Ph. D. Dissertation

LOW TEMPERATURE TRANSPORT IN SEMICONDUCTING POLYMER THIN FILMS

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A thesis submitted to the faculty of KAIST in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics. The study was conducted in accordance with Code of Research Ethics\textsuperscript{1}.

2013. 11. 26.

Approved by

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반도체 고분자 박막의 저온 전도 연구

강 현 구

위 논문은 한국과학기술원 박사학위논문으로 학위논문심사위원회에서 심사 통과하였음.

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ABSTRACT

Since Heeger, MacDiarmid, and Shirakawa reported that plastic can be electrically conductive in 1977, the era of conducting polymer has started. Because conducting polymers have both the electronic advantages and the material advantages, the applicability becomes enormously increasing. The future devices made of conducting polymers will be properly working while folded, rolled, or even crumpled. This specialty will result in a new generation of various portable devices, such as smart phones, tablet devices, or electronic books. Moreover, due to the printability on the large-area surface, we can readily realize large-screen displays, low-cost solar cells or high-capacity batteries soon. Furthermore, once a conducting polymer printer gets into general use, everyone can print the displays, logic circuits, or sensors on a A4 copy paper at home. However, despite its industrial development potential, how the charge carrier transport occurs inside of conducting polymers is still veiled. In this thesis, we investigated the transport mechanism in semiconducting polymer thin films from a physicist point of view through the low temperature experiments.

In the first experiment, the high-mobility amorphous copolymer, DTCPD-alt-CB, was studied. Generally, amorphous polymers are known to have higher disorder than crystalline polymers, resulting in lower charge carrier mobility. However, The transistors made of DTCPD-alt-CB revealed pretty high mobility in spite of its amorphous nature. Through the low temperature experiments, we could determine the charge transport mechanism and compare the resulting physical parameters with those obtained from other polymers. As a result, this polymer has low disorder and low barrier height for transport, reflecting the weak charge localization in the films. This breaks the consensus that amorphous nature always indicates high disorder in polymer systems.

In the second experiment, we could actively control the microstructure in polymer thin films and investigate the effect of the microstructure on the transport. Although it has been believed that the microstructure and the transport are closely related, in order to test this hypothesis, the microstructure need to be well-controlled, which was not a simple process before. In this project, we could control the microstructures through changing the cooling rate after the annealing process. As the cooling rate was decreased, the larger domains on the surface were observed in the AFM images. Moreover, 2D XRD measurement showed that the connectivity between domains was also improved for slow-cooled samples. Low temperature transport measurements were performed to study the effect of the microstructure control on the charge transport. The better connectivity leads to the lower activation energy (i.e. the barrier height), confirming the relation between the microstructure and the transport.

In the third experiment, we determined the transport mechanism in the conducting polymer thin film within a larger range of temperature, electric field, and charge carrier concentration. As a result, field emission becomes a dominant transport mechanism at low temperature under high electric field with high charge concentrations. This field emission process is thought to be following the one-dimensional path formed by the percolation in polymer networks. These series of results might provide the answer for the recent fundamental debate on the charge transport in the semiconducting polymers: “Is the transport one-dimensional or two-dimensional?”
In this thesis, we extensively studied the charge transport mechanism at various temperatures and electric field and were able to construct the transport mechanism map for semiconducting polymers.
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Chapter 1. Introduction

In 1977, Heeger, MacDiarmid and Shirakawa introduced the first conducting polymer by doping fibrils of high-quality polyacetylene with halogens or arsenic fluoride (AsF$_5$), opening a new era of conducting polymer. Since the conducting polymers have both advantages of the material properties of polymers and those of the electrical properties of conductors, the appearance of conducting polymers provides an inexhaustible supply of applications. The fanciful devices made of conducting polymers is expected to be working properly while folded, rolled, or even crumpled.

The polyacetylene is one of the first generation conducting polymers. At first, conducting polymers received attention mainly for their high conductivity. The conductivity was improved significantly and became comparable to that of dirty metal. However, the following achievement of the high performance semiconducting polymer devices and the improvement of solution processibility opened the era of the second generation of conducting polymers, the semiconducting polymers. (Fig. 1.1) The mobility now become an essential parameter for high performance. The mobility of the semiconducting polymers has caught up that of amorphous silicon, which is often compared with for large area applications. One of the advantage of this research field is that there are limitless kinds of polymers. New semiconducting polymers with more complex molecular structures are being introduced in succession. The era of the third generation conduction polymers has come [1, 2]. (Fig. 1.2)

Figure 1.1: Molecular structures of some of the important First and Second Generation semiconducting polymers.
1.1 Electronic structure of π-conjugated polymer chains

Semiconducting polymers have the chemical structure containing the linear conjugated carbon chains along the longitudinal backbone. Each carbon atom has six electrons and four of them are valence electrons which take part in chemical bonds. While carbon atoms in traditional polymers have tetrahedral symmetry with sp$^3$ hybridization, carbon atoms in conducting polymers have hexagonal symmetry with sp$^2$p$^z$ hybridization. In the latter configuration, three sp$^2$ wavefunctions are building physical σ-bonding structure with in-plane three carbon atoms and p$^z$ wave function results in the π-orbital orthogonal to the plane defined by the three σ-bonding. The electron residing in the p$^z$ wave function is in a first approximation independent of the structure due to its orthgonality. (Fig. 1.3) This decoupled p$^z$ electron behaves like a free electron in metal and gives these polymers special electronic properties.

A schematic band diagram for conjugated polymers is shown in Fig. 1.4. The wavefunctions of the π-bands are linear combinations of the p$^z$ wave functions from the carbon atoms in each repeat unit. In the one-electron approximation (i.e. neglecting the electron–electron Coulomb interaction), the number of sub-p-bands is determined by the number of carbon atoms in the repeat unit of the polymer.

The conjugation structure is held by the σ-bonds. Therefore any excitation of the electrons from σ band to σ$^*$-band leads to the structural instability. For this reason, traditional polymers with only sp$^3$ hybridizations tend not to have interesting electronic or optical properties. For conjugated polymers, however, excitations within the π-band are possible with smaller energy and do not accompany any bond breaking.

Although the π-electrons in the conducting polymers are delocalized along the chain, these pristine polymers are not metals. The polymerization of polyacetylene (PA) from the monomer yields a dimerized (bond alternating) structure. As sketched in Fig. 1.4, the molecular structure of “real” polyacetylene has alternating single and double bonds which are, respectively, longer and shorter than the equilibrium value of the bond length in uniform PA. In this structure, the π-electrons on neighboring carbon atoms form
weaker and stronger $\pi-\pi$ bonds resulting in the bond alternating structure. The bond alternation has been determined from analysis of X-ray diffraction data and from analysis of nuclear magnetic resonance data. The shorter bond length is 1.35 $\text{Å}$ and the longer bond length is 1.45 $\text{Å}$.

Such a bond alternating structure doubles the unit cell, thereby opening a gap in the electronic structure. As a result, because of the bond alternating structure, polyacetylene is a semiconductor.

In the dimerized form, the Su-Schrieffer-Heeger (SSH) Hamiltonian reduces to

$$H = \sum_{m,\sigma} \left[ (-t) + \alpha(u_{m+1} - u_m) \right] \times [c_{m+1,\sigma}^+ c_{m,\sigma} + c_{m,\sigma}^+ c_{m+1,\sigma}] \tag{1.1}$$

where $c_{m,\sigma}^+$ and $c_{m,\sigma}$ are the fermion creation and annihilation operators for site $m$ and spin $\sigma$, $u_m$ are the displacements from equilibrium, $t$ is the magnitude of hopping interaction, and $\alpha$ is a constant. Here,
\[ u_m = \langle u_m \rangle = (-1)^m u \quad \text{and} \quad t_m = t_0 + (-1)^m 2\alpha u = t_0 + (-1)^m \Delta \]

leads to

\[ H = \sum_{m, \sigma} \left[ (-t_0) \pm \Delta \right] \times \left[ c^+_{m+1, \sigma} c_{m, \sigma} + c^+_{m, \sigma} c_{m+1, \sigma} \right] \]

Diagonalization of the SSH Hamiltonian for dimerized trans-PA yields the band structure of the dimerized chain; the energy as a function of wave number \( k \) is given by

\[ E_k = \pm \sqrt{\epsilon_k^2 + \Delta^2} \]

where \( \epsilon_k = 2t_0 \cos ka \).

In the terminology of traditional semiconductor physics, the \( \pi \)-band and the \( \pi^* \)-band are corresponding to the conduction band (or lowest unoccupied molecular orbital, LUMO) and valence band (or highest occupied molecular orbital, HOMO), respectively. All the energy states in the \( \pi \)-band are filled and all states in the \( \pi^* \)-band are empty.

The bond alternation in PA is an example of the well-known “Peierls instability” of one-dimensional (1D) metals. Rudolf Peierls first showed that a 1D metal such as uniform PA structure without dimerization is always unstable to the lattice distortion with periodicity \( \Lambda \) where \( 2\pi/\Lambda = 2k_F \). The fundamental reason why such 1D metallic structures are unstable against any infinitesimal distortion of the lattice can be understood using the example of the uniform PA chain. Consider a distortion with periodicity \( 2a \). In the presence of bond distortion an energy gap opens precisely at the Fermi energy with magnitude proportional to the magnitude of the distortion. Upon opening the energy gap at the Fermi energy, the total energy of the occupied electronic states decreases as the gap pushes the occupied states to lower energy. Since the magnitude of the energy gap is proportional to the magnitude of the distortion, the average energy of the \( \pi \)-electrons decreases by an amount proportional to the distortion. This decrease in energy is partially compensated by the increase in the total bond energy that arises from the distortion away from uniform bond lengths. Thus, for a 1D metal, the decrease in average \( \pi \)-electron energy is always greater than the increase in lattice energy. The gap at the Fermi energy that opens as a result of this instability is often referred to as “Peierls gap”.

![Figure 1.5: Density-of-states distribution for ordered and disordered material.](image-url)
In semiconducting polymer systems, the band edge is not as sharp as that for inorganic semiconductors due to its inborn disorder. The broadened band by disorder forms a long band tail into the energy gap, as shown in Fig. 1.5. The band edge in disordered density-of-state separate the mobile states from the localized states. When Fermi level ($\epsilon_F$) lies outside of band edge, all the charges are localized and the trap-to-trap transport is allowed.

