3$, were deposited by thermal evaporation in glove box and sputtering, respectively.

Processing for type 9 devices:

Fig. 3.7 illustrates the fabrication procedures for type 9 devices which are designed for ESR measurements. A transparency was cut into 3 mm × 2.5 mm pieces as substrates followed by thermally depositing Cr (5 nm) and Au (25 nm) as S/D electrodes with dimensions 3 mm × 500 µm and 1.1 mm in separation. After that, a drop of PEDOT:PSS was spread out across the S/D electrodes and air dried for one day followed by vacuum drying for 2 hours. A mixture of 80 mg LiClO$_4$ (Aldrich) and 265 mg polyethylene oxide (Aldrich) dissolved in 14.5 g acetonitrile (Aldrich) was then spin coated on top of the vacuum dried PEDOT:PSS layer at 1500 rpm. This structure was then dried in vacuum for an hour. Another 3 mm × 1 mm piece of Al deposited transparency was brought in contact to laminate with the PEDOT:PSS/ LiClO$_4$ - PEO structure mechanically.
The 4-probe devices employ the layer structure of type 3 devices except having four electrodes across the channel. The schematic view of processes is in Fig. 3.8. A scotch tape was used to mask a channel on glass before spin coating PEDOT:PSS mixture. After drying PEDOT:PSS in the air for one day, Ag (30 nm) was thermally evaporated on the Teflon tape masked 4-probe electrodes. Then 1% PVP solution was spin coated at 2000 rpm on top of the 4-probe structure. Finally, Al (30 nm) was thermally evaporated on top of PVP layer to complete the fabrication as shown in Fig. 3.8.
3.1.4 Issues on Device Fabrication

Spin Coating method is used to cast the polymer solutions. For the processing shown in Sect. 3.1.3, it is important for a dielectric material to be dissolved in a proper solvent which does not destroy the coated PEDOT:PSS layer. An intermixture of a dielectric material and the PEDOT:PSS could happen for improper solvent chosen. And this can be discerned by the increase of PEDOT:PSS resistance.

Another problem could happen during processing is the final metal deposition step. It is important to deposit Al in a high vacuum \((P < 5 \times 10^{-6} \text{ torr})\) environment to prevent the oxidation of Al. Typically, 1 Å/s deposition rate at \(P = 5 \times 10^{-6} \text{ torr}\) is good enough to obtain good quality of Al. The aluminum deposition process is the critical step determining a successful device fabrication. Most of the time, Al diffuses into a dielectric layer due to carrying high thermal energy. However, compared with Au
deposition, Au carries even higher energy for higher melting point which exposes the diffusion problem more pronounced.

### 3.2 Device Characterization Techniques

In room temperature measurements, we characterize devices by performing conventional I-V measurement and time dynamic I-t measurements. Here, the measurement details will be summarized.

#### 3.2.1 Equipment and Setup

Two Keithley 487 meters are required for doing the basic characterization measurements. Keithley meters were used to supply voltage and measure the current flowing in the circuit simultaneously. The circuit set up for field effect devices is shown in Fig. 3.8.

As can be seen in Fig. 3.9, there are two electronic circuit loops, G-S and S-D loops. Both loops join at a common ground at the device S end. For each loop, the Keithley meter outputs a voltage as well as measuring the current simultaneously. The voltages supplied in the G-S and S-D loops are named $V_G$ and $V_D$, respectively. The corresponding currents measured in the G-S and S-D loops are denoted as $I_G$ and $I_D$, respectively. The output voltage limit for Keithley is $\pm500$ V and the current measurement limit is $\pm2$ mA. This circuit setup is the standard one to study three terminal devices. In the following two sections, the data acquisition will be discussed.
3.2.2 I-V Measurements

I-V measurements are designed to obtain the carrier $\mu_{\text{FET}}$ in a conventional field effect transistor. $\mu_{\text{FET}}$ is an important parameter to characterize the performance of a field effect device because it provides information about the sensitivity of carriers to the electric field as well as the properties of the material. In the I-V measurements, one scan $V_D$ under a fixed $V_G$. For each $V_G$ applied to the devices, there is always a set of $V_D$ being scanned and the corresponding $I_D$ and $I_G$ are measured. The $\mu_{\text{FET}}$ can be obtained using Eq. (2-26) and Eq. (2-27) and the threshold voltage $V_T$ can be extracted as well.

3.2.3 Time Dynamic (I-t) Measurements

In the time domain measurements, the channel was kept at a specific $V_D$. When a particular $V_G$ was applied, one monitored chronologically the evolution of $I_D$ with time.
The purpose for the time dynamic measurements is to obtain the carrier relaxation
dynamic in the system under external electric field.

3.3 Temperature Measurements

3.3.1 Field Effect in situ Time Dynamic Measurements

3.3.1.1 Equipment and Setup

Delta 9059 from Delta Design Inc. was used to carry out the temperature variation. The temperature range achieved in the environmental chamber in Delta 9059 is from 90 K – 473 K. Delta 9059 uses liquid nitrogen to cool down the environmental chamber. During cooling, a build-in thermometer controls the liquid nitrogen flow into the chamber. A vaporized nitrogen gas continuously purges the air inside the environmental chamber. As shown in Fig. 3.10 (a), the device was attached to the bottom of a metal copper box with a thermalcouple positioned right on top of it to measure the temperature. Two-probedevices (see Fig. 3.6) were used in the temperature dependence I-t measurements. The three electrical connections of the sample were soldered to the BNC connection inside the copper box. The metal box was placed in the center of the Delta 9059 environmental chamber and the BNC lines were hooked up to the electronic circuits outside the Delta 9059 with the arrangement shown in Fig. 3.9. The final experimental setup is shown in Fig. 3.10 (b).
3.3.1.2 Data Acquisition

The time dynamic measurement technique accompanied with temperature variation was performed to examine the field effect devices. At room temperature, a small $V_D$ was applied to the channel before $V_G$ applied. $V_G$ was applied for a 30 second period followed by resetting $V_G$ to 0 V. The evolution of the channel current and leakage current was recorded with a Labview program on a computer. A different temperature was then selected and the measurements repeated.

Figure 3.10: Temperature dependence time dynamic measurement setup. (a) Sample mounting. (b) Experimental setup.
3.3.2 Field Effect in situ DC conductivity Measurement

3.3.2.1 Equipment and Setup

The Delta 9059 from Delta Design Inc. was used to carry out the temperature variation from 90 K to 300 K in this study. In Fig. 3.11 (a), the device was attached to the bottom of a metal copper box with a thermalcouple positioned right on top of it to measure the sample temperature. The 4-probe device configuration (see Fig. 3.8) was employed in this measurement. The five electrodes (2 current inputs, two voltage probes and one gate electrode) were soldered to the inner BNC connection of the copper box. Then after loading the sample, the copper box was placed inside Delta 9059 (see Fig. 3.10(b)). And the five BNC connectors were connected externally to a Keithley 2400 and a Keithley 487. The Keithley 2400 was set to a four wire mode to supply current and measurement the voltage.

3.3.2.2 Data Acquisition

The standard 4-probe measurements were performed on the channel area. Due to the polarity dependence of the device output characteristics for I-V measurements, a very small negative current was applied to the ungrounded side of the device to obtain the correct $\Delta V$ in the linear regime. After applying $V_G$ at room temperature, the on/off ratio was measured to be $R_d(V_G)/R_d(0)$, then cooling was initialized. The system was slowly cooled down to 273 K to make sure that the air inside the Delta 9059 was completely purged out. Measured data was recorded during the cooling down cycle. Due to the
input impedance limit of Keithley meters in different ranges, it is necessary to double check the obtained value in a range higher than the current used one.

Figure 3.11: Temperature dependence conductivity measurement setup. (a) Sample mounting. (b) Experimental setup.

3.4 EPR Measurements

3.4.1 Field Effect *in situ* Room Temperature EPR Measurements

The Field Effect *in situ* EPR measurements studied in this thesis are comprised of two parts, room temperature and various lower temperatures. The experimental setup in former part will be discussed in this section while the latter part will be provided in Sect. 3.4.2. The common for both experiments is combining the I-t measurement setup and EPR instrument functions.
3.4.1.1 Equipment and Setup

**Bruker ESP 300 Spectrometer** was used to take the microwave absorption spectra of the sample. The *in situ* EPR spectra were taken in ESP spectrometer operating in X-band (9.5 GHz). There are two microwave cavities with dimensions 3 cm×3 cm×3 cm for each connected to each other. The cavities are located between two huge magnets. A microwave generator launches the microwaves down a waveguide to tune the cavity to the resonance state (see Fig. 3.112).

**Sample mounting:** A quartz tube with 3 mm in diameter and round shape at the bottom was used to load samples into the cavity. Device configuration (9) was used in the room temperature EPR study. Silver paste (Electron Microscope Sciences) was applied to fix the copper wire to the Au and Al contacts to hook up to the FET circuits (see Fig. 3.13). The measuring circuit in this experiment is shown Fig. 3.9 except keeping the device inside a quartz tube.

**Experiment Setup:** By loading the quartz tube shown in Fig. 3.13 into the EPR cavity 1, the *in situ* setup is complete,
Figure 3.12:  Bruker ESP 300 Spectrometer setup for detecting unpaired spin. The middle two big round shape plates are magnets. The cavities are sandwiched between two magnets.

Figure 3.13:  The sample mounting and electronic circuit for room temperature EPR measurement.
3.4.1.2 Data Acquisition

For the measurement performed here, the cavity was tuned to obtain the resonance microwave frequency. It is necessary to check the EPR spectrum with an empty cavity to verify the clean measurement environment. After that, room temperature EPR spectra are ready to be collected. First, the cavity is tuned with the sample to obtain a resonance frequency and a good tuning can be selected from a dip laying in the mid-height between two equal split cavity tuning spectrum. After obtaining the critical tuning spectrum, one can start to collect the absorption spectra from the sample. In these measurements, the EPR spectra were recorded under the conditions of floating $V_G$ and $V_G > 0$.