1.2 Polymer thin-film transistors (TFTs)

TFTs are best known for the consumer electronics components. Actually, ‘TFT’ is often confused with flat-panel display, like a CRT (cathode-ray tube) was confused with a old type of monitor or television. In fact, the TFT in these cases is the steering element of the display pixels, nothing more. The advantages of TFTs over MOS-FETs is that their production is more flexible. With a common substrate, consisting of the gate, the insulator and the source and drain electrodes, rapidly many different types of TFTs based on different materials can be made. The device is then ‘finalized’ by depositing the active layer and this can be done from drop-casting, LB-film, spin-coating, up to vacuum deposition. All done with the same substrate. Such flexibility in production is especially interesting for research, of course. The organic materials make full use of this flexibility, since they are easily solution processed and TFT fabrication is especially easy for organics. Some materials do not even need fancy environments (such as clean rooms, etc.) and can be drop-cast from a pipet on top of the substrate to result in working and stable TFTs, exactly the kind of devices the organic area needs to aim at.

1.2.1 Transistor types

In Fig. 1.6, the four main types of transistor configurations are presented [3].

Co-planar Bottom-gate

The co-planar bottom-gate structure describes a transistor in which the gate electrode is either the substrate (such as a heavily doped silicon wafer) or where the gate electrodes are patterned on an insulating substrate in which an insulating gate dielectric deposited above it. Source-drain electrodes are

![Figure 1.6: Different architectures of organic field effect transistors.](image-url)
patterned over the gate dielectric typically using lithographic processes (e.g. photo-lithography, electron-beam lithography). The semiconducting polymer film is then deposited above the fabricated substrates using solution-based processes (such as spin-coating, dip-coating or doctor-blade). The advantage of this structure is that with inert gate dielectrics such as silicon dioxide or metallic oxides, lithographic definition of the source-drain electrodes allows very narrow channel lengths, as low as tens of nanometers, to be fabricated. Lithographic processing also enables large quantities of device substrates to be produced in a short time, enabling design experiments for optimization of the processes for deposition of the polymer semiconducting layer. Thus the transistor fabrication is limited merely by the polymer processing step rather than the electrode fabrication process, enabling fast production of devices. The main disadvantage of the co-planar bottom-gate device structure is the problem of poor contacts; devices typically suffer from high contact resistance. This is either due to poor coverage of the polymer film on the edges of the contacts due to the surface tension of the semiconducting film or the metallic sticking layer used in the patterning of source-drain electrodes, which typically have an adverse effect on the work function of the source-drain contacts, impeding good current injection.

**Staggered Bottom-gate**

The staggered bottom-gate structure shares the same structure as the coplanar bottom-gate structure in the first two layers, the gate electrode and the gate dielectric. However, in the staggered bottom-gate structure, the semiconducting polymer layer is solution deposited first. The source-drain electrodes are then defined above the semiconducting layer, typically by thermal evaporation of a metal through a shadow evaporation mask. Due to the sensitivity of the polymer to reactants, only thermal evaporation is used due to the relatively low energy of the process; other higher energy metal deposition processes such as electron-beam evaporation and sputtering, will result in damage to the film. The main benefit of using the structure is that highly reactive metal electrodes can be fabricated as final evaporation and the subsequent testing can be done in an inert environment. Another advantage is that processing can be done without use of lithographic or clean-room type processing which is expensive. The last benefit is that the evaporation of the metallic contacts enables direct contact of the metal to the semiconducting layer, resulting in good source-drain contacts. The disadvantages of this structure are that the structural limits of the shadow mask only enable transistors with channel lengths of micron scale to be fabricated and that radiative heat from the evaporation source may adversely affect the semiconducting material.

**Staggered Top-gate**

The fabrication steps of the staggered top-structure are the exact reverse of the staggered bottom-gate structure. The source-drain contacts are patterned onto a (typically flexible) substrate, followed by deposition of the polymer semiconducting layer. The gate dielectric is the deposited on top of the semiconducting layer and finally the gate electrode is deposited on top of the dielectric by an aligned evaporation. The great advantage of this structure is that it mimics the typical structure of inorganic transistors that are well known in industry, thus allowing these structures to be easily modeled and fitted to industrial standards. Another advantage is, due to lithographic definition of the source-drain contacts, narrow source-drain contacts can be fabricated and the quantities of devices produced are typically large. The main disadvantage of the structure is that the dielectric layer has to be deposited onto semiconducting layer via solution processing due to the chemical sensitivity of the polymer layer, limiting the type of dielectrics that can be used. Source-drain contact resistance also is typically poor.
as explained in the section on the co-planar bottom-gate structure. Of all transistor structures, this is used typically for all polymer active layer/polymer dielectric/solution processed gate electrodes due to the limitations of processing imposed on this structure.

**Co-planar Top-gate**

In analogy to the staggered top-structure, fabrication steps of the co-planar top-gate structure are the exact reverse of the co-planar bottom-gate structure. The semiconducting layer is first deposited on a substrate and the source-drain electrodes are evaporated via shadow mask on top of the polymer layer. A gate dielectric is then deposited on top of the semiconducting layer and then capped by deposition of the gate electrode. The advantages and disadvantages of the this structure is the similar to the staggered bottom-gate structure in that the use of shadow mask allow good contacts and deposition of more reactive metals, but limits the minimum length of the channels. The co-planar top-gate structure also share the advantages and disadvantage of the staggered top-gate structure due to the final deposition steps of the gate dielectric and gate electrode, the limit of the type of dielectric layer that can be deposited and that the structure is similar to structures typically used in industrially-fabricated transistors. Again, it is also possible to fabricate an all solution processed transistor with this structure.

1.2.2 Transistor model

The field effect transistor utilizes the capacitive effect of the dielectric insulator to modulate the thin layer of charge accumulated at the interface of the dielectric and the semiconductor (and the corresponding quantity of charge at the gate electrode) by variation of the voltage between the gate and the source. The quantity of charge that accumulates at the semiconductor-dielectric interface in turn determines the magnitude of the current that flows when a bias is applied between the source-drain electrodes. The single postulate in the model is to treat the device as a simple parallel plate capacitor. All charge on both sides of the insulator is immediately at the interface, without band bendings or other ways to distribute the charge in another way. As such, the charge at any place in the device is directly proportional to the voltage drop at the insulator, like in a classical capacitor \( C = Q/V \). In this simple starting model, it is assumed that all charge is composed of free holes only:

\[
\rho(x) = C_i[V(x) - V_G] \tag{1.4}
\]

where \( \rho(x) \) is the charge density at position \( x \) along the channel, \( C_i \) the capacitance of the dielectric, \( V(x) \) the local potential in the channel and \( V_G \) the uniform potential at the gate. Note that the density of charge is per square meter, thus effectively treating the active layer as two-dimensional. At any point in the channel, the current \( I_{ds} \) is then given by the product of the local free charge density, the local electrical field \( E_x = -dV(x)/dx \), the charge-carrier mobility \( \mu \) multiplied by the device width \( W \).

\[
I_{ds}(x) = \rho(x)\mu W \frac{dV(x)}{dx} \tag{1.5}
\]

The differential equation can easily be solved when appropriate boundary conditions are used, namely \( V(0) = 0, V(L) = V_{ds} \) and \( I_{ds}(x) = I_{ds} \) for all \( x \) (indicating there are no current sources in the channel). The general equation describing the source-drain current-voltage characteristics can then be derived as the following equation:

\[
I_{ds} = \frac{(W/L)\mu C_i[V_{ds}(V_G - V_T) - 1/2V_{ds}^2]} \tag{1.6}
\]
Figure 1.7: (a) Typical transfer characteristics for an organic transistor. (b) Typical output characteristics for an organic transistor for various $V_G$.

where $I_{ds}$ is the source-drain current, $W$ is the width of the source-drain channel (length of source or drain electrode), $L$ is length of the channel (distance between source and drain), $\mu$ the mobility, $C_i$ the capacitance of the dielectric, $V_{ds}$ the source-drain voltage, $V_G$ the gate voltage and $V_T$ the threshold voltage. Using the gradual channel approximation which assumes that the source-drain voltage is low enough such that the charge layer is uniform between the source-drain electrodes, the equation simplifies to:

$$I_{ds} = \left(\frac{W}{L}\right) \mu C_i \left[V_{ds}(V_G - V_T)\right]$$

(1.7)

This regime is referred to as the linear regime, because assuming constant mobility, the channel current increases linearly with the additional charge induced in the channel. At high voltages such that $V_{ds} \gg (V_G - V_T)$, the electric field induced by the gate at the drain contact is negligible, with no accumulated carriers within the region (a depletion regime). This is known as the pinch-off point, and due to this, source-drain current saturates (does not increase) even as source-drain voltage increases. The saturation current is described as:

$$I_{ds} = \left(\frac{W}{L}\right) \mu C_i (V_G - V_T)^2$$

(1.8)
Fig. 1.7a shows the typical source-drain IV characteristics of a PBTIT transistor, which separate curves for a different gate voltage. The linear regime is shown at low source-drain voltages, but as voltage increases, the current flattens out, an indication of saturation.

The mobility values derived in the subsequent experiments are saturation mobilities, in which Eq. 1.3 is used. By taking the derivative of $|I_{ds}|^{1/2}$ as a function of $V_G$, the following relationship can be determined:

$$\mu = \frac{L}{C_iW} \frac{d(|I_{ds}|^{1/2})}{dV_G}$$

(1.9)

Fig. 1.7b shows the transfer curve in which $|I_{ds}|$ is plot as $V_G$ on the right y-axis and $|I_{ds}|^{1/2}$ is plot as $V_G$ on the left axis for a constant $V_G$ (in this case $V_G = -60$ V). By taking the gradient of $|I_{ds}|^{1/2}$ versus $V_G$ curve and correcting it with the coefficient $C_i(W/L)$, the mobility can thus be derived.

1.3 Transport mechanisms

This section summarizes the mechanisms considered to explain electronic transport in organic and polymer devices [4]. Four tables comprise a concise smorgasbord of expressions for researchers to consider when attempting to understand the behavior of new materials or devices. $F$ is the electric field, $\phi_e$ effective barrier height, $w$ relevant width of barrier or depletion region, $\Delta E$ the appropriate activation energy, $N_A$ the doping concentration, $N_V$ the density of states in the valence band, and $A$ the junction area.

Fig. 1.8 summarizes transport mechanisms for metal/semiconductor and metal/insulator interfaces that rely primarily on thermal energy. Mechanisms include thermionic emission, field emission, diffusion theory, and combinations thereof. Schottky emission is field-enhanced thermionic emission from the metal, whereas Frenkel–Poole emission is field-enhanced thermal excitation of trapped carrier. Fig. 1.9 summarizes tunneling mechanisms, including tunneling with square, triangular, trapezoidal, and parabolic barriers. Zener tunneling describes valence band to conduction band tunneling. Tunneling processes may benefit from multiple steps via traps or thermal fluctuations. Fig. 1.10 summarized expression for nearest-neighbor hopping and variable-range hopping. Fig. 1.11 contains expressions for other transport mechanisms, including “Ohmic” conduction, ionic conduction, space-charge-limited currents, field-dependent mobilities, and combinations thereof.
<table>
<thead>
<tr>
<th>Process</th>
<th>Expression</th>
</tr>
</thead>
</table>
| Thermionic emission                              | \( J = J_0 \exp(qV/kT)(1 - \exp(-qV/kT)) \)
\[ J_0 = A^\varepsilon T^2 \exp(-q\phi_a/kT) \]
\[ A^\varepsilon = m^\varepsilon q^2/8\pi^2\hbar^3 \]
\[ -120(m^3/m)[\text{Acm}^{-3}K^{-2}] \]
\[ n = \left[ 1 - (\phi_a/\phi_V) \right]^{-1} \]
\[ qE_{\phi 0} \ll hT \]

| Thermionic field emission                        | \( J = J_0 \exp(V/E_{\phi 0})(1 - \exp(-qV/hT)) \)
\[ E_{\phi 0} = E_{\phi 0} \exp(0)(qE_{\phi 0}/kT) \]
\[ h/2m^2 \]  
\[ qE_{\phi 0} \approx hT \]

| Field emission                                   | \( J = J_0 \exp(V/E_{\phi 0})(1 - \exp(-qV/hT)) \)  
\[ qE_{\phi 0} \gg hT \]

| Diffusion theory                                 | \( J = J_{0D}(\exp(qV/kT) - 1) \)
\[ J_{0D} = q\mu V F^0 \exp(-q\phi_a/kT) \]
\[ F^0 \approx -\left[ 2qN_A(V_n - V - kT/q) \right]^{1/2} \]

| Thermionic emission & diffusion                  | \( J = J_0 \exp(qV/kT)(1 - \exp(-qV/kT)) \)  
\[ J_{\text{TED}} = \frac{1 + \nu_f}{\nu_f} \]
\[ A^\varepsilon T^2 \]
\[ qN \nu_f \]
\[ \nu_f \approx [q\mu/kT \exp(-q\phi_a/kT)]^{1/2} \]
\[ \nu_f/\nu_f \text{ is the ratio of the thermal velocity to the effective diffusion velocity through the depletion layer} \]

| Thermionic emission plus interfacial layer       | \( J = J_0 \exp(qV/kT)(1 - \exp(-qV/kT)) \)
\[ n = \frac{1 + \delta}{\delta + \delta q D_{\text{ss}}} \]
\[ \delta \text{ is the interfacial layer thickness} \]
\[ D_{\text{ss}} \text{ is the density of surface states in equilibrium with the metal} \]
\[ D_{\text{ss}} \text{ is the density of surface states in equilibrium with the polymer semiconductor} \]

| Schottky emission                                | \( J_0 = A^\varepsilon T^2 \exp[-q(\phi_a - \sqrt{qF/4\pi e}/kT)] \)

| Frenkel-Poole emission                           | \( J_0 = \sigma^0_F \exp[-q(\phi_a - \sqrt{qF/4\pi e}/kT)] \)
\[ \sigma^0_F = qN \mu_a (kT)^2 \text{ in a semi-crystalline material} \]
\[ \sigma^0_F = qN \mu_a (kT)^2 R^{1/2} \text{ in an amorphous material} \]
\[ N \text{ is the derivative with respect to energy of the density of emission states per unit volume per unit energy} \]

Figure 1.8: Thermionic emission mechanisms
<table>
<thead>
<tr>
<th>Process</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunneling through square barrier</td>
<td>( J = \sigma_0 V; \quad \sigma_0 = \frac{q^2 \sqrt{2m\hbar \phi_c}}{4\pi^2 w} \exp\left[-\frac{2w}{\hbar \sqrt{2m\hbar \phi_c}}\right] \quad V \ll \phi_c )</td>
</tr>
<tr>
<td>Tunneling through triangular barrier</td>
<td>( J = \sigma_0 F^2 \exp\left[-\frac{4q^2 m^* (q\phi_c)^{3/2}}{3q\hbar F}\right] )</td>
</tr>
<tr>
<td></td>
<td>( \sigma_0 = \frac{q^5}{16\pi^2 h (q\phi_c)} )</td>
</tr>
<tr>
<td>Modified Fowler-Nordheim</td>
<td>( J = \sigma_0 F^2 \exp[C_1 - C_2 F + F_w] )</td>
</tr>
<tr>
<td>Zener tunneling</td>
<td>( J = q\nu N_s \exp\left[-\frac{4q^2 m^* (q\phi_c)^{3/2}}{3q\hbar F}\right] )</td>
</tr>
<tr>
<td></td>
<td>( \nu = q\alpha F / h ) is the frequency of electron oscillations in the</td>
</tr>
<tr>
<td></td>
<td>valence band (( \alpha ) is the lattice constant)</td>
</tr>
<tr>
<td></td>
<td>( \phi_c ) equals the energy gap for band to band tunneling</td>
</tr>
<tr>
<td>Tunneling through trapezoidal barrier</td>
<td>( J = \sigma_0 F^2 \exp\left[-\frac{23q^2 m^* (q\phi_c)^{3/2}}{12q\hbar F}\right] )</td>
</tr>
<tr>
<td></td>
<td>( \sigma_0 = \frac{1.1q^2}{8\pi^2 \hbar \phi_c} \quad V \gg \phi_c )</td>
</tr>
<tr>
<td>Tunneling through trapezoidal barrier with non-uniform thickness</td>
<td>( J = \sigma_0 V^2 \exp(\lambda \exp(-\gamma / V) - 1) )</td>
</tr>
<tr>
<td></td>
<td>( \sigma_0 = \frac{8\pi\hbar \phi_c \exp(\gamma / V) - 1}{1} )</td>
</tr>
<tr>
<td></td>
<td>( \gamma = \frac{23q^2 m^* (q\phi_c)^{3/2}}{12q\hbar F} )</td>
</tr>
<tr>
<td></td>
<td>( \omega ) is the mean barrier thickness</td>
</tr>
<tr>
<td></td>
<td>( \lambda ) is the mean number of steps in thickness</td>
</tr>
<tr>
<td>Multi-step trap assisted tunneling</td>
<td>( J = \sigma_0 V \exp[-\gamma / \phi_c - V] )</td>
</tr>
<tr>
<td></td>
<td>( \sigma_0 = \frac{q^2 a N_f / 2\pi^2 \hbar c}{1} )</td>
</tr>
<tr>
<td></td>
<td>( \gamma = -(8\pi / 3h) \sqrt{m^* \hbar \phi_c / N_f} )</td>
</tr>
<tr>
<td></td>
<td>( N_f ) is the trap concentration</td>
</tr>
<tr>
<td></td>
<td>( \phi_c ) is the tunneling barrier for each step</td>
</tr>
<tr>
<td></td>
<td>( \phi_t ) is the number of steps required to traverse the layer</td>
</tr>
<tr>
<td>Multi-step trap assisted tunneling</td>
<td>( J = \exp(-\sqrt{F_c / F}) )</td>
</tr>
<tr>
<td>Thermal fluctuation induced tunneling through parabolic barrier</td>
<td>( J = J_0 F \exp\left[-\frac{T_1}{T + T_0} (1 - F/F_0)^5\right] )</td>
</tr>
<tr>
<td></td>
<td>( kT_1 = q\phi_c ) is effective barrier height</td>
</tr>
<tr>
<td></td>
<td>( \omega = \frac{T_1}{T_0} \frac{\hbar}{2q^2 \sqrt{2m\hbar \phi_c}} )</td>
</tr>
<tr>
<td></td>
<td>( F_0 = \sqrt{kT_1 / eA} ) field required to lower the top of the</td>
</tr>
<tr>
<td></td>
<td>potential barrier to the cathode</td>
</tr>
</tbody>
</table>

Figure 1.9: Tunneling mechanisms
<table>
<thead>
<tr>
<th>Process</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hopping to nearest neighbor</td>
<td>( J = J_0 \exp(-\Delta E/kT) \sinh(qRF/kT) )</td>
</tr>
<tr>
<td></td>
<td>( J_0 = 2qRFkTN(E_F) \exp(-2\Delta E) )</td>
</tr>
<tr>
<td></td>
<td>( R, \Delta E ) = distance between states, overlap parameter, and energetic separation</td>
</tr>
<tr>
<td></td>
<td>( kTN(E_F) ) = concentration of states within ( kT ) of the Fermi energy</td>
</tr>
<tr>
<td></td>
<td>( \nu = \text{hop frequency} )</td>
</tr>
<tr>
<td>Variable range hopping</td>
<td>( J \propto \exp(-C/T^{1/4}) )</td>
</tr>
<tr>
<td>Variable range hopping</td>
<td>( C = 2 \left( \frac{3 \alpha}{2\pi} \right)^{1/2} \left( \frac{\Phi^2}{kN(E_F)} \right)^{1/4} )</td>
</tr>
<tr>
<td></td>
<td>( R = (1/8\pi N(E_F) \pi kT)^{1/4} )</td>
</tr>
</tbody>
</table>

Figure 1.10: Hopping mechanisms

<table>
<thead>
<tr>
<th>Process</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Ohmic” conduction</td>
<td>( J = \sigma_F F \exp(-\Delta E/kT) )</td>
</tr>
<tr>
<td>Ionic conduction</td>
<td>( J = \frac{N_i^0 e^2}{T} \exp(-\Delta E/kT) )</td>
</tr>
<tr>
<td></td>
<td>( N_i ) = the concentration of carrier ions</td>
</tr>
<tr>
<td>Space-charge-limited</td>
<td>( J = \frac{q^2 \mu V^2}{8e^2 \tau^2} ) with no traps, or</td>
</tr>
<tr>
<td></td>
<td>( J = \left[ \frac{1}{2N_i kT (d+1)} \right] \left( \frac{q \mu N_i}{W^{d-1}} \right) \left( \frac{2l+1}{l+1} \right)^{1/4} V^{l-1} )</td>
</tr>
<tr>
<td></td>
<td>( N_i(E) = N_i \exp(-E/kT)_i ) is the trap distribution</td>
</tr>
<tr>
<td></td>
<td>( l = T/T_i &gt; 1 )</td>
</tr>
<tr>
<td>Murgatroyd space-charge-limited</td>
<td>( J = \frac{9}{8} \epsilon \mu \Delta V \exp(0.89 \sqrt{\Delta V/\epsilon}) )</td>
</tr>
<tr>
<td></td>
<td>( \Delta V = V - V_{ts} )</td>
</tr>
<tr>
<td>Meyer-Neldel mobility</td>
<td>( \mu = \mu_0 \exp\left[-\Delta E \left( \frac{1}{kT} - \frac{1}{\Delta E_{MN}} \right) \right] )</td>
</tr>
<tr>
<td>Gaussian disorder model</td>
<td>( \mu = \mu_0 \exp\left[-\frac{2\sigma^2}{3kT} + C \left( \frac{\sigma^2}{kT} \right)^2 - 2.25 \right] \sqrt{F} )</td>
</tr>
<tr>
<td>Correlated Gaussian disorder model</td>
<td>( \mu = \mu_0 \exp\left[-\frac{3\sigma^2}{5kT} + 0.78 \left( \frac{\sigma^2}{kT} \right)^{3/2} \left( \frac{\mu_{F}}{\sigma} \right) - 2 \right] \sqrt{F} )</td>
</tr>
<tr>
<td>Field-dependent mobility</td>
<td>( \mu(E) = \mu_0 \exp\left[-\frac{\Delta}{kT} + B \left( \frac{1}{kT} - \frac{1}{kT_0} \right) \sqrt{F} \right] )</td>
</tr>
</tbody>
</table>