3.4.2 Field Effect in situ Temperature Dependence EPR Measurements

3.4.2.1 Equipment and Setup

The instrument, electronic circuits and experimental setup discussed in this section are identical with Sect. 3.5 except varying temperature and sample sealing was added. The sample inside the EPR quartz with a homemade metal tool which can hold two small O-rings in the Ar gas filled glove box. The electrical wires are tightly pressed between two O-rings (see Fig. 3.14) and the FET device circuits are connected. The quartz was then installed into the ESR cavity of an Oxford 900 He continuous flowing cryostat. The Oxford temperature controller was used to control the helium flow inside the cryostat. The temperature performed in this study ranged from 5 K–300 K.
3.4.2.2 Data Acquisition

The measurement techniques are the same as Sect. 3.5. After taking the room temperature EPR signals, the sample was cooled down to a base temperature of 5 K and gradually warmed up while collecting periodically the absorption spectra at different temperatures.
CHAPTER 4

ROOM TEMPERATURE STUDY OF ELECTRIC FIELD EFFECT IN PEDOT:PSS

4.1 Motivation

4.1.1 Screening Effects Prediction in PEDOT:PSS

Fully doped PEDOT:PSS is capable of carrying one charge per every three repeat units with a metallic band structure based on the UV-Vis-NIR absorption spectrum. It is known that a conventional metal will induce an equal amount of opposite charges on the surface to prevent external electric field penetration. For the metallic-like polymer having carrier concentration \( \sim 10^{21}\text{cm}^{-3} \), the Debye screening length is

\[
\lambda_D = \frac{1}{k_0} = \frac{\varepsilon_0 k_B T}{e^2 \rho} = \frac{3(8.85 \times 10^{-14} \text{ F/cm})(25.6 \text{meV})}{(1.6 \times 10^{-19} \text{ C})(e)(10^{21} \text{ cm}^{-3})} = 6.5 \times 10^{-9} \text{cm} = 0.65 \text{Å}.
\]

In this case, the metallic polymer is expected to behave as a conventional metal with a sheet of negative charges induced at the interface to prevent the penetration of the electric field.
4.1.2 Experimental Observation of Screening Effect in PEDOT:PSS

Various types of devices were fabricated by incorporating several dielectric materials but all with the same active component. All types of devices listed in Table 3-2 were tested in the laboratory environment at room temperature using the testing circuits shown in Fig. 3.8. An unexpected conductance change in PEDOT:PSS was observed in device type 1, 2, 3, 5, 6, and 9. Fig. 4.1 illustrates an example of the field effect phenomenon in the type 1 device under the gate electric field applied. The black curve shows the drain current $I_D$ which represents the PEDOT:PSS conductance. The PEDOT:PSS conductance can be modulated up to three orders of magnitude difference during $V_G$ applied. The typical screening effect was not observed in the metallic polymer which was a motivation for this study.

![Figure 4.1: Field effect phenomenon in PEDOT:PSS.](image)

Figure 4.1: Field effect phenomenon in PEDOT:PSS.
Due to structural similarity, the conventional field effect transistor model was initially assumed and the corresponding I-V measurements were performed to understand the unexpected field effect phenomenon in PEDOT:PSS.

4.2 I-V Characterization

Type 3 devices in Table 3-2 with channel dimensions \((L \times W \times t)\) 578 \(\mu\)m \(\times\) 850 \(\mu\)m \(\times\) 83 nm were studied. The dielectric PVP was 46 nm thick measured by Alpha-Step 500 surface profiler (Tencor). A certain potential was applied to the gate electrode and the current flowing in the PEDOT:PSS layer was recorded while varying the drain voltage. A full \(V_D\) scan was started from \(+5 \text{ V} \rightarrow 0 \text{ V} \rightarrow -5 \text{ V} \rightarrow 0 \text{ V} \rightarrow +5 \text{ V}\). This scanning process was repeated at every different gate voltages. And each \(V_D\) scanning process starts 5 minutes after a new \(V_G\) was applied.

4.2.1 Experimental Results

The responses of the PEDOT:PSS channel to various vertical electrical fields by the potential applied on the gate electrode are shown in Fig 4.2. The \(V_D\) scanning rate was 25 mV/s. Apparently, gate voltages substantially change the I-V characteristics. Increment of the gate voltage decreases the channel conductance. The I-V curves are observed to be polarity dependent and also show a hysteresis. In the first quadrant \((I_D, V_D)=(+, +)\) (see Fig. 4.2 (a)), at low \(V_G\) \((>0)\), the I-V curves are mostly linear and the nonlinearity occurs at high positive \(V_G\). The discontinuity of I-V curves at \(V_D= +5 \text{ V}\) is due to the initiation of scanning \(V_D\) set at \(+5 \text{ V}\). All I-V curves do not match in both drain voltage
scanning directions. For the third quadrant \((I_D, V_D) = (\cdot, \cdot)\) (see Fig. 4.2 (b)), both linear and saturation regions appear in each curve. A clear hysteresis behavior can be observed upon drain voltage sweeping. For a given \(V_G\) and \(V_D\), the drain current is larger in the direction of increased \(|V_D|\). Comparing both quadrants, the I-V characteristics in the third quadrant are similar to a conventional MOSFET. A pronounced modulation in the channel conductance was obtained for \(V_D < 0\) V.

By lowering the scanning rate to 10 mV/s, the hysteresis is minimized (see Fig. 4.3) since the system is more static. When the gate electrode is physically disconnected from the circuit, the PEDOT:PSS channel exhibits a linear I-V behavior, which implies the contacts between PEDOT:PSS and Ag electrodes are ohmic. This metal-organic conductor-metal junction presented in our structure is different from a conventional metal-semiconductor-metal junction. For a conventional FET, the active channel is equivalent to two back-to-back diodes operating under an imposed bias. The reverse biased diode dominates the output current characteristics. In our device, the intrinsic metal-organic conductor junction behaves as a simple resistor. No hysteresis was observed up to 1 V/s scanning rate in the case of disconnecting the gate electrode to the circuits. However, applying gate voltages substantially changes the I-V characteristics. The charge conduction is further suppressed as \(V_G\) increases.

Based on the similarity of I-V characteristics to the MOSFETs, a conventional MOSFET model was used to obtain \(\mu_{FET}\) by using Eq. (2-27). Fig. 4.4 shows the square root of \(I_D\) in the saturation region \((I_{D(sat.)})\) vs. \(V_G\), one can obtain \(V_T \sim 7\) V for this device.
Figure 4.2: I-V characteristics of a device in the (a) first quadrant and (b) third quadrant.

Figure 4.3: I-V characteristics of a device in the third quadrant with 10 meV/s scanning rate.
Due to the leakage current, the device shown in Fig. 4.3 can not be completely turned off. The slope, \( m = \frac{W \mu_{\text{FET}} C_i}{2L} = -1.49 \times 10^{-3} \ (\sqrt{A/V}) \) for the \( \sqrt{I_{D(sat)}} \) vs. \( V_G \) plot which yields an extracted mobility of \( \mu_{\text{FET}} = 52 \ \text{cm}^2/(\text{Vs}) \) for carrier conduction with \( L = 578 \ \mu\text{m}, W = 850 \ \mu\text{m} \) and \( C_i = \frac{\varepsilon}{d} = \frac{3(8.85 \times 10^{-12} \ F/m)}{460 \times 10^{-10} \ m} = 5.8 \times 10^{-4} \ F/m^2 \).

Figure 4.4: Third quadrant \( \sqrt{I_{D(sat)}} - V_G \) plot for Fig. 4.4.

### 4.2.2 Discussion

Fig. 4.2 and Fig. 4.3 show the depletion mode operation of PEDOT:PSS devices at positive gate biases. For the conventional depletion mode operation, the majority carriers are repelled away from the semiconductor-insulator interface which gradually removes the conducting channel. However, for the metallic like PEDOT:PSS, the assumption of
depletion model contradicts with the charge screening nature of a conductor. This electric-field modulation effect is still observed when the PEDOT:PSS layer is 10 μm thick. Further, the relatively high mobility 52 cm$^2$/ (Vs) obtained in our devices and reported by Okuzaki et al. ($\mu_{\text{FET}} = 170 \text{ cm}^2/(\text{Vs})$) [37] obtained from the I-V characteristics also implies the failure of the conventional charge depletion pictures. Thus, the observed dramatic change in the highly doped polymer conductance can not be understood by modeling it as a conventional metal or semiconductor.

The hysteresis current output characteristic is an indication of a charging-discharging phenomenon during the device operation. From estimating the RC time constant ($\tau$) for the Al - PVP - PEDOT:PSS capacitor in our device, it takes about 0.3 s for carriers to charge and discharge the PVP capacitor by taking $C = 283.6$ pF, $\varepsilon \sim 3$ for the polymer and $R \sim 1 \text{ G}\Omega$. $R$ was selected from the experimental data when $V_G = 0$ V and $V_D = -0.05$ V which yields the largest value. $\tau$ decreases as the gate voltage is applied for smaller gate-source resistances. However, the estimated time constant can not fully explain the hysteresis I-V curves observed. We propose that ion motion is involved under the applying gate field. Ions such as Na$^+$, H$^+$, K$^+$ etc. may be present in both PEDOT:PSS [151] and PVP layers. These ions can be driven by the electric field resulting in a slow response with respect to the electric field. Therefore, ion motion can play a crucial role in the origin of the metallic polymer based device operation.
4.3 Dielectric Layer Characterization

A capacitor structure was used to characterize the dielectric material, PVP. The area (A) for the Al metal electrodes are 850 µm × 700 µm and the thickness of PVP layer is 1.14 µm.

4.3.1 DC Conductivity and AC Conductivity Measurements

Fig. 4.5 shows the I-V measurement of the PVP capacitor in air. The voltage scanning was started from 0 V → +30 V → 0 V → -30 V → 0V with scanning rate 167 mV/s. The I-V measurement shows that a hysteresis appears during voltage scanning. A possible explanation for this hysteresis behavior is impurities originally present in the materials driven by the electric field. By linearly extrapolating the resistance from the I-V

![Figure 4.5: The I-V measurement of Al/PVP/Al structure.](image-url)

\[ \rho = 5.2 \times 10^{10} \text{ ohm-cm} \]
curve, the resistivity for PVP is around $5.2 \times 10^{10}$ ohm-cm. The ac conductivity measurement for this capacitor is shown in Fig. 4.6. The frequency dependent conductivity yields $\sigma(\omega) = \frac{1}{\rho(\omega)} = C\omega$, where $C$ is a constant. This dependence is a signature of hopping transport in amorphous materials. The capacitance at $\omega = 0$ is around 65 pF.

![Figure 4.6: The ac conductivity measurement of Al/PVP/Al structure.](image)

4.4 Transient Current Study

To further understand the ion motion inside PEDOT:PSS, a transient current study of the channel conductance was performed. Two-probe measurements were used in the transient current studies with 30 second and a long period gate voltage “pulses”.

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4.4.1 Short Time Gate Voltage “Pulse”

In order to prevent degradation of devices, a short 30 second duration was used for various gate potentials and a constant 0.1 V drain voltage was applied to record the conductance of PEDOT:PSS. The sample studied here has channel dimensions \((W \times L)\) 380 \(\mu\)m×950 \(\mu\)m covered with a 600 Å thick PEDOT:PSS layer as the active component, with a 300 Å thick PVP insulating layer and a 300 Å thick Al gate electrode. The gate potential pulses ranged from 0 V to 4 V, which was increased with a 0.5 V step size (see Fig. 4.7(a)) and the associated drain current also varied accordingly. Here, the drain current has not reached a stationary regime within the 30 second pulse and the recovery time takes even longer after \(V_G\) is restored to zero.