Figure 1.11: Other mechanisms
Chapter 2. Experimental Details

2.1 Dielectric Surface Passivation

One of the critical processing steps is the passivation of the silicon dioxide dielectric surface with trichloroalkylsilanes [3]. Trichloroalkylsilanes permanently react with the silicon hydride and silicon hydroxide bonds on the surface in the reactions:

\[
\begin{align*}
X\text{-SiH} + \text{SiCl}_3(C_xH_{(2x+1)}) & \rightarrow X\text{-Si-SiCl}_2(C_xH_{(2x+1)}) + \text{HCl} \\
X\text{-SiOH} + \text{SiCl}_3(C_xH_{(2x+1)}) & \rightarrow X\text{-SiO-SiCl}_2(C_xH_{(2x+1)}) + \text{HCl}
\end{align*}
\]

forming a single monolayer of alkyl chains emanating from the surface of the oxide. It has been hypothesized that the monolayer of alkyl chains on the oxide surface effectively interdigitates with polymer chains, resulting the chains to stand upright, with the conjugation perpendicular to the surface. This allows the chains to collectively stack against each other, resulting in mesoscopically ordered, domains of stacked chains.

Octyltrichlorosilane (OTS) and octadecyltrichlorosilane (ODTS) are commonly used as a self-assembled monolayer (SAM) for passivation. Normally, soaking in 0.1 % OTS with toluene solvent for about 5 h is enough to form the SAM. For a fast reaction, soak in 2 % OTS solution being heated at 60–90°C for

Figure 2.1: A schematic diagram on the right describes the passivation of the surface of SiO\textsubscript{2} with an alkyltrichlorosilane and how the passivation orders the polymer deposited above it.
about 10-20 min. After the reaction, the samples are then cleaned in a bath of pure toluene and then stored in a second bath of toluene to prevent contamination from the environment. A sample is placed on the spinner and spun with nitrogen blown on the surface of the substrate to remove residual toluene. Evaporate the residual toluene on the hot plate at 80°C.

On the other hand, polypropylene-co-1-butene (PPcB) can be used to removed hydroxyl groups from the substrate surface. The PPcB solution is prepared at 20mg mL\(^{-1}\) concentration in Decahydron-aphthalene. To completely dissolve, the PPcB solution is stirred on the hot plate at 200°C for 1h. The PPcB layer is spin-cast from hot solution at 5000 rpm in air. After deposition, the samples were dried on hot plate at 200°C. For PPcB with low molecular weight, more then 2 min at 200°C can evaporate PPcB layer. In that case, dry at 190°C for 10 min.

### 2.2 Active layer deposition

The substrates are cleaved to form individual devices and then stored until devices need to be made. On such an occasion, the substrates are first cleaned, dried and then exposed to ozone plasma for one hour to activate the surface such that the substrate can be silylated more readily. The samples are then taken into a glove box, and in the inert environment, the samples are surface-treated as describe above. The polymer solution, heated to the desired temperature, is then spin-cast at a variety of spin-rate (typically 3000 RPM) onto the passivated substrate, followed by annealing to induce better morphology or formation of the liquid crystalline phase, and then the hotplate in which the samples are lying upon is turned off and the samples are allowed to cool. The thicknesses of the polymer thin films deposited in this fashion are typically around tens of nm.

### 2.3 Electrode evaporation

#### 2.3.1 Bottom-gate bottom-contact transistors

Bottom gate, bottom contact transistor samples fabricated by the Heeger group typically consist of a gate electrode of heavily-doped silicon (Si) (which also acts as the substrate which the transistors are on) and a gate dielectric of thermally grown oxide, with gate and source-drain electrodes of typically a high work-function metal (such as gold (Au) and platinum (Pt)) patterned on the oxide. Typically, contact to the gate electrode/Si substrate is made either by removal of the silicon oxide using a buffered hydrofluoric acid etch on selected areas defined by photolithography or by breaking the resist-capped oxide surface using a diamond scribe. Metal contacts to the gate are fabricated by electron beam evaporation. An initial layer of about 100 Å of titanium (Ti) is evaporated, serving two purposes: firstly, as an intermediate sticking layer to allow gold, which typically has poor adhesion to most materials, to adhere to the substrate, secondly, Ti acts a getter to remove surface oxide that forms when Si is exposed to the ambient (some of the oxygen atoms on the Si surface will dissolve into Ti layer), allowing good contact of the metal to gate electrode. Approximate 900 Å of Au is then evaporated in the same vacuum onto the Ti layer. Gold does not oxidize as strongly as Ti, preventing the gate contact from degrading with time due to formation of oxide. The metal lift off process is then completed by the removal of the gold capped resist, with only the areas of Si exposed either by lithography or scratching to have remaining layers of metal adhering to them.

The source-drain electrodes are then defined on the oxide surface by photolithography. Contact
lithography, which typically has a resolution of 1mm, is used to define open areas on the oxide surface in which metallic source-drain electrodes of 1mm in width and channel lengths of 5mm and above will be defined by electron-beam evaporation. Thereafter, 30 Å of Ti, followed by 500 Å of Au is deposited, and then subject to resist removal. The completed substrate is exposed to oxygen plasma at 100W for 4 minutes to completely remove any residual traces of resist that may affect the quality of semiconducting layer to be subsequently deposited.

2.3.2 Bottom-gate top-contact transistors

The surface treatment and polymer film deposition procedure is same as the described above. The only difference is the metal electrode deposition after the polymer film formation. Various metals can be used as the electrodes depending on the difference between the work function of the metal and the energy level of HOMO or LUMO of the semiconducting polymers. Thermal evaporation is a common method to deposit the electrodes. In the thermal method, metal mass is fed onto heated semimetal (ceramic) evaporators known as “boats” due to their shape. In a high vacuum (~ 1 µTorr), a pool of melted metal forms in the boat cavity and evaporates into a cloud above the source. The thickness of the metal can be controlled by the thickness monitor and the shutter installed under the samples.

2.4 Electrical testing system

The electrical testing system in UCSB consists of three Keithley 2400 SourceMeters. Two of the SourceMeters acts as voltage drivers for gate voltage and source-drain voltages. The last SourceMeter acts as a sense probe, measuring the voltage at the center of the channel to determine conductance of the sample during measurement. All the measurement systems share the same ground.

Keithley 2636 SourceMeters were used for the electrical testing system in KAIST. This sourcemeter has independent dual channels acting as gate and source-drain voltage drivers. In different configuration, one channel can be used to apply the current and measure the voltage drop for 4-probe measurement of resistance while the other channel can apply the gate voltage. All the measurement systems share the same clean ground or the isolated ground.

2.5 Low temperature system

2.5.1 Cooling system using liquid helium Dewer

The system was designed such that there is an option to test the samples in vacuum of around 20 mTorr. The upper side of the probe from which the BNC connections to the electrical testing system was welded with a steel cup with a rubber O-ring seal. A detachable aluminum cover with BNC connections screwed on, sealed with vacuum epoxy, is used to seal the cup from the ambient. Cryogenically insulated, shielded copper wires are attached to the BNC connectors and are threaded through the hollow steel rod, ending at the sample holder. A steel tube with an UltraTorr opening is attached to the cup, allowing connection to a vacuum pump or the helium outlet to fill the probe with helium as a heat transfer medium. An adjustable valve connected the steel outlet enable control of flow of air into and out of the probe.

The sample holder consists of a copper block, with an IC chip holder screwed on top of it. The sample holder screws onto the end of the steel rod which has a copper screw-hole welded to it, with a
Figure 2.2: Sample wiring. The T-shape is the gold electrodes. Gap between two electrode is the semiconducting polymer channel. Wiring is carried out with 0.08 mm tin-coated copper wires and Dotite D-500 silver paint.

Figure 2.3: Optical microscope image of a transistor device.
grooved steel flange located above it. The IC chip holder is machined with a rectangular hole in the middle such that part of the copper block juts out of it. The copper wires come out from an opening of the rod are soldered onto certain pins of the IC chip holder and to the DT-400 silicon diode temperature sensor. The temperature sensor is embedded with GE varnish into the copper block via a hole tapped into the underside of the block and sealed with GE varnish and Teflon tape. A Minco polyimide-sealed heater is attached to the top of the jutting section of the copper block using GE varnish. Utilizing a Scientific Instruments temperature controller, the temperature sensor and the heater work in tandem to accurately control the temperature of the sample, depending on how the user adjusts the probe, to an accuracy of 1% or less. Finally, to prevent the wires from slipping out of the opening, Teflon tape is used to wrap and seal the wires. To seal the sample holder from the outer environment and to create a
vacuum environment to test the sample, a hermetic steel cup, with a circular groove on the rim of the
cup was created. To seal the sample holder, a ring of indium is used as the O-ring, and the cup is sealed
to the flange on the probe via screws, creating a vacuum-tight seal.

A sample stage chip holding the transistor was also fabricated to fit into the IC chip holder of the
sample holder. The chip consists of an IC chip holder that was machined with opening large enough
to fit the jutting section of the copper block, an additional section of the holder was also machined to
accommodate the heater wires. A section of a sapphire wafer was cut to fit the opening and attached over
the opening of the chip holder with epoxy. The sapphire wafer acts as the stage in which the transistor
sample is attached to using thermal grease. Connections to the pins of sample stage chip are made by
attaching thin gold wires from the contact pads of the transistor to the pin ‘cups’ of the chip using silver
paste. This sample stage chip then clips onto the IC chip holder, with the sapphire stage flush against
the copper block, allowing thermal, electrical and mechanical connections to the probe. To perform a
measurement on the sample, the sample is attached to the sapphire stage with thermal grease, gold wires
are connected to the contact pads of the sample to the pin ‘cups’ sample stage chip with silver paint.
All this is performed in an inert environment, typically a glove-bag with nitrogen flowing in it. The
sample stage chip is then plugged onto the IC chip holder and the cap is attached to the probe with an
indium seal. The top half of the probe is connected to a vacuum pump and the system is evacuated by
opening the adjustable valve to the pump and closed when the lowest pressure is reached. The probe
is then inserted into the dewar with the Wilson seal with the dewar cover covering the opening of the
dewar. The Wilson seal not only ensures that minimum amount of He escapes, but also serves to hold
the probe in position. The probe is lowered into the dewar and cooled until around 40K, whereupon He
gas is introduced to the probe via the adjustable valve. The He acts as an efficient heat transfer medium
to the sample despite the isolation of the sample holder to the bath.

2.5.2 Cooling system using mechanical refrigerator

We used Leybold two-stage cryocooler system (so called GM refrigerator). The expansion of the
helium gas in the cold head results in refrigeration. Inside the cold head is a dual-diameter piston-like
mechanism, a “displacer”, which is driven by an electric motor. As the displacer moves up and down
in the cold head cylinder, an inlet valve and exit valve opens and close. The high pressure helium
gas is fed into the refrigerator through the inlet valve. The low pressure helium is exhausted from the
refrigerator through the drive motor to provide additional cooling to the motor. These Joule-Thomson-
like cooling cycle enables to cool the cold head down to 6.5K. The main advantage of this system is that
this is expensive-helium-free system. For the transport measurement, we used the feedthrough for SMB
c coaxial cables, which are essential for the low level current measurement. Inside the system, low thermal
conductive coaxial cables made of stainless steel were used to prevent heat from being transferred through
the cables. Sample stage made of aluminum was installed on top of the cold head by screws for good
thermal contact. Samples are attached on the sample stage by GE varnish. Sample stage temperature
was measured by DT-660 silicon thermometer with LakeShore 330.

As temperature decreases, the current level also decreases. The current below $10^{-12}$ A is comparable
to the noise from the mechanical vibration generated by the refrigerator. For transport measurement
at lower temperatures, the heat switch was prepared. It consists of two stages thermally isolated by
the plastic columns with bad thermal conductivity. One stage is screwed on top of the cold head and
the other stage is thermally isolated. 1mm-diameter capillary is connecting the two stages, strongly
thermally-linked to the both stages. Helium gas flows from the outside of the system, gets cooled on the
cold head and it cools the isolated stage and goes outside again. The cooled helium gas can provide the cooling power to the isolated stage. When the capillary is pumped out thoroughly, the cooling power becomes almost zero. This is the basic working principle of this heat switch. After thermal equilibrium, the refrigerator and the heat switch are turned off at the same time, maintaining the temperature over at least 5 min. During the equilibrium, transport measurements were carried out.
Chapter 3. High mobility amorphous polymer

We developed a new high performance amorphous donor–acceptor conjugated copolymer consisting of a dithienylcyclopentadienone subunit as an electron acceptor and carbazole derivative as an electron donor. X-Ray diffraction analysis shows no scattering patterns, indicating that a disordered amorphous solid is formed. Atomic force microscopy (AFM) images show an amorphous surface morphology regardless of the annealing temperature. A high on/off current ratio of approximately 10⁶ and high field effect mobility of 2.2 × 10⁻² cm²V⁻¹s⁻¹ were obtained with stable output characteristics. The high performance of the amorphous copolymer is ascribed to the relatively low activation energy and low characteristic temperature obtained from a low temperature transport analysis, reflecting that localization of the charge carrier is not substantial in the film [5].

3.1 Introduction

The fabrication of flexible and inexpensive electronic devices has been facilitated by laboratory successes with organic field-effect transistors (OFETs) [6, 7, 8, 9]. The practical applications of high-performance electronic devices, however, are limited by their low charge carrier mobility. Most organic materials have mobilities that are several orders of magnitude lower than those of conventional inorganic semiconducting materials. Recently, OFETs with a relatively high charge-carrier mobility, comparable to that of amorphous silicon, were reported. The higher mobility was attributed to the structural order of the polymer backbone [10, 11, 12, 13, 14].

A relatively high charge carrier mobility was also achieved in a new class of polymers synthesized with the goal of reducing the electronic band gap using donor–acceptor conjugated architectures along the backbone [15, 16, 17, 18, 19]. Low band gap conjugated copolymers adopting strong acceptors exhibit high charge carrier mobilities [16]. Considering these advantages, the synthesis and OFET performance of copolymers based on dithienylcyclopentadienone derivatives with regioregular thiophene based moieties were reported [20].

Although the consensus is that the lack of structural order in amorphous polymer devices results in poor mobility [21, 22], a relatively high mobility of the order of 10² cm²V⁻¹s⁻¹ was recently reported in an amorphous copolymer [23]. This success has focused attention on amorphous polymer OFETs because amorphous semiconductors offer advantages such as spatial homogeneity and reproducibility in device performance. The origin of the high mobility in amorphous polymers has not been clearly understood, although intrachain transport must play an important role [24, 25].

The present study reports a high-performance amorphous donor–acceptor conjugated copolymer synthesized with soluble dithienylcyclopentadienone derivative (3-(4-(nonan-3-yl))-7,9-di(thiophen-2-yl)-8H-cyclopenta[a]acenaphthylene-8-one, DTCPD) as an electron-deficient acceptor and 2,7-carbazole derivative (9-(heptadecan-9-yl)-2,7-carbazole, CB) as an electron-rich donor. We modified the DTCPD-alt-4,40-dialkyl-[2,20]bithiophene (DAT) by substituting CB for DAT moieties, which leads to self-assembled structural regularity [20]. CB moieties exhibit exceptional chemical and ambient stability and enable convenient substitutions of various functional groups [26, 27]. X-Ray diffraction patterns and AFM images indicate that a disordered amorphous solid is established. We found relatively a high charge carrier...
mobility, $\mu = 2.2 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and investigated the temperature dependence of charge carrier transport in the copolymer to understand the origin of the high performance.

3.2 Experimental details

3.2.1 Absorption and steady-state photoconductivity

Thin film polymer samples for photoconductivity measurements were spin-cast onto alumina substrates at 1000 rpm using 1 wt% solution. Metallic (Au) electrodes (80 nm-thick) were directly deposited onto the polymer layer by thermal evaporation using a shadow mask. The width of the gap (Auston switch sample geometry) between the two electrodes was 50 mm and the length 0.6 mm. The 500 V voltage bias applied between two electrodes generated an electric field of $10^5 \text{ V cm}^{-1}$. Photoconductivity measurements were performed in a dynamically pumped cryostat. For this measurement, light from a tungsten source was passed through a monochromator, and was then mechanically chopped at 170 Hz, which enables photocurrent measurement using the sensitive lock-in amplifier technique. The incident power spectra were recorded after each run with a calibrated silicon photodiode in order to normalize the photoconductivity data to Amps per Watt (A/W).

3.2.2 Ultraviolet photoelectron spectroscopy

Thin films for UPS measurement were fabricated inside a $N_2$ atmosphere by spin-coating on gold substrates using same solution and the samples were transferred via an airtight sample holder to the UPS analysis chamber. Samples were subsequently kept in a high-vacuum chamber overnight to remove solvent residues. The UPS analysis chamber was equipped with a hemispherical electron energy analyzer (Kratos Ultra Spectrometer) and a UV (He I) source and was maintained at $1 \times 10^9 \text{ Torr}$. UPS spectra were collected along a direction normal to the surface with a photon incidence angle of 35°.

3.2.3 Thermal annealing

All thermal annealing processes were carried out on a calibrated and stabilized heat stage (HCS600V, INSTEC) under $N_2$ atmosphere. After annealing, the devices were placed on a metal plate at room temperature to cool down.

3.2.4 X-ray diffraction measurements

Thin film samples for XRD measurements were prepared by spin-coating on SiO$_2$/Si substrates pre-coated with OTS using the same solution which was prepared for making the FET devices. X-Ray diffraction (XRD) measurements were carried out in air on a Panalytical X’Pert Pro (PW 3040) with a Cu Ka source ($\lambda = 1.5405 \text{ Å}$).

3.3 Amorphous thin film

The absorption spectrum covers a broad spectral range including the visible (VIS) and near infrared (NIR) as shown in Fig. 3.1b. The higher energy absorption peak centered at 426 nm shows a bathochromic shift compared to the DTCPD monomer peak at 400 nm or the 2,7-carbazole homopolymer peak at 396 nm [28, 29]. The lower energy absorption peak centered at 797 nm is due to DTCPD.
Figure 3.1: UV-VIS absorption spectra (red solid curve) of DTCPD-alt-CB film and corresponding photoconductivity (blue dotted curve). There is no photo-response following excitation into the NIR band.

Figure 3.2: (a) X-Ray diffraction patterns of DTCPD-alt-CB as solution processed films after annealing at various temperatures. (b) Atomic force microscopy images of DTCPD-alt-CB thin film annealed at various temperatures.

substitution and is responsible for the VIS and NIR absorption. The energy of the highest occupied molecular orbital (HOMO) level is 4.94 eV, as determined by UPS measurements.

We measured the steady-state photoconductivity spectra (photo-current as a function of the exci-
tation wavelength) to identify the photo-generation of charge carrier. The absence of any photocurrent in response to absorption in the low energy feature centered at 797 nm is similar to the results obtained from DTCPD-alt-DAT copolymers [20]. This result is not consistent with expectations for a low band gap semiconducting polymer in a cyclopentadienone platform [30]. This puzzling discrepancy implies independent and localized cyclopentadienone moieties. Note that the NIR absorption spectra are similar to those of DTCPD monomers [28]. In addition, it is likely that the ketone part on the backbone of the copolymer becomes an electron trap site and affects the charge transport along the backbone.

X-Ray diffraction (XRD) study was performed to investigate the structural order in the film. Crystalline peaks were not detected when cast and remained absent after annealing at various temperatures, as shown in Fig. 3.2a. In addition, amorphous solid formation in the film was confirmed by atomic force microscopy (AFM) images shown in Fig. 3.2b. Although annealing at 150 °C improves the surface morphology, no evidence of the crystalline structure was developed. On the contrary, annealing at temperatures greater than 200 °C causes significant roughness in the surface morphology TEM images also show the amorphous nature of the film.

### 3.4 Transistor characteristics

The output and transfer characteristics of a DTCPD-alt-CB conjugated copolymer thin film transistor with top contact geometry were investigated (Fig. 3.3a). The conjugated copolymer shows a typical p-type semiconductor characteristic operating in accumulation mode (Fig. 3.3b). A high on/off current ratio of approximately 106 is obtained from the drain-source current (Ids) versus the gate voltage (VG) graph. The output characteristics indicate stable device performance and provide evidence of reliable saturation when drain-source voltage (Vds) is comparable or greater than VG (Fig. 3.3c).