In each gate bias-on cycle, the initial channel conductance changes approximately linearly with time. This suggests that ions drift into the conducting polymer with a constant velocity at least in the initial short period of the application of gate potentials. The linear modulation of the channel current due to the initial constant drift of the ions is shown in Fig. 4.7(b), the expanded chart for \(V_G = 3.5\) V for instance. We describe the initial time dependence of drain current as

\[
I(t) = I(0)(1-kt),
\]

where \(k\) is the response rate of the conducting polymer to the gate potential and \(I(0)\) stands for the drain current right before the gate potential is applied. By extracting the response rates from various gate potentials, we derive the relationship

\[
k = k_0 \exp\left(\frac{V_G}{V_0}\right),
\]
where \(k_0 = 6 \times 10^{-6} \text{ (1/s)}\) and \(V_0 = 0.556 \text{ V}\) in this device as shown in Fig. 4.7(c). This relationship suggests the exponential dependence of hopping rate for ions on the gate fields. The other explanation for this exponential dependence of \(k\) on \(V_G\) is the rate of electrochemical reaction which generates ions as mentioned in section 2.1.2.2.

To clarify the possible mechanisms of this exponential dependence, we first study the equilibrium states in the active channel by applying gate potentials for a longer time period.
Figure 4.7: The results of 30 second gate voltage “pulse” modulation. (a) Modulation of $I_D$ upon applying $V_G$ from 0 V to 4 V with a 0.5 V step. The channel conductance is returned to its original state before a gate voltage is applied. (b) The expanded chart for $V_G = 3.5$ V cycle. The pink line is the fitting line. (c) The fitting result of the response rate of the drain current corresponding to various gate voltages.
4.4.2 **Long Period Gate Voltage “Pulse”**

In the case of a long period $V_G$ “pulse” situation, the drain voltage was kept at -1 V and the applied gate potential ranged from 0 V to 4.5 V with a 0.5 V step size. The gate voltage was reset to 0 V after each potential step. The channel dimensions ($W\times L$) for this device are 900 $\mu$m $\times$ 500 $\mu$m. The PEDOT:PSS layer is 800 Å thick followed by a 500 Å thick PVP layer on top and finished with a 300Å thick Al gate electrode.

Both the modulated drain and gate currents were monitored in the measurement. The gate voltage was reset to zero after the channel current reached a minimal constant value (see Fig. 4.8(a)). And the gate potential was applied while the channel was at about 90 % recovery. As can be seen in Fig. 4.8(b), there is an equilibrium state (off-state) corresponding to an applied gate potential and this suggests that electrochemical reaction driven by the gate potential may not be the main working mechanism. To restore the original channel conducting state (on-state), no negative bias voltage is required. In these polymer FETs, the leakage current was observed to be a few tens nA at $V_G > 0$ V, and a few tens pA at $V_G = 0$ V. The leakage current at a zero gate bias suggests that the drain current recovery is mostly due to the resetting of ions diffusing back to their original positions. Thus, injecting ions into the polymer film changes the conductivity of highly doped polymer. And the switching-off time depends on the gate potential.
Figure 4.8: Drain current modulation of long period gate voltage “pulse”. (a) The modulation of drain current by keeping gate voltages for long time periods. The modulation profile of gate voltage is shown on the top of the panel. (b) The zoom in of cycle $V_G = 2V$. The gate voltage, drain current and gate current are shown in the panel.
4.4.2.1 System Relaxation Analysis

The drain current for a given gate-on period was fit with a stretched exponential function,

\[
\Delta I(t) = \Delta I_0 \exp\left[-\left(\frac{t}{\tau}\right)^\alpha\right]
\]

(4.3)

\[\Delta I(t) = I(t) - I(t'),\]

\[\Delta I_0 = I(0) - I(t'),\]

where \(t'\) is the time taken to approach equilibrium, \(\tau\) and \(\alpha\) are fitting parameters. Fig. 4.9(a) shows the fitting results of the drain current relaxation in the \(V_G = 0.5\) V and 4 V applied condition. According to the fitting results, the average value of \(\alpha\) is around 1 (see Fig. 4.9(b)). Therefore, a simple exponential function will be good enough to describe the polymer system under an electric field. However, the relaxation of the system can not be described by only one relaxation process. As indicated in Fig. 4.9(a), there are two relaxation processes involved in this system at \(V_G = 4\) V. For the fitting results of using simple exponential in Fig. 4.10(a), two relaxation processes occur when \(V_G > 2\) V. The fast relaxation time of the system modulated by the ions under different applied \(V_G\) in this device ranges from 3 seconds to 3 minutes. An exponential relationship can be obtained for the fast dynamic relaxation vs. \(V_G\) as seen in Fig. 4.10 (b).
Figure 4.9: The dynamic relaxation fitting of $I_D$ in the gate voltage applied condition. (a) Stretched exponential fitting for the $V_G = 0.5$ and 4 V. (b) Value of exponent $\alpha$.

Figure 4.10: Replotting dynamic relaxation fitting of $I_D$ in the gate voltage applied condition. (a) Simple exponential fitting for the $V_G = 2$ and 2.5 V. (b) log $\tau - V_G$ relation for fast relaxation process.
The gate potential determines the off-state of the polymer channel. The ratio of on to off state conductance ($\sigma_{on}/\sigma_{off}$) is plotted with its corresponding $V_G$ as shown in the inset of Fig. 4.11. As the gate voltage increases higher than a critical voltage ($V_C$), the on/off ratio decreases as expected. Fitting was attempted using $\sigma_{on}/\sigma_{off}$ vs. $V_G$ with

$$\frac{\sigma_{on}}{\sigma_{off}} = \left(1 - \frac{V_G'}{V_C'}\right)^\gamma$$

(4.4)

$$V_G' = V_G - V_T,$$
$$V_C' = V_C - V_T,$$

where $V_T$ is the smallest voltage causing 1 % change in channel conductance, $V_G'$ is the actual gate voltage causing conductance modulation, and $V_C'$ is the actual critical voltage to turn off the channel conductance. For the device shown in Fig. 4.11, $V_T \approx 0$ V, $V_C' = 4$ V and $\gamma = 2.9$. The value of $\gamma$ is almost the same in other devices with different channel W/L ratios.
4.4.2.2 Leakage Current Analysis

Because the leakage current is always present in the device when the gate potential is applied, this issue was carefully examined. Unlike conventional FETs, the leakage current present in these FEDs does not simply behave as a capacitor charging current. In Fig. 4.8(b), take \( V_G = 2.5 \) V for example, the variation of the gate current, \( I_G \), was recorded simultaneously with drain current. Clearly, \( I_G \) starts with an initial increase followed by a substantial decrease. The channel conductance is gradually suppressed as gate charges are continuously injected into the polymer film for the first few minutes. Since PEDOT:PSS carries one hole charge per every three PEDOT repeat units (a unit
(cell), the injected charges can be quantified in terms of a unit cell. The evolution of injected gate charges per PEDOT:PSS cell, $Q_{\text{total}}$/cell, with respect to the normalized channel resistance $R/R_0$ at different gate voltages is plotted in Fig. 4.20 (a).

Apparently different gate voltages lead to different equilibrium states (see Fig. 12(a)). For a specific applied $V_G$, further injection of gate charges does not change the resistance of the active channel significantly which suggests that a gate current is the combination of both ionic and electronic currents. The ionic current originates from ion migration and the electronic current is the electron flow in and out the source and gate electrodes at equilibrium state. Charging current does not have significant contribution to the monitored gate current since it only occurs during the initial 0.3 seconds ($RC$ time constant) and is beyond instrument resolution. By subtracting the electronic current, all curves corresponding to different gate voltages almost collapse into one curve as shown in Fig. 4.12 (b). This suggests that the percolation phenomenon occurs during ion injection. This deviation occurs at different gate potentials; therefore, we replot $R/R_0$ with respect to $Q_{\text{ion}}$/cell according to the scaling relationship stated in Eq. (2-61),

$$\frac{R_0}{R} = \left(1 - \frac{Q_{\text{ion}}/\text{cell}}{Q_C}\right)^{-\beta},$$

where $Q_C$ is the critical charge per cell and $\beta$ stands for the scaling index of the system. $\beta \approx 1$ for a $(1 + \varepsilon)$-dimensional conducting network where $\varepsilon < 1$ [132]. From Fig. 4.12(b) we can see that the accumulated ion charge controls the channel resistivity and around 2% ion charge per cell is enough to lead to high on/off ratio.
Figure 4.12: (a) The accumulation of gate charge with time per unit cell with different gate voltages. (b) Reploting of the accumulated gate charges after subtracting the electronic current.
4.4.3 Discussion

In the transient current study, the long switching time between different conducting states indicates that the motion of ions plays a role in the system which is consistent with the observed hysteresis in I-V characteristics. For 30 second gate pulse measurements, the channel response rate is $k \propto \exp [V_G (V)/0.556]$, which shows that ions hop exponentially with the gate electric field. Because the hopping frequency ($f$) for an ion under electric field ($E$) is proportional to [152]

$$f \propto \exp\left[\frac{eER}{2k_BT}\right],$$

we can estimate the hopping distance ($R$) for ions is

$$\frac{eR}{2k_BTd} = \frac{1}{0.556} \Rightarrow \frac{eR}{2(25.6meV)(30nm + 60nm)} = \frac{1}{0.556} \Rightarrow R = 8nm.$$

For an ion with a mass much greater than that of an electron, it is difficult for an ion to hop over 5-6 repeat units of PEDOT:PSS. A possible explanation of this inconsistency is the fact that some fraction of the total voltage drops across the dielectric layer so that the true electric field inside the PEDOT:PSS is smaller than the applied $V_G$.

On the other hand, the exponential dependence of $k$ on $V_G$ can also be interpreted as the rate of electrochemical reactions which generates ions as mentioned in Sect. 2.1.2.2. However, by keeping $V_G$ for a longer duration, equilibrium states were observed at different gate biases. The existence of static states is contradictory to the theory of mass transport in electrochemical process [45] that the charge transfer persists until one of the species vanishes.
The relaxation of the carriers in PEDOT:PSS under applied gate potentials is described by multiple relaxation processes. We fit the drain current to a stretched exponential (see Eq. 4.3). The results show that a simple exponential function is good enough to describe the general relaxation of the system. There are two major relaxation processes of the carriers under ion motion. In general, one can expect that the first “fast” mechanism should prevail at the initial period of time and the second “slow” mechanism should dominate later. A fast relaxation process can range from a few seconds to several tens seconds followed by a slow relaxation. The fast relaxation reveals the response of a polymer system under non-equilibrium conditions against ions present while the slow relaxation indicates the thermalization of the system to its new configuration. Therefore, the multiple relaxation process accounts for several factors such as ion diffusion, ion redistribution, electron-ion interaction and the change of polymer conformation.

From analyzing the ion flow through the leakage current measurements, we found that around 2% holes in the PEDOT:PSS being substituted by ion charges is enough to change the conductance up to three orders of magnitude (see Fig. 4.11(b)). The small fraction of ion compensation inside the polymer, which leads to completely blocking the charge transfer paths, suggests that the ions migrate to the polymer backbone to destroy the percolation in the conducting channel. As proposed by Nilsson et. al. [40], the electrochemical switching of PEDOT:PSS conductance through mediate ions (M⁺):

\[
\text{PEDOT}^+\text{PSS}^- + M^+ + e^- \rightarrow \text{PEDOT}^0 + M^+\text{PSS}^- \quad (4.7)
\]

The \(e^-\) is transported inside the PEDOT:PSS film and M⁺ migrates into the polymer film in order to maintain charge neutrality in the PEDOT:PSS film. The reduction of PEDOT
to its neutral state is possible by gaining electrons from the circuit but not the key mechanism for the small fraction of charge compensation on the PEDOT backbone. The deviation of curves from linear fitting lines in Fig. 4.12(b) may due to thermalization or conformational changes of the polymer after ion ingress to the system, which is a slower relaxation process. The obtained percolation evidence clarifies the device operation mechanism. Compensating charges on the polymer backbone is not the major contributor of ions in this kind of devices. An electrochemical mass transport process may be involved in this doping system; however, it is not the main working mechanism.

According to the chain linked granular model [103], the conducting polymer systems can be viewed as well ordered crystallites embedded in a poorly conducting disordered media. The conducting network is formed by charge hopping from one well ordered grain to another through intermediate states in the disordered regions. Due to the screening effect in the crystallites, the ions migrate to the disordered region and columbically interact with the dopants, PSS\(^-\), lowering the local potential in the PEDOT:PSS backbone. Therefore, the observed ionic current is the nonfaradic current when ions ingress to the amorphous PEDOT:PSS region to charge and discharge the interfacial region between PEDOT\(^+\) and PSS\(^-\). No charge transfer occurs during the double layer formation.

The double layer formation explains the unusual ion hopping distance. In our calculation, we assume that the voltage drops uniformly across the dielectric layer and PEDOT:PSS. In fact, since there is double layer forming in the dielectric layer, most of the voltage drop is across the double layer [45]. The real electric field inside
PEDOT:PSS should be $E_r = m E$, where $m < 1$. Thus, the real ion hopping distance is $R_r$. Therefore,

$$E_r R_r = m E R_r = E(m R_r) = E R.$$  \hfill (4-8)

This gives

$$R_r = \frac{R}{m}.$$ \hfill (4-9)

So, the obtained ion hopping distance earlier is magnified by a factor of $1/m$.

The critical ion charge concentration ($Q_C$/cell) to modulate the hopping sites is around 2% ion charges per cell from the analysis of leakage current. The small fraction of ions coulombically interacts with PSS$^-$ thereby indirectly modulating the local potential energy of the trapped holes on the polymer backbone. The holes become more mobile and hop away to the electrodes to maintain charge neutrality (see Fig. 4.13). Therefore, the ion screening effect introduces disorder in the system resulting in changing the available density of states around the Fermi level in the disordered region.

![Potential energy modulation of hole charge by ion screening.](image)

Figure 4.13: Potential energy modulation of hole charge by ion screening.
4.5 Summary

The unexpected penetration of a gate electric field inside metallic polymer, PEDOT:PSS, is observed. A conventional MOSFET model was initially assumed to characterize these organic conductor based devices. Although the output and transfer characteristics are similar, the extracted $\mu_{\text{FET}} \sim 100 \text{ cm}^2/(\text{Vs})$ from I-V curves using conventional MOSFET is two orders of magnitude larger than that estimated from the conductivity. This contradictory result for mobility indicates that conventional MOSFET model is invalid in the devices studied here.

The sweeping rate dependent I-V curves in closed gate-source (G-S) circuit condition imply the charging and discharging behavior upon varying $V_D$. This hysteresis behavior is either due to a large capacitance of the dielectric layer or a slow motion of hole carriers on the PEDOT backbone. The slow switch-on and -off on the order of several minutes is not consistent with the estimated $RC$ time constant which is less than 0.3 s for a PVP capacitor. Thus, we propose that the ion motion is responsible for the observed field effect phenomenon.

To understand the role of ions in the PEDOT:PSS conductance suppression, transient current measurements are performed. In the short gate voltage “pulse” study, the obtained large ion hopping distance (8 nm) indicates that the gate voltage is not homogeneously distributed across the dielectric and PEDOT:PSS. A significant fraction of the gate electric field is dropped at the Al/dielectric dipole layer. The forming of electrical double layer at the Al/dielectric interface indicates that positive charged ions inject into PEDOT:PSS. The long period gate voltage “pulse” measurements provide information
on PEDOT:PSS system relaxation under ion insertion and the evidence for the role of ions. The conductance of PEDOT:PSS due to ion presence under gate electric field can be described by a simple exponential function. Two relaxation processes are involved in the carrier relaxation at high electric field. The fast relaxation is attributed to the drifting of ions by a gate field while the slow relaxation comes from the thermal equilibrium of the PEDOT:PSS to its new configuration. The relation between the $\sigma_{on}/\sigma_{off}$ and $V_G$ can be described by power law formula.

The leakage current provides the information of ion flow. From analyzing the evolution of channel conductance with injected ion charges, two major conclusions can be drawn: (1) instead of $V_G$, the injected ion concentration controls the channel’s final state and (2) $\sim 2\%$ ion charges present in the PEDOT:PSS system is enough to completely suppress the charge conduction on PEDOT:PSS backbone. Since various final static states are observed and no negative gate voltage is required to retrieve the PEDOT:PSS conductance, the charge transfer between injected ions and the polymer backbone could happen but not the main reason causing the observed electric field effect. Therefore, the recorded leakage current mostly is a nonfaradic current.

Only $\sim 2\%$ of hole charges to be replaced by inserted ions is enough to destroy the charge conduction networks. The small fraction of charge compensation indicates that the PEDOT:PSS conductance suppression is not entirely caused by electrochemical dedoping of the conducting polymer. In terms of the chain-link granular model [103], the injected ions can migrate into the disordered region due to the porous nature of conducting polymers. The role of ions inside PEDOT:PSS is to screen the coulombic
interaction between the PSS\textsuperscript{−} and the hole charge on the polymer backbone. This can be analogous to the compensation of donors and acceptors in Si. The local hole potential energy screened by injected ions in the disordered region modulate the available density of states around the Fermi level for charge conduction. Thus, the observed field effect phenomenon can be attributed to modulation of conductivity in the disordered regions in the presence of injected ions.

More evidence regarding the role of ions was collected in the temperature measurements in Ch. 5 and electron spin resonance measurements in Ch. 6 to support the mechanism proposed here.
CHAPTER 5

FIELD EFFECT

_in situ_

TEMPERATURE MEASUREMENTS

As proposed in Ch. 4, the unusual electric field effect phenomenon in a metallic polymer originates from ion motion. A percolation phenomenon was observed when ions were driven inside the conducting polymer system. In this chapter, the roles of ion motion and physical quantities of ions are examined by temperature measurements. A dielectric material with known ion specie, Li\(^+\), is used to compare and support the previous conclusion in Ch. 4 and is the main focus of this chapter for obtaining physical quantities. A very small drain voltage \(V_D = -0.2\) V and gate voltage \(V_G = 0.5\) V, or floating voltage were used for investigating the Li\(^+\) ion motion in this study. A detailed description of ion diffusion behavior inside a conducting polymer is discussed. Finally, a physical mechanism in the disordered region of conducting polymer undergoes conductance suppression in the presence of ions is addressed.
5.1 *in situ* Time Dynamic Measurements

Type 1, 3 and 6 devices listed in Table 3-2 were studied in this chapter. The thickness of dielectric layers are 4 µm (OA), 50 nm (PVP) and 50 nm (LiClO₄ – PEO) for type 1, 3, and 6 devices, respectively. As the transient current results show in chapter 4, the conductance of PEDOT:PSS drops upon applying a gate voltage. To prevent degradation of the material under a long duration of gate electric field, a short gate voltage “pulse” was applied to study the temperature behavior of field effect phenomenon. Based on the devices' performance, a 30 second time period was selected for \( V_G \) applying duration with the exception of 150 seconds for devices with the OA dielectric.

Figure 5.1 shows the device operation incorporating three kinds of dielectric materials at room temperature and 280 K (290.5 K for devices using OA as dielectric). As can been in Fig. 5.1, the channel conductance decreases around 50% upon applying \( V_G = 20 \text{ V}, 4 \text{ V} \) and 0.5 V for devices using OA, PVP and LiClO₄-PEO as dielectric. When the temperature is lowered to 290.5 K or 280 K, the field effect is suppressed in all three kinds of devices. The temperature sensitive phenomenon for the device performance indicates ion motion is involved.

Due to the hopping motion of ions, a maximum hopping rate was calculated by taking the first derivative of drain current (\( I_D \)) with respect to time (t). In Fig. 5.2, two maxima rates for \( I_D \) was obtained for devices incorporating OA and this result suggests two kinds of ion motions are driven by gate field while one kind of ion for PVP and LiClO₄-PEO devices.
Figure 5.1: Device operation at room temperature and below room temperature. The dielectric materials using in the devices are (a) OA, (b) PVP and (c) LiClO₄-PEO.
5.1.1 Under Gate Electric Field

Considering the motion of interstitial ions, the ions have to overcome a potential barrier $U$ to move to a position nearby. In the presence of electric field, the barrier height is modified by an amount of $\frac{1}{2} eER$. Thus, the ion hopping frequency ($f$)

$$f \propto \exp\left[\frac{U - \frac{1}{2} eER}{k_B T}\right]$$  \hspace{1cm} (5.1)

is parallel to the electric field. And the average ion hopping barrier ($E_a$) can be obtained from the $I_D$ response rate with respect to temperature $T$ through

$$\frac{d[I(t)/I(0)]}{dt} = \exp\left[-\frac{E_a}{k_B T}\right].$$  \hspace{1cm} (5.2)

To understand the relationship between the ion motion and device performance, the transient current measurements were carried out from 230 K to 300 K for PVP and LiClO$_4$-PEO devices.

The channel conductance in both devices decreases 50% within 30 seconds at room temperature by applying different gate voltages subject to individual performance. The purpose for this is to make sure that both devices have the same channel configuration after injecting ions. Fig. 5.3 (a) shows an example of one cycle time transient response of $I_D$ modulation from 230 K to 300 K for a LiClO$_4$-PEO device. The gate currents at various temperatures were recorded when a gate voltage was applied (see Fig. 5.3 (b)). The temperature analysis of the response rate for PVP and LiClO$_4$-PEO devices are shown in Fig. 5.3(c). The $E_a$ for ions in PVP and LiClO$_4$-PEO devices are around 338.4 meV and 182.6 meV in the temperature range of 230 K to 300 K, respectively. The
corrections for ion hopping barrier in the absence of electric field were estimated to be 20 meV and 2.5 meV for PVP and LiClO₄-PEO devices, respectively, assuming that R = 0.5 nm and the voltage drop is uniformly distributed across the dielectric and PEDOT:PSS.