The influence of thermal annealing treatment on transfer characteristics at various temperatures is shown in Fig. 3.4a. The threshold voltage (VT) fluctuations after annealing have not been clearly understood so far. For comparison, field effect mobility, threshold voltage and on/off ratios of the OFETs of various annealing temperatures are listed in Table 3.1. Fig. 3.4b depicts the FET mobility after annealing. The mobility increases steadily as the annealing temperature is raised sequentially up to 150 °C. Further increase of the annealing temperature reduces the mobility gradually, consistent with the poor morphology observed by the AFM measurement. Here, carrier mobility enhancement was

<table>
<thead>
<tr>
<th>T/°C</th>
<th>Mobility/cm²V⁻¹s⁻¹</th>
<th>VT/V</th>
<th>Ion/Ioff</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>8.17 × 10⁻³</td>
<td>-9</td>
<td>10⁵</td>
</tr>
<tr>
<td>120</td>
<td>1.61 × 10⁻²</td>
<td>11</td>
<td>10⁶</td>
</tr>
<tr>
<td>150</td>
<td>2.18 × 10⁻²</td>
<td>15</td>
<td>10⁶</td>
</tr>
<tr>
<td>170</td>
<td>2.19 × 10⁻²</td>
<td>11</td>
<td>10⁶</td>
</tr>
<tr>
<td>190</td>
<td>1.87 × 10⁻²</td>
<td>0</td>
<td>5 × 10⁵</td>
</tr>
<tr>
<td>220</td>
<td>1.47 × 10⁻²</td>
<td>-5</td>
<td>5 × 10⁵</td>
</tr>
<tr>
<td>250</td>
<td>9.19 × 10⁻⁴</td>
<td>-10</td>
<td>2 × 10⁴</td>
</tr>
<tr>
<td>300</td>
<td>4.11 × 10⁻⁴</td>
<td>-25</td>
<td>5 × 10³</td>
</tr>
</tbody>
</table>
not substantial in comparison with the effect in liquid crystalline polymer devices, which showed the enhanced mobility by an order of magnitude. The moderate enhancement is most likely connected to the amorphous nature of the thin film and to the improved film morphology, whereas the strong annealing effect is ascribed to thermally-assisted structural rearrangement. On the contrary, an intriguing thermal annealing effect was reported in a highly disordered polymer [31]. Despite improvement of structural order after thermal annealing, the charge carrier mobility decreased by an order of magnitude, suggesting that structural order does not always lead to high mobility.

3.5 Low temperature experiments

The transport mechanism was assessed by temperature dependent mobility measurements. For the low temperature experiments, we used bottom contact geometry (Fig. 3.5a). This showed the reduced mobility ($3.4 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) indicative of significant contact resistance at the source and drain [32].
Figure 3.4: (a) Transfer curves in saturation regime annealed at various temperatures and (b) hole mobility of DTCPD-alt-CB FET as a function of annealing temperature from room-temperature to 300 °C.

Figure 3.5: (a) Schematic diagram of bottom contact FET architecture, (b) transfer curves in saturation regime at various temperatures.
The contact resistance decreased as gate bias increased, consistent with previous literature [33]. We found that the ratios of contact resistance to channel resistance was not substantially dependent on the temperature. Temperature dependent field effect mobility was obtained from the transfer characteristics in the saturation regime at various temperatures. (Fig. 3.5b) The transport is thermally-activated, as shown in Fig. 3.6a. We found strong \( V_G \) dependence of the activation energy of charge carrier mobility as shown in Fig. 3.6b. The relation between activation energy and gate bias is well-described by Eq. (3.1) below [34, 35].

\[
E_a(V_{GT}) = E_{a0} - 2kT_t \ln|V_{GT}/V_0|
\]  

There are two fitting parameters: \( E_{a0} \) is the bias-independent activation energy, i.e. the effective potential wall for charge carrier hopping, and \( T_t \) is the characteristic temperature, i.e. the width of the disorder-broadened exponential density of localized states. Here, \( k \) is the Boltzmann constant, \( V_{GT} \) is the difference between the gate voltage and the threshold voltage, and \( V_0 \) is a reference gate voltage which generates the reference charge concentration \( (N_0 = 10^{17}) \) at the interface. Note that the fitting is depicted as a solid line in Fig. 3.6b. We found unexpectedly small values of \( E_{a0} = 268.1 \ (\pm 5.9) \) meV and \( T_t = 342.2 \ (\pm 12.4) \) K compared to previously reported amorphous polymers of PTV (418 meV and 380 K)[36] and PPV (450 meV and 540 K) [37]. In fact, the activation energy is fairly close to those obtained from liquidcrystalline polymers or oligomers such as PQT-12 (245 meV), DH6T (260 meV)

Figure 3.6: (a) Temperature dependence of mobility at various gate biases, (b) gate bias dependence of activation energy. The solid line is a fit to Eq. (3.1).
or 6T (313 meV) [34]. Additionally, we attempted to fit the field effect mobility with the amorphous
organic transistor theory of Vissenberg et al. [36], where the mobility is described as a function of
a pre-exponential factor to the conductivity \( \sigma_0 \), wave function overlap parameter \( \alpha \) and characteristic
temperature \( T_t \):

\[
\mu = \frac{\sigma_0}{e} \left[ \left( \frac{T_t}{T} \right)^4 \sin \left( \frac{\pi T}{T_t} \right) \right]^{\frac{2}{(2\alpha)^3 B_c}} \left( \frac{T}{T_t} \right)^{p/2^3 - 1}
\]  

(3.2)

Here, \( e \) is the elementary charge, \( B_c \sim 2.8 \) is the critical number for the onset of percolation in
three dimensions, and \( p \) is defined as the charge concentration substituted for \((C_i V G T)^2/2kT \epsilon\), where \( C_i \)
is the capacitance of insulating layer and \( \epsilon \) is the dielectric constant of semiconducting layer. The fits
of the temperature dependence of the mobility yield a reasonable characteristic temperature (~340 K)
with a relatively large overlap parameter (~2.4 Å), comparable to those of better stacked and ordered
semiconductors [36, 38]. Large effective overlap parameters are often obtained from better stacked and
ordered semiconductor layers. It is, however, surprising that an amorphous polymer device without
crystalline ordering exhibits such a high overlap parameter.

3.6 Conclusions

In conclusion, the transport in the amorphous donor–acceptor conjugated copolymer, DTCPD-alt-CB
was studied. No XRD peak was observed even after post-annealing. AFM images show amorphous
surface morphology regardless of annealing temperature. Although there is a clear and relatively intense
absorption band in the NIR, photo-excitation into this NIR band yields no photoconductive response.
A high field effect mobility of \( 2.2 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and large on/off current ratio of approximately \( 10^6 \)
were obtained with stable output characteristics. In comparison to the other disordered polymers, the
low activation energy \( E_{a0} \) and the low characteristic temperature \( T_t \) were deduced from the temperature
dependent transport analysis. This reflects a weak localization of the charge carrier in the thin film,
justifying the relatively high mobility obtained from DTCPD-alt-CB FETs.
Chapter 4. Microstructure vs. transport

We present the effect of recrystallization rate on the microstructure and charge transport properties of high-performance semiconducting polymer, poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTTT), thin films. Differential scanning calorimetry (DSC) measurements indicate that the cooling rate directly influences the recrystallization process. In addition, atomic force microscopy (AFM) studies with an X-ray diffraction diagram demonstrate that slow cooling leads to well-connected large domains with enhanced three-dimensionally ordered structures, whereas fast cooling results in misaligned small domains with rough surfaces. At various temperatures, transport characteristics show an increase in the charge carrier mobility and a reduction in the activation energy with decreasing cooling rate of the films. Cooling rates slower than 15 °C/min induce the saturation of mobility and activation energy. These results assert that the cooling rate is a crucial factor for ordering in a microstructure as well as for the high performance of polymer thin films [39].

4.1 Introduction

Semiconducting polymers have become an essential class of materials for potential flexible electronic devices [40]. The charge carrier mobility, an index for practical applications, has been increasing steadily and is now comparable to that of amorphous silicon. The structural order within the polymer thin film is considered to be one of the most crucial factors, and accordingly, the relationship between the microstructural morphology and the charge transport has been extensively studied [41, 42, 43, 44, 45, 46, 47, 48]. The microstructure of polycrystalline polymers is typically characterized by the crystalline grains. Within a grain, charge transport is rather fast through a backbone chain and along the stacking direction with \( \pi-\pi \) overlap. Therefore, the mobility of a thin-film device is mainly limited by grain boundaries, which behave as a bottleneck of charge transport.

Kline et al. investigated the correlation between the mobility and various morphologies of poly(3-hexylthiophene) (P3HT) controlled by different molecular weights (MWs) [49]. They found that polymers with a high MW formed nodular-like structures that were more disordered than rod-like grains in polymers with a low MW. Nonetheless, the mobility of the higher-MW P3HT was several orders of magnitude higher than that of the lower-MW P3HT. This unusual inconsistency between the mobility and the order in the morphology was attributed to the fact that the connectivity between the grains of the lower-MW polymer is much worse than that of the higher-MW P3HT. Atomic force microscopy (AFM) topography reveals well-defined grain boundaries in the lower-MW P3HT, while the grains in the higher-MW P3HT are better connected because of the interconnecting polymer chains propagating through several grains, which enhances the connectivity. The significance of the connectivity between the grains was also investigated by utilizing directionally crystallized P3HT films. Transport characteristics measured in the direction parallel to the aligned grains showed that the charge transport barrier was lower and the mobility was higher than those measured in the direction perpendicular to the aligned grains, although more grain boundaries were expected in the direction parallel to the aligned grains [50]. The higher mobility was interpreted as better connectivity due to the existence of elongated polymer chains connecting two neighboring grains. These observations indicate that in addition to the appearance of crystalline grains,
the connectivity between the grains is an important factor for charge transport. Various microstructures have been realized by modifying chemical designs (e.g., regioregularity [12, 8] and MW [49, 51]), by applying different processing methods (e.g., using various boiling-point solvents [52, 53] and changing deposition conditions [44, 54]), or by employing different post-treatments [55, 56]. Within liquid crystalline polymers in particular, thermal annealing – a typical example of post-treatment – plays an important role in self-healing, that is, in reducing the grain boundaries and increasing the average grain size. For instance, annealing of poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTTT) thin films induces an extraordinary three-dimensional (3D) terrace structure that is composed of lamellar sheets stacked by interdigitated side chains in between [55, 57].

The annealed film is then cooled down in order to form the solid thin film from the liquid crystalline phase. The recrystallization is a non-isothermal process, and accordingly, the cooling rate through the transition may affect the recrystallization process and the resultant microstructures of the thin films. This non-isothermal process is, however, not extensively studied; therefore, the correlation between the cooling rate and the microstructure is not yet known.