Figure 5.2: (a) Normalized \( I_D \) for devices using three different dielectric materials under short gate voltage “pulse”. (b) First derivative of \( I_D \) with respect to \( t \) when gate field is applied for devices using OA, PVP and LiClO₄-PEO as dielectric.

Comparing \( U \) for both devices suggests that the impurities in PVP are heavier than \( \text{Li}^+ \) ions in PEO. As the temperature drops below room temperature, the injected \( \text{Li}^+ \) ion charges (\( Q_{\text{ion}} \)) decrease and the corresponding field effect is suppressed (see Fig. 5.3 (d)). At \( T = 230 \) K, the field effect is nearly absent. At this temperature the ion motion is frozen which causes the PEDOT:PSS conductance change to stop.
Figure 5.3: Temperature dependence I-t measurement data for LiClO$_4$-PEO device (a). The corresponding gate currents at various temperatures when $V_G$ is 0.5 V are summarized in (b). Activation energy (c) for devices under gate electric field made from LiClO$_4$-PEO and PVP as dielectric. The injected Li$^+$ charges for $V_G = 0.5$ V at various temperatures are shown in (d).
5.1.2 Without Gate Electric Field

The diffusion behavior of Li\(^+\) ions is now examined from the channel conductance under a G-S open circuit condition. The I\(_D\) response under G-S circuit open can be described by

\[ I(t) = I(0)t^{-\alpha}, \quad (5.3) \]

where \(0 < \alpha < 1\) as shown in Fig. 5.4. The Li\(^+\) diffusion behavior was measured at various temperatures shown in Fig. 5.3 (a). The room temperature result is plotted in the inset of Fig. 5.4 (a). The exponent \(\alpha\) can be obtained from the slope of log I(t)- log t plot. The values obtained for \(\alpha\) ranging from \(10^{-1}\) (298 K) to \(10^{-3}\) (230 K) are summarized in the inset of Fig. 5.4 (b). The decrease of \(\alpha\) with decreasing temperature suggests a thermally activated energy for Li\(^+\) ion diffusion.

![Figure 5.4](image_url)

**Figure 5.4:** Temperature dependence diffusion behavior of retrieving channel conductivity. The room temperature fitting result is shown (a). (b) shows the results for \(T = 280 \text{ K} - 230 \text{ K}\). The value of \(\alpha\) corresponds to different temperatures is summarized in inset chart of (b).
5.2  *in situ* DC conductivity Measurements

The devices studied in this section have four 200 µm wide silver probes thermally deposited with equal spacing across the PEDOT:PSS channel. The standard four-probe method was performed to investigate the resistivity of the channel. The channel dimensions are 1 mm and $W = 0.9$ mm with at least 90% gate electrode coverage.

Because the output I-V characteristics of a device are both $V_D$ polarity and $V_G$ dependent (see Fig. 4.3), different magnitudes of current were applied to choose the resistivity value in the linear region for each static channel off-state.

5.2.1 Quasi-1D VRH

In the disordered system, the charge transport process is hopping. The hopping conductivity ($\sigma$) can be described by Mott's law [101] as Eq. (2.51) and the corresponding activation energy is given as Eq. (2.52).

The results of temperature dependent resistivity measurements are shown in Fig. 5.5. Each linear curve corresponds to a temperature variation of a specific static channel resistance ($R_f$) at $V_G$ normalized to the resistance ($R_0$) when $V_G = 0$V at room temperature.

For the PEDOT:PSS system, when $V_G$ equals zero ($R_f/R_0 = 1$), the normalized channel resistance follows a Quasi-one dimensional variable range hopping ($d = 1$) in the temperature range from 80 K to 300 K, as shown by the dashed fitting line in Fig. 5.5. The characteristic temperature $T_0$ obtained from the slope is around 1300K. When the ratio $R_f/R_0$ increases, the slopes become steeper and this implies that $T_0$ increases with the
off-state channel resistivity. As the channel resistance changes 100 times, $T_0 \sim 1.3 \times 10^5$ K. Because $T_0$ measures the degree of disorder in the disordered regions, the increase of $T_0$ suggests that the PEDOT:PSS system is driven into a more disordered regime throughout the whole bulk film.

### 5.2.2 Disorder Parameter

The result obtained in Sect. 5.2.1 indicates the average barrier height for charge carriers to overcome increases as PEDOT:PSS is driven into a more disordered state. The injected $Q_{ion}/$cell controls the PEDOT:PSS conductance such that a further examination of $Q_{ion}$ vs. $T_0$ is necessary. Since $\sim 2\%$ of hole charges are being screened
by ions (result from Ch. 4), one can assume a weak modulation of $\xi$ by ions, the available states within hopping energy range are mainly responsible for the carrier conduction. According to Eq. (2.52),

$$T_0 \propto \frac{1}{N(E_f)\xi} \propto \frac{1}{(n_{\text{pss-}}/W_{\text{disorder}})\xi}$$

by assuming a uniform distribution of the concentration of counterions PSS$^-$ among the PEDOT within the carrier hopping energy range, $W_{\text{disorder}}$. The available concentration of hopping sites within the hopping energy range changes when ions are inserted. The amount of changes, $\Delta n_{\text{pss-}}/W_{\text{disorder}}$ is proportional to $Q_{\text{ion}}/\text{cell}$. Therefore, we consider $T_0/T_{0f}$ vs. $Q_{\text{ion}}/\text{cell}$ through the first order linear approximation

$$\frac{T_0}{T_{0f}} = 1 - \lambda \left( Q_{\text{ion}}/\text{cell} \right), \tag{5.4}$$

where $T_{0f}$ is the activation energy for a $R/R_0$ modulation and $\lambda = \frac{1}{n_{\text{pss-}}/W_{\text{disorder}}}$. The parameter $\lambda$ extracted from Fig. 5.6 is around 5.3 and this corresponds to 18% of PSS$^-$ being compensated by ions. The large concentration compensation (18%) of PSS$^-$ by inserted ion charges implies that not all inserted ions reside within the carrier hopping energy range.
5.3 Discussion

Results of the temperature dependence measurements relate to both the physical quantity and the role of ion motion in the fully-doped PEDOT:PSS based FETs. From temperature dependent transient current measurements for three different dielectric material based devices, the field effect response of PEDOT:PSS originates from the insertion of impurity ions into dielectric materials. Space between the polymer chains provides opportunity for the ions to enter, so the ion current depends on chain movements [153], ion size, ion-polymer interaction, etc. Thus, diffusion in conjugated polymers is not Fickian [154,155].

The flow of ion produces an ionic current

\[ j_i = n_i q \mu_i E - qD \frac{\partial n_i}{\partial x}, \]  

(5.5)
where $n_i$ is the ion concentration, $\mu_i$ is the ion mobility and $D$ is the diffusion coefficient. The first term on the right side is the drift current due to the electric field and the second term is the ion diffusion current \([45,47]\). The drift term dominates for short periods of time when $V_G$ is imposed, and the diffusion term governs the recovering process. The 30 second voltage pulse period is within the ion drift regime. The ions hop into the PEDOT:PSS film with a hopping frequency proportional to $\exp[-E_a/(k_BT)]$. The maximum ion hopping rate occurs at $dI_D/dt = 0$. There are two kinds of unknown ions in the OA dielectric and one kind of ion specie in PVP and PEO-LiClO$_4$ materials.

Since ion hopping is a thermally assisted process, the barrier for ions to overcome can be obtained from the rate of drain current change with temperature. In the temperature range from 230 K to 300 K, the activation energies for ions without an electric field are $338.4\pm20$ meV and $182.6\pm2.5$ meV for PVP and PEO-LiClO$_4$, respectively. The unknown ions contained in PVP are more massive than Li$^+$ ions, therefore, lighter ions generally with smaller sizes are able to move faster as well as be driven by the electric field. The total amount of ions injected, $Q_{\text{ion}}$, decreases as temperature decreases which is consistent with the thermally activated motion of ions. The reduction in the amount of injected ion charges results in smaller conductance changes of PEDOT:PSS at low temperatures.

The ion diffusion mechanism dominates the drain current recovering process. It is known that ion motion will reach homogeneous diffusion in a short time after the external perturbation is removed. The ion diffusion outside the conducting polymer with no applied field can be fit to the power law relation $I(t) \propto t^\alpha$. For Li$^+$, $\alpha$ is 0.18 at room
temperature and $\sim 10^{-2}$ for temperatures ranging from 240 K to 280 K. According to Eq. (2.16) for ion diffusion into a porous electrode, the exponent $\alpha = (D_r-1)/2$ gives $D_r = 1.36$. The morphological structure for ions to diffuse inside PEDOT:PSS has dimensionality of 1.36. Pyun et al. [156] have reported $D_r = 2.2$ for Li$^+$ ions diffusing inside Li$_x$V$_2$O$_5$ electrode. The power law fitting results can be also interpreted as the cooperative rearrangement of polymer segments due to Li$^+$ ions diffusion. The studies of molecular diffusion in polymers have been carried out by holographic method [157, 158] and the Forced Rayleigh scattering (FSR) [159]. The experimental results of dye molecular diffusion in amorphous polymers from both methods show the multiple relaxation processes of polymers in the presence of molecular diffusion. The theoretical calculation by Kotelyanskii et al. [160] concludes that reduction of the local polymer dynamics decreases the volume available for diffusion. This theoretical result could be used to explain the ion diffusion behavior below room temperature discussed here. However, the molecular diffusion mechanism studies [157, 158, 159, 160] directly monitor the concentration variation of molecules instead of considering a charge transfer or charge compensation process between diffusion species and conducting polymers. As ions diffuse inside a polymer, subtle movements of polymer chains are possible to make space for ion moving. However, a polymer chain would have to undergo a large conformation change in order to make a significant contribution to the hopping conductance. The electrical signal of the polymer obtained here is more related to the probability of ions compensating for the hopping sites during diffusion. Thus, the
interpretation of fractal electrode surface for an electrochemical chemical cell is chosen to explain these results.

The diffusion coefficient, $D$, can be estimated from the power law diffusion region in the recovering cycle by assuming one dimensional $\text{Li}^+$ diffusion and no conformational change of PEDOT:PSS. $D$ is obtained through

$$l^2 = 4D\Delta t,$$

(5.6)

where $l$ is the thickness of PEDOT:PSS and $\Delta t$ is the time duration for static diffusion of $\text{Li}^+$ ions. Combining Fig. 5.3(a) and Fig. 5.4, we see that at least 90 % recovery of the channel conductance is within the static diffusion region. Therefore, the estimated $D$ for $\text{Li}^+$ inside PEDOT:PSS is on the order of $10^{-14}$ cm$^2$/s. Comparing with the literature, for $\text{Li}^+$, $D=10^{-13}$ cm$^2$/s in polyacetylene [154], $3\times10^{-10}$ cm$^2$/s in polythiophene [154], $4\times10^{-9}$ cm$^2$/s in poly(N-methylpyrrole) [161], and $5\times10^{-10}$ cm$^2$/s [161] in polypyrrole by electrochemical methods at room temperature. Therefore, improving device switching speed requires a proper host conducting polymer system should be designed.