In this chapter, we report that the cooling rate in the recrystallization from the liquid crystalline mesophase to the solid phase strongly influences on the microstructural morphology of PBTTT thin films and charge transport characteristics. Non-isothermal behavior in the recrystallization process is monitored by differential scanning calorimetry (DSC) measurements at various cooling rates. Microstructures of the films with different cooling rates are examined using AFM and two-dimensional grazing incidence wide-angle X-ray scattering (2D GIWAXS) experiments. Thin-film transistors (TFTs) with each resulting film as an active layer are fabricated. The transport characteristics show the dependence of charge transport on cooling rate from room temperature down to low temperatures.

### 4.2 Experimental details

Commercially available PBTTT-C14 (Merck Chemical Co.) was used as is. Thermal analysis of PBTTT was implemented using a differential scanning calorimeter (DSC 204 F1, NETZSCH). Powder PBTTT (3.69 mg) was used; it was heated at a rate of 10 °C/min and cooled at various rates under N₂ gas flow. Thin-film fabrication was performed in a glove box filled with N₂ gas. A heavily n-doped silicon (Si) wafer with a thermally grown 200 nm silicon dioxide (SiO₂) layer was used as a substrate. Before fabrication, substrates were completely dried at 120 °C on a hot plate in the glove box after sonication with acetone followed by ethanol. The substrates were treated with octatrichlorosilane (OTS) to make the surface hydrophobic. PBTTT solution was prepared at 0.5 wt% concentration in chlorobenzene. The heated solution (125 °C) was spin cast onto the substrate at 3000 rpm resulting in approximately 30 nm-thick films.

For an accurate measurement of sample annealing/cooling temperature at its equilibrium, a thermometer was attached to a large-mass metal plate which was placed on a conventional hot plate. Samples were placed on the metal plate and annealed at 150 °C above the liquid crystalline phase transition temperature for 10 min. Average cooling rates over the exothermic region were determined by monitoring temperature of the metal plate. AFM images were taken with Dimension 3100 (Veeco Instruments) operating in the tapping mode.

2D GIWAXS measurements were conducted at the 4C2 beamline of the Pohang Accelerator Laboratory at Pohang University of Science & Technology [58]. A monochromatized X-ray radiation source of 8.979 keV (wavelength λ = 0.138 nm) with a size of 0.5 mm (height) × 0.8 mm (width) was used.
Figure 4.1: DSC curves of PBTTT powder for various cooling rates.

Table 4.1: Exothermic peak parameters for various cooling rates.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Peak position (°C)</th>
<th>∆H (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>77.6</td>
<td>15.21</td>
</tr>
<tr>
<td>20</td>
<td>90.3</td>
<td>20.87</td>
</tr>
<tr>
<td>10</td>
<td>97.5</td>
<td>26.48</td>
</tr>
<tr>
<td>3.5</td>
<td>112.9</td>
<td>26.02</td>
</tr>
</tbody>
</table>

A 2D charge-coupled device (CCD) detector (MAR USA) producing 2D data of 2084 × 2084 pixel was used (where each pixel size is 57.6 × 57.6 µm²). Samples were loaded on a homemade z-axis goniometer in a vacuum chamber. The exposure time for the measurements was 60 s.

TFT devices were fabricated with conventional top-contact geometry. The heavily n-doped substrate worked as a gate electrode. Source and drain electrodes were formed on the spin-coated polymer layer by thermal evaporation of 70 nm Au using a patterned shadow mask. The channel length (L) and channel width (W) were 50 µm and 2000 µm, respectively, with W/L = 40. All electrical measurements were performed with the Keithley 2636 Dual-Channel System SourceMeter. For temperature dependent transport measurements, samples were mounted on the cold head of a GM refrigerator (130GM, Leybold Cryogenics) where a Si thermometer (LakeShore Cryotronics) was attached. Every measurement was conducted after full thermal equilibrium was reached.

4.3 Microstructure control

4.3.1 Non-isothermal recrystallization behavior

When a PBTTT film is formed on the substrate by deposition, innate defects hinder the construction of ordered microstructure. Annealing these films above the liquid crystalline phase transition temperature (T_H) induces side-chain melting and freely moving polymer backbones. Subsequent cooling of the films induces the well-ordered structures because defects in the films are removed, resulting in a 3D terrace structure with domains of typically several hundred nanometers in lateral size. This is the basic
mechanism of self-healing via thermal treatment in the liquid crystalline polymers. Upon cooling below the recrystallization temperature ($T_C$), most of the high-quality structural order formed in the liquid crystalline phase is preserved by side chain interdigitation, which is attributed to the origin of the exceptional 3D registry between the layers in PBTTT. Simultaneous X-ray diffraction (XRD) measurements along the thermal cycle show that a reorganized structure is maintained throughout the recrystallization process [59].

We systematically studied the recrystallization process by measuring the thermal properties of PBTTT powder by DSC. The samples were first heated at a fixed rate of 10 °C/min and subsequently cooled at various cooling rates from 3.5 to 40 °C/min. The exothermic heat flow curves for various cooling rates are shown in Fig. 4.1. The exothermic behavior at a cooling rate of 10 °C/min is consistent with previously reported results [55, 59]. When the sample is cooled from the liquid crystalline phase, the DSC curve shows a peak owing to the recrystallization transition, which is strongly dependent on the cooling rate. The key parameters of the recrystallization transition are listed in Table 4.1. Fast cooling through the recrystallization temperature prohibits the release of sufficient heat for the recrystallization and homogeneous interdigitation of the polymers. Thus, as the cooling rate increases, the exothermal peak shifts to lower temperatures, which is the typical characteristic of the meta-stability in the first-order phase transition. The enthalpy change ($\Delta H$) of the recrystallization for the fast-cooled sample does not reach the value obtained from the slow-cooled sample. The insufficient recrystallization time prob-
ably leads to poor interdigitation and inhomogeneous recrystallization (see Supplementary data). We performed the measurements with powdered PBTTTs and presumed that the recrystallization process in the polymer thin films is not unusually different from that of powdered polymers.

### 4.3.2 Effect of cooling rate on PBTTT microstructure

In order to directly study the effect of recrystallization rate on the microstructure of PBTTT thin films, the topography images were obtained using AFM (Fig. 4.2). All the samples were annealed at 150 °C for 10 min and cooled at various rates. Small (50–100 nm) water-droplet-like domains were observed in the fast-cooled sample in Fig. 4.2b. In the slow-cooled samples, on the other hand, relatively large (several hundred nanometers) and flat domains were observed, as shown in Fig. 4.2e and f. Recent TEM studies showed that the large lateral domains in the terrace structure are composed of crystalline subunits (~10 nm in size) [46]. Thus the large domains are not directly characterizing the size of grains but reflecting possibly enhanced connectivity between the grains with relatively small angles. A variety of domain sizes displayed in Fig. 4.2 can be interpreted by the indication that slow recrystallization leads to better connectivity among PBTTT molecules and consequently larger ordered domains, as is proposed in the previous section. Samples cooled at intermediate cooling rates show progressive improvement in morphology.

Another noticeable effect of slow cooling on the terrace structure is the flattening of surface layers to smoother surface morphologies. While the quenched sample exhibits rough surface morphology with small domains distributed over five or more layers, slow-cooled samples show smoother morphology with mostly one or two layers appearing on the surface. The root-mean-square (RMS) roughness of the films, shown in Fig. 4.3, quantitatively indicates the improvement of the surface morphology as the cooling rate decreases. Finally, RMS roughness saturates to about 1.3 nm with a cooling rate less than 15 °C/min. The substrate roughness was found to reduce the lateral domain size and the extent of long-range order, prevent the terrace formation, and suppress the field-effect mobility [54]. From this perspective, formation of large and smooth domains in the 3D terrace structure is likely to be an essential component for realization of high-performance polymer thin films.

The effect of the cooling rate on the long-range order in the polymer was determined by 2D GIWAXS

![Figure 4.3: RMS roughness values obtained from the AFM surface images for the films with various cooling rates.](image)
measurements. The 2D diffraction patterns for the various samples shown in Fig. 4.4 exhibit several noticeable differences. One is the d-spacing in the normal direction to the substrate. The d-spacing can be obtained from the out-of-plane diffraction peak position, i.e., the qz direction slice at qxy = 0, as shown in Fig. 4.5. The d-spacing of the diffraction peak in the fastest cooled film was 21.7 Å. As the cooling rate decreased, the d-spacing decreased and saturated to 20.7 Å for samples cooled slower than 15 °C/min, which is consistent with the results of the previously reported XRD analysis showing that the layer spacing changes with the thermal cycle [59]. The cooling rate dependence of the d-spacing can be explained by the different recrystallization times of melted side-chains. Above \( T_R \), side-chain melting expands the vertical layer spacing, and subsequent cooling down through \( T_C \) leads to the formation of interdigitated side-chains, reducing the layer-to-layer distance. It can be inferred that if melted side-chains have insufficient time to recrystallize, layer packing does not occur sufficiently; in contrast, sufficient recrystallization time guarantees relatively close-packing of the layers. It is worthwhile to mention that in-plane diffraction patterns show negligible cooling rate dependence (not shown here), which is consistent with the previous literatures [56]. This suggests that annealing modifies only the lamellar stacking and not the π-stacking.

Another prominent feature found in the 2D GIWAXS measurements is the shape and the intensity of Bragg peaks, from which the extent of layer ordering and tilting orientations can be compared. Figs. 4.6a–c show the 2D patterns of the (200) Bragg peaks of polymer films for different cooling rates. A perfectly aligned structure would exhibit an elliptical pattern in the Bragg peak, whereas a misaligned structure would exhibit an arc-shaped pattern [54, 60]. The elliptical shape of the Bragg peak in the slow-cooled sample clearly demonstrates the lack of tilted layers in this sample in comparison to the as-spun sample or the quench-cooled sample. We also examined at the horizontal (qxy-direction) slice of
the (200) peak intensity, as shown in Fig. 4.6d. The width of the peak is related to the lateral length of the ordered structure along the surface, in other words, the lateral domain size. The tilting of domains broadens the width of the horizontal peak intensity. The sharp and narrow peak of the slow-cooled sample indicates the highly oriented large in-plane domains. Since each layer is mutually supported by adjacent layers during recrystallization, side-chain interdigititation also enhances the lateral ordering, resulting in formation of large-size domains [59].