To further understand the physical phenomenon inside the conducting polymer layer in the presence of ions, charge transport measurements on the active channel using a standard four-probe technique were performed. As seen in Fig. 5.5, the PEDOT:PSS is driven into an insulating regime with applying gate potentials, which reveals an increase in degree of disorder in the gate voltage imposed system. Charge carriers hopping in the CP backbone have to overcome a higher barrier as the conductivity drops due to the insertion of ion charges. The barrier height depends on the carrier hopping distance and energy difference between initial and final states. As the results from Ch. 4 indicated a
2% replacement of hole charges by ions charges is enough to suppress PEDOT:PSS conductance. Thus, $\xi$ (localization length) can be considered as a weak modulation. Mainly, the presence of ions in PEDOT:PSS modulates $N(E_F)$ through the entire active material. When ions diffuse interstitially between polymer chains, a local polymer-ion interaction may induce disorder in the host polymer.

5.4 Summary
The origin of device operation based on fully doped PEDOT:PSS is reported. Devices with three kinds of dielectric materials show the suppression of the field effect phenomenon below room temperature. By calculating the amount of injected ion charges associated with the temperature, the correlation between ion charges and decreasing channel conductance was obtained. The decreasing of injected ion charges results in a nonapparent field effect under the same $V_G$ applied at low temperatures.

For the thermally assisted hopping of ions, we obtain the activation energies for ions without a field inside PVP and LiClO$_4$-PEO in the temperature range from 230 K to 300 K are $338.4 \pm 20$ meV and $182.6 \pm 2.5$ meV, respectively. For ion diffusion outside PEDOT:PSS, the corresponding $I_D$ response can be described by a power law fitting, $I(t) \propto t^\alpha$ with $\alpha = 0.18$ at room temperature and $\sim 10^{-2}$ for temperature between 240 K and 280 K. The small exponent reveals a slow diffusion process. The diffusion coefficient for the Li$^+$ inside PEDOT:PSS was estimated to be on the order of $10^{-14}$ cm$^2$/s. By comparing with the literature, an optimized device switching speed can be overcome by choosing a more appropriate host material.
The conductivity decrease in the conducting polymer due to ion presence occurs throughout the whole bulk. $T_o$ measures an increase in degree of disorder in poorly conducting regions as PEDOT:PSS conductivity drops. This disordering comes from either longer ion hopping distance or more localized polaronic states. As discussed, 2% hole charge replacement does not modulate the potential energy of other localized polaron states. Therefore, inserted ion charges modulate the available hopping sites in the conducting polymer layer. The observed conductance variation of metallic polymer, PEDOT:PSS, can be understood as conductance suppression in the disordered regions caused by longer hopping distance of charge carriers. More evidence is presented in Chapter 6 to support this argument.
CHAPTER 6

FIELD EFFECT in situ ESR MEASUREMENTS

The role of ion motion in the disordered region has been discussed in Ch. 5. In this chapter, the issues of electrochemical dedoping and the motion of ions in the ordered regions will be considered.

Polarons and bipolarons are the charge species responsible for conducting electricity in the highly doped polymer system. Polarons carry magnetic moments and can be distinguished from diamagnetic bipolarons by means of electron spin resonance (ESR) spectroscopy. The field effect phenomenon reveals the transition of metallic polymer into an insulator state. In this chapter, ESR spectroscopy is used to elucidate the origin of field effect induced conductor-nonconductor transition in metallic polymer.

6.1 Room Temperature ESR Measurements

Type 9 devices listed in Table 3-2 were used in this study. The thickness of PEDOT:PSS, electrolyte, and Al layers are 0.7 µm – 2 µm, 0.9 µm -2 µm, and 25 nm, respectively. Fig. 6.1 shows the room temperature drain current modulation (bottom
Figure 6.1: The output characteristics of the device under gate potential modulation.

As can be seen in Fig. 6.1, there is a sharp decrease in channel conductance during the applied gate potential and the conductance automatically returns to the original state (on-state) without applying negative gate voltage. The ESR spectra were taken (1) right
before (on-state) and (2) static state (off-state) during applied a gate potential as well as (3) during the return of the channel conductance to its original state (on state). These (1), (2) and (3) steps for each applied gate potential is considered as a cycle, marked with arrows indicating on the top panel of Fig. 6.1. The leakage current ($I_G$) was also monitored. Two cycles of in situ ESR spectra for gate potential $V_G = 0.5$ V and 1 V were taken and shown in Fig. 6.2.

As shown in Fig. 6.2, the ESR spectra taken in conditions (1) (black curve), (2) (red curve) and (3) (blue curve) for each cycle are displayed. The drain current modulation (the ratio of on-state to off-state channel conductance, $\sigma_0/\sigma_f$) for $V_G = 0.5$ V and 1 V yield 22 % and $10^5$ %, respectively. Independent of gate voltage applied, the first derivative of ESR signals for both cycles do not show any Dysonian effect. Concerning the floating gate conditions, the ESR spectra show reversibility which indicate that there is no change in the properties of PEDOT:PSS film after inserted ions diffuse away. Applying a potential on gate electrode substantially changes the ESR spectrum (see red curve in Fig. 6.2 (a), (b)). There are apparent changes in lineshapes of ESR spectra in both cycles including the $\Delta H_{pp}$ and absorption intensity.

The integrated ESR spectra for cycle 2 are shown in Fig 6.3. Both Lorentzian (red curve) and Gaussian function (blue curve) were used to fit the integrated ESR spectra. The Lorentzian lineshape yields better fit. The double integration of the first derivative ESR spectra is subjected to the relative total concentration of paramagnetic centres. The correlations of field effect and ESR analysis for both cycles are summarized in Fig. 6.4.
Figure 6.2: ESR spectrum for $V_G = 0.5$ and 1 V cycles. The black and blue curves are for the before and after the gate voltage applied, respectively. The red curve is taken when the channel approaches the static state during applied gate voltage.
In Fig. 6.4, the □ indicates the percentage of conductance changes ($\sigma_0/\sigma_f$) for the PEDOT:PSS channel. The percentage of $\Delta H_{pp}$ variation under gate electric field present is represented by ●. As can be seen in Fig. 6.4, the channel conductance modulation was 22% and $10^5\%$ for $V_G = 0.5$ V and 1 V, respectively. Considering the variation of polaron concentration (▲), around 3% (or 18%) reduction leads to a 22% (or $10^5\%$) decrease in channel conductance. The corresponding injected ion charges are 0.008 charge/cell and 0.26 charge/cell for 22% and $10^5\%$ conductance suppression, respectively. There is no linear correlation between the variation of the channel conductance and that of total spin concentration. A few percent reduction in polaron population is enough to suppress charge conduction in the polymer matrix. In addition, the $\Delta H_{pp}$ increases as the channel conductance decreases. The presence of the Li$^+$ ions inside the conducting polymer influences the spin environment, thereby the spin relaxation time is modulated resulting in $\Delta H_{pp}$ change.
Figure 6.3: Lineshape of ESR spectra for both with and without $V_G$ applied for cycle 2. The red line is the Lorentzian fitting curve and the blue is Gaussian result.

Figure 6.4: Summary of the drain current modulation and corresponding ESR spectra results for each cycles. The symbols □, ▲, and ● represent the drain current modulation percentage under applying $V_G$, the corresponding variation of spin concentration, and the variation of $\Delta H_{pp}$, respectively.
6.2 Temperature Dependent ESR Measurements

In this section, we report the electronic states of charge carriers in the ordered regions in the presence of inserted ions by temperature dependent ESR measurements. The double integration of the first derivative of an ESR spectrum gives the relative total concentration of polarons in the system. This relative polaron concentration is equivalent to a relative magnetic susceptibility. Since the XRD measurement suggests partially crystalline morphology for PEDOT:PSS, spins inside PEDOT:PSS are composed of localized spins (Curie spins) and delocalized spins (Pauli spins). Both types of spins contribute to the magnetic susceptibility (see Eq. (2.76)). The Pauli spins are attributed to delocalized charge carriers in the ordered regions and the Curie spins arise from localized polaron charges in the disordered regions. Thus, the temperature dependence of the magnetic susceptibility is described by Eq. (2.78).

Fig. 6.5 shows the temperature dependent results of relative magnetic susceptibility for the device with floating and 0.98 V gate voltage applied. A 67% conductance change in PEDOT:PSS was obtained at \( V_G = 0.98 \) V. The relative \( \chi_p \) was obtained by linearly fitting \( \chi - T \) (dotted lines) over the entire temperature range based on Eq. (2.78). The ratio of \( \chi_p \) for floating gate condition to 0.98 V is \( \chi_p[\text{floating}]/\chi_p[0.98V] \approx 1 \). Further, the Pauli susceptibility can be related to the density of states at the Fermi level through Eq. (2.75) such that one can rewrite \( \chi_p[\text{floating}]/\chi_p[0.98V] = N(E_F) \ [\text{floating}]/N(E_F)[0.98V] \approx 1 \). There is almost no change in the \( N(E_F) \) at the Fermi level when the PEDOT:PSS conductance is suppressed.
Generally, the ESR linewidths are determined by spin-spin (hyperfine, dipolar, ect.) interactions, narrowing mechanisms (spin diffusion, rotation, and exchange interaction) and spin-lattice relaxation. For systems which do not have complicated lineshapes (homogeneously broadened (Lorentzian lines)), the spin-spin interactions and effects of any narrowing mechanisms can be described in terms of an effective spin-spin relaxation time $T_2$. In our samples, we obtain a Lorentzian line shape in both $V_G = \text{floating}$ and a specific potential cases. For an ESR spectrum with a Lorentzian line shape, the half-width at half maximum linewidth can be written

$$
\Delta H = \gamma^{-1} \left( \frac{1}{T_2} + \frac{1}{2T_1} \right),
$$

(6.1)
where $\gamma$ is the gyromagnetic ratio and $T_I$ is the spin-lattice relaxation time [133]. In conducting polymers the hyperfine and dipolar broadening of a resonance will be limited by narrowing due to spin diffusion [162]. Therefore, increases in conductivity will increase the effectiveness of spin diffusion to narrow ESR linewidth because of a decrease in $T_2^{-1}$.

The ratio of conductance for PEDOT:PSS with ($\sigma(0.98 \text{ V})$) and without ($\sigma$(floating)) gate potential applied in the sample studied in this section is $\sigma$(floating)/$\sigma(0.98 \text{ V}) \approx 3$ at room temperature. Assuming the hyperfine and dipolar interactions in these samples are the same, $1/T_2$ contributes less to the total linewidth in $\sigma$(floating) than in $\sigma(0.98 \text{ V})$ situation. However, the experimental linewidth of device in the open gate circuit condition is larger than that of $V_G = 0.98 \text{ V}$ for the entire temperature range (see Fig. 6.6). Furthermore, from the $\sigma(T)$ [163] of the device, the $1/T_2$ linewidth contribution should decrease as the temperature increases. However, the device only shows a $1/T_2$-dominated linewidth below 50K at $V_G = 0.98 \text{ V}$. Both in gate circuit floating condition and in $V_G = 0.98\text{V}$ above 50K, we observe linear increasing of linewidth with increasing temperature which is consistent with a $1/(2T_1)$-dominated linewidth feature. The estimated slope (dotted lines) of $\Delta H_{pp}$ are 0.0327 and 0.0296 GK$^{-1}$ for $V_G = $ floating and 0.98 V, respectively. $V_G = $ floating case gives faster relaxation time $T_1$ which may be possibly explained in terms of the spin-spin interaction between the conduction electrons of the metallic island and the localized spins of localized polarons in the surrounding disordered regions giving rise to added relaxation routes.
Hasegawa [164] has proposed the studies in the dynamical properties for systems containing magnetic ions in metals where localized spins and conduction electrons interact through exchange interaction by using the modified Bloch equation of motion. Under the isothermal limit [165], the effect spin-lattice relaxation is roughly given by the Koringa relaxation rate

$$\Delta H_{pp} \propto N(E_F)^2 T,$$

where $N(E_F)$ is the density of states at the Fermi level. In this case, the linewidth is expected to increase linearly with temperature in the region shown in Fig. 6.6. By using Eq. (6.2) and the slopes from Fig. 6.6, we obtain

$$\frac{d\Delta H_{pp}[\text{floating}]}{dT} / \frac{d\Delta H_{pp}[0.98V]}{dT} \approx 1.1,$$
and this result gives

\[ \frac{N(E_F)^{\text{floating}}}{N(E_F)^{0.98V}} \approx 1.05, \]  

(6.4)

which is roughly consistent with the result obtained from comparing the Pauli susceptibility.

In summarizing the temperature dependent ESR study, there is almost no change in the density of states at the Fermi level in the ordered region upon applying gate electric field. The \( T_2 \) processes appear to dominate due to the ESR linewidth narrowing with increasing temperature for a device under gate electric field below 50 K. At high temperatures, a Korringa relaxation mechanism between conduction electrons and localized electrons is attributed to the linearly increasing linewidth with temperature as well as the larger line broadening for a high conducting state. The Lorentzian lineshapes of the PEDOT:PSS based device imply the three-dimensional delocalization of conduction electrons.

### 6.3 Discussion

The transient current response due to gate electric field modulation shown in Fig. 6.1 implies that \( \text{Li}^+ \) ions were driven in and out the PEDOT:PSS channel by controlling the gate potential. The typical evidence for ion motion accounts for the return of the channel conductance with an open gate circuit which implies the \( \text{Li}^+ \) ions diffuse back into the dielectric layer. This response of the drain current supports the ion-leveraged operation in these kinds of devices [36].
The in situ ESR measurements clarify the charge carrier motion inside a PEDOT:PSS based FET under electric field modulation. The reversible modulation of ESR signals under the gate-source circuit open condition reveals no change of PEDOT:PSS properties after Li$^+$ ions diffuse out of the conducting polymer. By electrically driving Li$^+$ ions into PEDOT:PSS, the presence of ions suppresses charge conduction of the polymer system. Around an 18% reduction in carrier concentration is able to reduce the polymer conductance up to three orders of magnitude which does not follow the fundamental physics relationship for $\Delta \sigma = (\Delta n) e \mu$, where $n$, $e$, and $\mu$ are free carrier concentration, electron charge, and carrier mobility, respectively. This suggests that not only $n$ but also $\mu$ are being modulated by inserted ions. According to the electrochromic effect [20,21], the conductance switching of conducting polymers is through chemical doping-dedoping process by ions. In such case, the chemical reaction from Eq. (4.7), $\text{PEDOT}^+\text{PSS}^- + \text{Li}^+ + \text{e}^- \rightarrow \text{PEDOT}^0 + \text{Li}^+\text{PSS}^-$, is expected to occur. The reduced form of PEDOT is spinless and accompanies with an apparent color change. The experimental result of total spin concentration reduction can be expected as Eq. (4.7). However, it is not necessary to reduce the entire conducting polymer film to achieve a pronounced PEDOT:PSS conductance modulation. Three orders of magnitude suppression of PEDOT:PSS conductivity by a ~18% loss in conduction charges implies electrochemical dedoping process is not the key mechanism.

On the other hand, bipolaron formation can also cause a decrease in spin concentration. However, to maintain charge neutrality of an entire device, the formation of bipoarons carrying two positive charges is not possible.
The device with 67% conductance modulation by sacrificing ~ 4.8% of its spin concentration shows that there is almost no change in $N(E_F)$ with gate electric field applied. Modulating the conductance of PEDOT:PSS by injecting ions without apparently reducing the density of states of Pauli spins in the ordered region suggests that charge transfer does not likely occur between injected ions and the conducting polymer.

From Prigodin et al. [103] a polymer with chains coherently aligned in densely packed regions form metallic bundles and the polaron wave functions are three-dimensionally delocalized within these metallic grains. Surrounding regions are disordered and polaron wave functions are localized. Charge transport occurs between metallic islands by hopping through available states in the disordered regions. The Li$^+$ ions driven by the electric field are not expected to diffuse inside the metallic islands and this is confirmed by the Pauli spin measurements. The majority of Li$^+$ ions spread over the disordered regions and modulate the conductance in those regions. This explains the decrease of the polymer conductance without sacrificing the density of states at the Fermi level inside the crystalline islands.

From the decrease of $\Delta H_{pp}$ upon an applied gate potential suggests that Li$^+$ ions may be screening the interaction between polarons and PSS$^-$ dopants. Therefore, Li$^+$ ions can diffuse close to the PSS$^-$ ions in the disordered regions to screen the coulombic interaction between polarons and PSS$^-$ dopants. This screening effect decreases the local potential energy of the polarons on the PEDOT:PSS backbone resulting in a more mobile state. To maintain charge neutrality, those ion modulated states will eventually transfer to the electrodes. Therefore, the carriers mostly hop over longer distances to conduct
electricity in the presence of ions. The spatial modulation of available resonance sites decreases the electron hopping probability.

6.4 Summary

The slow switching time and the PEDOT:PSS conductance recovering under open circuit conduction confirms Li$^+$ participating in the device operation. By injecting Li$^+$ ions triggered by a gate electric field into the conducting polymer layer, a dramatic decrease in polymer conductance with only a few % reduction in total spin concentration was observed and this suggests that charge transfer between Li$^+$ ions and polymer may occur but is not the main origin of device operation.

The in situ temperature dependence ESR results show no apparent modulation of $N(E_F)$ in the ordered region as the channel conductance decreases by 67%. This result further implies that the major origin of charge suppression is in the disordered regions. The presence of Li$^+$ ions in the disordered regions modulating the local energy around the polarons results in the removal of intermediate hopping sites. Only ~ 2% of the hopping sites being removed is enough to suppress the conductivity of PEDOT:PSS thoroughly. The decrease in the concentration of intermediate hopping sites causes the hole carriers to hop over longer distance to conduct electricity leading to the decrease of carrier mobility. Thus, a conductor-nonconductor transition in the disordered regions is a base for conducting polymer transistors.
CHAPTER 7

DESIGN AND APPLICATION

7.1 Design

The temperature examination results conclude that ion species determines the sensitivity of the field effect phenomenon. Generally, ions having smaller sizes with low activation energies are more mobile and produce significant field effect. From the diffusion analysis, the thickness of the active layer and the diffusion coefficient determine the time to retrieve the polymer conductance. Therefore, by controlling the ion species, one can design applications for field effect devices which cover a large frequency range.

In the very low switching regime (~ hour), non-volatile Ram (NRAM) would be a favorable choice. In the moderate switching regime (~ minutes), devices can be use in low frequency circuits would be a good choice. In the fast switching regime (~ms), FETs can be a good alternative for α-Si FETs.

In section 7.2, the application of NRAM devices is demonstrated. The device shown in the following incorporates PEO as the dielectric material.
7.2 Application: Non-Volatile Ram

An application of the field effect structure studied in this thesis is reported in this section. Type 5 devices listed in Table 3-2 were used to demonstrate the NRAM operation. The time dynamic response of field effect incorporating PEO as a dielectric layer is shown in Fig. 7.1. A -0.1 V drain voltage and 3 V or -3 V gate voltages were applied to the structure. As can be seen in Fig. 7.1, it takes ~ 60 seconds for the PEDOT:PSS system to reach equilibrium when $V_G = 3$ V applied and two hours to retrieve the PEDOT:PSS conductance. However, $V_G = -3$ V shorten the recovery time and the PEDOT:PSS stays at a different static state. By applying $V_G = 3$ V and -3 V, the conductance of PEDOT:PSS film can be driven into two different static states. These two distinct conductance states can be used to store information in terms of “1” and “0”.

Figure 7.1: Time dynamic response of device incorporating PEO as a dielectric material.
We use $V_G$ as the writing line to write the “1” ($V_G = -3$ V) or “0” ($V_G = 3$ V) state, and $V_D$ is the reading line to read the data stored. There is no $V_D$ is required to keep the stored information. Figure 7.2 and Fig. 7.3 show the example of NRAM operation. In Fig. 7.2 and Fig. 7.3, 60 seconds pulses are written to the PEDOT:PSS structure to initiate a conductance state. After the writing, a -0.1 V drain voltage is applied to examine the status of the PEDOT:PSS conductance. As can be seen in Fig. 7.2, the information can be stored for 30 minutes before losing the contrast. The longer time storage is shown

![Graph showing NRAM operation for 30 minutes data storage.](#)

**Figure 7.2:** NRAM operation for 30 minutes data storage.
in Fig. 7.3, the written information is gradually lost as time continuous because of the recovery of PEDOT:PSS conductance under $V_G = 0$ V. However, there is still sufficient contrast to distinguish “1” and “0” for 1 hour storage period.

As mentioned at the beginning of this chapter, the data storage time can be optimized with proper design of the ion species.

Figure 7.3 : NRAM operation for 1 data storage.
CHAPTER 8

CONCLUSION AND SUMMARY

8.1 Electric Field Effect in a Metallic Polymer

The study of the electric-field effect in a heavily doped conducting polymer by using FET structure was presented. It was unexpected to observe the penetration of gate electric field into a metallic polymer due to the screening nature of the metal. Conventional MOSFET model, transient current studies, temperature measurements, and electron spin resonance were used to investigate the origin of the gate electric field encroachment of a metallic polymer. The hysteresis I-V curves and temperature sensitive field effect behavior indicate that ion motion is involved in the conductance modulation of PEDOT:PSS. The role of ions in the organic conductor-based FETs is studied.

The following sections summarized the work done in this thesis starting from an assumption of a MOSFET model to final clarification of the physical mechanism for the field effect phenomenon.
Failure of Conventional MOSFET Model

The physical mechanism behind those organic conductor based transistors is different from Si-based FETs even though the output and transfer characteristics are similar. The failure of the conventional semiconductor transistor model to explain the experimental results is seen from the unusual mobility obtained $\mu_{\text{FET}} \sim 100 \text{ cm}^2/(\text{Vs})$, the time dynamic analysis and the increase of $T_0$ with the off-state channel resistivity.

The bulk mobility of PEDOT:PSS (0.2 cm$^2/(\text{Vs})$) estimated from conductivity is approximately two to three orders of magnitude less than the $\mu_{\text{FET}} \sim 100 \text{ cm}^2/(\text{Vs})$ extracted from the I-V curves using the conventional MOSFET model. The switch-on and -off time of the order of several minutes is not consistent with the estimated RC time constant of a PVP capacitor. The increase of activation energy with applied gate voltages does not support a picture of gradual moving of the Fermi level away from the valence band at semiconductor-dielectric interface under gate field.

Electron-Ion Coupled System

The electric-field effect in the conducting polymer is driven by ion motion. This can be seen from I-V curves, transient current measurement and temperature dependent studies. The hysteresis in I-V curves suggests a charging and discharging behavior due to ion motion. The slow switching speed mimics an ion driven conductance modulation. In addition, the temperature dependence of I-t measurements show the suppression of the electrical field effect at the temperature 10 K below the room temperature which is direct evidence of ion motion.
The ions come from the impurities residing in the dielectric layer. This is found from the difference in I-V curves under open G-S circuit and $V_G = 0$ V as well as temperature sensitivity of the field effect. The experimental observation is consistent with the theoretical explanation for electrochemical potential alignment for a thermal equilibrium system.

The 30-second gate voltage “pulse“ measurements lead to conclusions: (1) the response rate of the majority charge carriers depends exponentially on $V_G$ and (2) an ion hopping distance (~80 nm) by assuming a uniform voltage drop across the dielectric and conducting polymer layers. The exponentially dependent response rate could be interpreted as either due to an electrochemical charge transfer (or ion generation) or due to injected ion hopping rate. However, from the existence of different equilibrium channel states, the automatic recovery of the drain current at zero (or floating) gate bias, and the in situ ESR measurements, the redox process may happen in this originally highly doped polymer but it is not the main working principle. The unusual long ion hopping distance indicates a relative large portion of voltage dropping across the dielectric layer. The natural explanation for this high voltage drop is an electrical double layer formation at the interface (Al/dielectric) of the dielectric layers.

The relaxation processes of the conducting polymer under gate electric field can be described by a simple exponential function. There are two relaxation mechanisms of hole charges under ion motion. The fast relaxation is due to the response of polymer system under non-equilibrium conditions while the slow relaxation represents the thermalization
of the system to its new configuration. The fast relaxation process ranges from 3 seconds to 3 minutes in the system studied here.

The leakage current provides the information about both electronic and ionic current. Around 2% of hole charges on PEDOT:PSS being replaced by ion charges destroys the charge percolation of the conducting polymer.

**Physical Properties of Ions/ Ion Diffusion**

Devices made from three different dielectric materials show the suppression of field effect phenomenon below room temperature. The decreasing of injected ion charges results in a nonapparent field effect under same $V_G$ applied below room temperature which implies an ion triggered field effect phenomenon. The activation energies for ions without field are $338.4 \pm 20 \text{ meV}$ and $182.6 \pm 2.5 \text{ meV}$ for ions inside PVP and Li$, respectively, in the temperature range from 230K to 300K. The back diffusion of ions out of PEDOT:PSS can be described by the power law $I(t) \sim t^\alpha$ with $\alpha = 0.18$ at room temperature and $\alpha \sim 10^{-2}$ between 240 K–280 K. The morphological dimensionality for ion diffusion inside PEDOT:PSS is 1.36 at room temperature. The estimated diffusion coefficient for the Li$^+$ inside PEDOT:PSS is on the order of $10^{-14} \text{ cm}^2/\text{s}$ which is an order of magnitude smaller than that reported in polyacetylene [154]. Therefore, the temperature measurements provide valuable information for the ion motion inside a conducting polymer which is essential for design practical devices.
Transport Mechanisms inside Conducting Polymer

The increasing activation energy with decreasing hole conductivity demonstrates the reduction of ordering in the disordered region in PEDOT:PSS. Room temperature in situ ESR studies on devices with Li$^+$ ions show that a $10^3$ times decrease in polymer conductance is caused by ~18% loss in total spin concentration. This result agrees with the percolation phenomenon from the leakage current analysis. No apparent change of $N(E_F)$ for 67% channel conductance reduction by sacrificing 4.5% total spin concentration. The unchanged $N(E_F)$ in the metallic grains under applying electric field implies the major conductivity suppression is in poorly conducting regions. The presence of Li$^+$ ions in the disordered regions reduces the local potential energy around the polarons. The ESR linewidths show faster spin relaxation rate in the absence of gate voltage than that with gate electric field. The decreasing interaction between conduction-electrons and localized spins due to ion presence in the amorphous region causes the spin-spin interaction dominating at low temperature.

Therefore, the modulation of hole conductivity may be associated with the ionic compensation of counterion charge in the disordered regions. We have found that a small degree of ion compensation produces a large effect on active channel conductance. Presumably, this large effect is related to the percolation nature of charge transport in the conducting polymer over acceptors. From $\sigma = n q \mu$, the ingress of ions modulates the hole conductivity by means of hole mobility through the longer hopping distance for charge carriers.
The Mott-Anderson model [73, 74, 80] has often been used to explain the MIT phenomenon. However, the Mott-Anderson transition is based on homogeneous energy disorder leading to charge localization and is not suitable for the structure studied in this thesis.

**Phenomenological Model**

A ion motion is responsible in the electric field penetration inside a metallic polymer. Around 2% reduction of intermediate hopping sites is enough to suppress charge conduction inside PEDOT:PSS. In terms of the chain-link granular model [103], the electronic states inside the metallic grains are unchanged because $N(E_F)$ remains constant under the gate voltage applied. The major conductivity suppression occurs in the disordered region which is supported by the increase of $T_0$ with the increase of channel resistance. Thus, the decrease of resonance hopping sites causes the increase of charge carrier hopping distance, reducing the charge carrier hopping rate. Therefore, the mobility of hole charges decreases. Thus, the observed field effect phenomenon in metallic polymers can be understood as a conductor-nonconductor transition.

**8.2 Improvement of Device Performance for Practical Applications**

There are many design issues involved in the transistor studied in this dissertation. Mainly, there are two major portions, gate voltage-on and gate voltage-off half cycles.

In the gate voltage-on half cycle, there are two major points to be aware of. One is the quality of interface between the dielectric and the conducting polymer, and the other
is the selection of ion species. The interface between the dielectric and the conducting polymer serves as the bottleneck for ion passing. A poor interface can trap ions resulting in high voltage application and poor performance. Therefore, careful selection and processing environment are important to have a smooth interface. Besides, ion mobility is also crucial. An indirect way to choose an ion species is through the activation energy. Light and small ions are easily driven by electric field and show a smaller activation energy.

In the gate-off half cycle, the diffusion coefficient of the ions is the major concern. For a transistor application, a high diffusion coefficient is preferred to enhance the switching speed.

Through understanding the ion motion as well as its properties, one can play with possible combination to design several kinds of ion-leveraged devices such as transistors, low frequency devices and memory devices. This is a great advantage for conducting polymers because only one type of conducting polymer is needed in the circuit board. By intentional adding ion species into dielectric layer, one can fabricate various kinds of devices for various kinds of functions. This outstanding “all-in-one” feature greatly reduces the production cost and enhances the functionality. Therefore, metallic polymer “transistors” can be considered as a promising candidate for plastic electronics.

8.3 Suggestions for Future Work

There are several kinds of experiments in various aspects can be done to clarify the field effect in “metallic” polymers. In the viewpoint of charge transport measurements,
thermalelectric power \((S)\), microwave dielectric constant \((\varepsilon_{\text{mw}})\) and microwave conductivity measurements \((\sigma_{\text{mw}})\) are recommended. In the conducting polymers, the general temperature dependence of thermal power can be written as
\[
S(T) = \frac{\sigma_{1D} f_{1D} S_{1D}(T) + \sigma_{3D} f_{3D} S_{3D}(T) + \sigma_m f_m S_m(T)}{\sigma_{3D} f_{1D} + \sigma_{3D} f_{3D} + \sigma_m f_m}, \tag{8-1}
\]
where \(S_m\), \(S_{1D}\), and \(S_{3D}\) are thermalelectric power in metallic crystalline domains and relatively well-organized chains in disordered regions, quasi-1D VRH in the disordered regions, and 3D VRH between metallic islands and between localized states; \(\sigma\) is the conductivity assuming a constant thermal conductivity; \(f\) is the volume fraction. The temperature behavior of thermalelectric power in those three regions are different: \(S_m \propto T\) \([75]\), \(S_{3D} \propto \sqrt{T}\) \([75]\), and \(S_{1D} \propto 1/T + \text{const} \) \([166]\). Thus, the nonlinear thermalelectric power can be fitted as
\[
S(T) = (A_1 + A_2 / T) + A_3 \sqrt{T} + A_4 T, \tag{8-2}
\]
where \(A_1, A_2, A_3\) and \(A_4\) are effective coefficients related to the volume fractions and relative electrical conductivities of the material domains. Commonly, one of those terms in Eq. (8-2) will dominate for a given sample crystallinity and temperature range. In the highly crystalline sample, \(S_m\) is expected to dominate at high temperature while \(S_{1D}\) dominates at low temperature in less crystalline samples. Based on the model built on this project, one expects to see the thermalelectric power changes in the 1D hopping regions and possibly in the metallic grains if electrochemical reaction occurs. Microwave dielectric constant and conductivity measurements help to estimate the
localization and delocalization length scales in quasi-1D systems. The temperature
dependent for more order sample at low temperature
\[ \varepsilon_r(T) \propto T^2 \]  \hspace{1cm} (8-3)
and
\[ \sigma_{mw}(T) \propto aT^3 + bT^2, \]  \hspace{1cm} (8-4)
where \( \varepsilon_r \) is the real part of the microwave dielectric constant, \( a \) and \( b \) are proportionality
constants. For more disordered samples,
\[ \varepsilon_r(T) \propto T \]  \hspace{1cm} (8-5)
and
\[ \sigma_{mw}(T) \propto cT^2 + dT, \]  \hspace{1cm} (8-6)
where \( c \) and \( d \) are the proportionality constants. One can estimate the localization length
or delocalization length with and without gate electric field as well as get more evidence
for supporting the model used in this thesis.

The other part of the interesting thing is to do further study on the fractal
morphological structure of conducting polymer as an electrode. Impedance spectroscopy
is a good starting place. Furthermore, it is also necessary to do the study in different
polymer systems as well as various dopants to sort out the relationship between dopants
and host polymers in order to improve device performance.
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