In addition, the higher-order mixed-index Bragg peaks, which are an index of 3D ordering, exhibit strong dependence on the cooling rate in the direct comparison of the (h10) peaks, as depicted in Fig. 4.7. The intensity data were collected from the slice of the 2D diffraction patterns at the (010) peak point along the qz direction. Although higher-order mixed-index peaks are indistinguishable in the as-spun sample and the fast-cooled samples, they become discernable in the slow-cooled samples, as (h10) and (h03) peak series labeled in Fig. 4.4f.

We did not study the microstructures of TFT at the dielectric interface which dominates the 2D transport in TFT. However, it is not unnatural to think that the cooling rate influences overall film structure of about 30 nm thickness including the dielectric interface.
Figure 4.6: 2D X-ray scattering near the (200) Bragg peak of a film of PBTNTT (a) as-spun, (b) quenched and (c) slowly cooled at 0.8 °C/min. The peak patterns were plotted on the same intensity scale. (d) $q_{xy}$ scan of the (200) peak for the corresponding films.

Figure 4.7: $q_z$ scan along the (h10) peak series for various cooling rates.
4.4 Transport measurement with TFT device

In order to study the effect of different morphologies on charge transport, the transfer characteristics of PBTTT TFTs with a top-contact configuration were investigated (Fig. 4.8a). All the devices exhibited high performance p-type TFT characteristics operating in the accumulation mode. The cooling-rate-dependent charge carrier mobility measured in the saturation region is shown in Fig. 4.8b. The mobility tends to increase as the cooling rate decreases. When the cooling rate is sufficiently low (lower than 15 °C/min), the mobility saturates at a certain value and becomes unaffected by further decrease in the cooling rate. The saturated mobility obtained from the slow-cooled samples is few times higher than the mobility from the quench-cooled sample.

To investigate the relationship between the recrystallization rate and the charge transport further, transport measurement was carried out at various temperatures. All the mobilities were measured in the saturation region at fixed effective gate bias, i.e., \( V_G - V_t = 20 \text{ V} \). The mobility monotonically decreases as temperature decreases. This temperature dependence becomes stronger with increasing cooling rate, as shown in Fig. 4.8b. The activation energy, i.e., the slope of mobility as a function of temperature, is calculated and plotted in Fig. 4.8c, showing a clear increase with increasing cooling rate. All the activation energy values are in reasonable agreement with those in previous work [46]. The activation energy also saturates for a sufficiently slow cooled sample, which is consistent with the behavior of raw mobility as a function of the cooling rate.

The relatively small mobility in the fast-cooled PBTTT film is closely related to its higher activation energy, which can be treated as an effective energy barrier that obstructs the charge transport. The dominant source of charge transport obstruction is grain boundaries, which is proliferated upon faster cooling. In other words, smaller mobility with higher activation energy can be attributed to its microstructure, which contains small and rough domains with worse connectivity induced by fast recrystallization. Sufficiently slow cooling results in well-connected, smooth, and large-size domains; the critical value of the cooling rate is found to be around 15 °C/min.

4.5 Conclusions

We have demonstrated the effect of recrystallization rate on the morphology and charge transport properties of a PBTTT thin film. DSC measurements at various cooling rates confirmed that the cooling rate plays an essential role in the recrystallization process. The connectivity between domains increases through recrystallization, resulting in larger domains. The microstructures obtained at various cooling rates were extensively studied by AFM and 2D GIWAXS. Slower cooling leads to well-connected large domains with 3D ordering, whereas faster cooling induces misaligned small domains. The charge carrier mobility increases with decreasing cooling rate and saturates for a cooling rate slower than the critical value of 15 °C/min. The activation energy obtained from the temperature dependent transport measurement showed that the charge transport obstruction tends to reduce as the cooling rate reaches the critical value. The smaller activation energy observed in the sufficiently slow cooled sample is attributed to the improved microstructure of the thin film.
Figure 4.8: (a) Cooling rate dependent transfer characteristics of PBTTT TFTs. The inset depicts the TFT configuration used in this study. (b) Cooling rate-dependent mobility measured at various temperatures. (c) Activation energies are obtained for various cooling rates.
Chapter 5. Nonlinear transport at low temperatures

5.1 Introduction

In the last decade, a large number of high performance conjugated polymers have been introduced and applied to a variety of electronic devices, including thin-film transistor, photovoltaics, or light-emitting diodes. The mobility of conjugated polymer has already exceeded that of amorphous silicon and now is approaching 10 cm$^2$V$^{-1}$s$^{-1}$ [61]. Even though we are taking advantage of the era of conjugated polymers, we are still missing a coherent picture of how the charge transport should be described in polymer systems.

One of the key issues in this research field would be “which charge transport is more dominant, intrachain or interchain?” Since charge carriers are rather delocalized along the polymer backbone, the mobility along the chain is much higher than the mobility along the pi-pi stacking direction. Therefore, if we make the device in which the charge carrier path is only along the chain direction, the performance of the device will be maximized. However, in real situations, since polymers have limited length much shorter than the device gap-length, charge should jump between the adjacent polymer chains. Moreover, even in the chain, there are localized sites such as kinks, impurities, etc. Therefore, interchain transport is unavoidable in the conjugated polymer thin films. This interchain-intrachain-mixed transport results in two-dimensional (2D) transport in poly(3-hexylthiophene) (P3HT) [12]. Highly regioregular P3HT chains tend to stand on the substrate with its side chains. The backbone and pi-pi stacking directions become parallel to the surface. In this situation, the interchain transport through the pi-pi stacking is the bottleneck of the total transport. Therefore, interchain transport become dominant in the whole electronic system. However, after a decade, one-dimensional (1D) transport was suggested in the high performance polymer, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTm) [62]. In this argument, the interchain transport is no longer a bottleneck for the transport. Charges are assumed to move through the backbone chains mainly. At the end of the chain, the charges can follow another adjacent backbone chains immediately. The interchain barrier is low enough not to disrupt the 1D transport along the successive intrachain transport. Therefore, the previous question, "intrachain transport or interchain transport?" would be equivalent to this new question, "1D transport or 2D transport?"

Another intriguing issue is the weak dependence of conductivity (or mobility) on temperature at low temperatures and the nonlinearity shown in the similar regime. Normally, since all the charge carriers tend to be localized in traps near the energy gap in organic materials, the transport mechanism is thermally assisted hopping. As temperature decreases, the phonon assistance also decreases. The mobility also decrease as temperature decreases following the Arrhenius relation below.

$$\mu = \mu_0 \exp \left( -\frac{E_a}{k_B T} \right)$$  \hspace{1cm} (5.1)

where $\mu_0$ corresponds to the trap-free mobility and $E_a$ is the activation energy, which is the barrier height for charge carriers to hop over. The ln $\mu$-1/T plot (Arrhenius plot) shows linear dependence and the slope indicates the activation energy. In the higher mobility organic materials, the less activation energy is
Figure 5.1: Arrhenius plot of the temperature-dependent mobility of sexithiophene (6T) and octithiophene (8T) based thin-film transistors. The oligomer was deposited at various substrate temperatures to control the grain size. RT: room temperature.

needed for charges to transport. Moreover, high mobility organic materials, especially small molecules, time to time show significantly weak temperature dependence at low temperatures. An Arrhenius plot is shown in Fig. 5.1 for sexithiophene (6T) deposited at room temperature (small grains) and 6T octithiophene (8T) deposited at high temperature (large grains) [63]. In the film with small grains the mobility follows the Arrhenious equation and remains thermally activated down to 100K. Below 100K, the mobility becomes too small to be measured. By contrast, in films with large grains the mobility is thermally activated only at high temperatures. It becomes practically temperature independent at low temperatures. To account for this, charge transport at low temperatures is thought to be dominated by tunneling across the grain boundary barriers [64, 65].

To explain this weak temperature dependence and nonlinearity at low temperatures, various types of tunneling mechanisms were suggested but no systematic studies were carried out. Especially, the nonlinearity shown in I-V curve and the weak temperature dependence were thought as independent phenomena to each other.

5.2 Luttinger Liquid controversy

Recently Yuen et al. showed that conjugated polymers at high carrier densities behave as one-dimensional metals, an observation that deeply opposes our intuitive understanding of the charge-carrying states in polymers, and provides a new experimental playground for the study of low-dimensional quantum systems [62]. Hereafter, a whole sentence of the introduction for this intriguing observation is quoted to help understanding this phenomenon [66].

As shown by Landau in the 1950s [67], electrons in two- and three-dimensional metals behave qualitatively as quasi-free particles; the only effects of any interaction with other electrons are (1) the modification of their effective mass and (2) the possibility of being scattered. For this reason — and even although in practice the interaction between electrons is not weak compared with the electron kinetic energy — our understanding of electron dynamics in two and three dimensions is entirely based on this single-electron picture known as Fermi liquid theory. In one dimension, however, the correlation between
electron motions has a much more dramatic effect. Excitations from the ground state cannot be described in the single-electron framework and are better thought of as collective excitations of the electrons of the system. The peculiarity of these one-dimensional (1D) systems, known as Luttinger liquids, have been described theoretically over the past 60 years [68], whereas a few experimental realizations of Luttinger liquids have only been identified more recently [69, 70, 71].

In a Luttinger liquid it is more difficult for the electrons to be thermally excited to a charge-conducting state, because of the correlation between electronic motions, and the tunneling transport is suppressed at low bias or low temperature in comparison with a ‘normal’ metal. The theory shows that, in an ideal Luttinger liquid, the current is proportional to some characteristic power of the voltage and the temperature. This is in strong contrast with 2D and 3D Fermi liquids in which the current is simply proportional to the voltage and the conductivity decreases with increasing temperature. The ‘fingerprint’ of a Luttinger liquid is its current–voltage characteristic, which is predicted to have a typical universal behavior.

\[
I = I_0 T^{1+\alpha} \sinh (\gamma eV/k_B T) \Gamma((\beta + 1)/2 + i\gamma eV/\pi k_B T)^2
\]

where \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( I_0 \) and \( \gamma \) are constants independent of \( T \) and \( V \), and \( \Gamma(x) \) is the gamma function.

Yuen et al. identified this fingerprint in two experimental systems based on the conjugated polymer poly(2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene) (PBTTT; Fig. 5.2). In one case the polymer was electrostatically doped by very high gate voltages in a field-effect transistor, where charge densities in the range of \( \approx 10^{19} \text{ cm}^{-3} \) were achieved. Another set of measurements with the polymer electrochemically doped to reach charge carrier concentrations of up to \( 10^{21} \text{ cm}^{-3} \) confirmed that the Luttinger liquid behavior is persistent over a very large range of carrier concentrations. (Fig. 5.3 and Fig. 5.4)

The results of Yuen et al. are extremely surprising because their system is structurally very far from an idealized 1D wire. Systems that have previously been convincingly characterized as Luttinger liquids include carbon nanotubes [69], atomic wires on insulating surfaces [70] and inorganic crystalline nanowires [71]. In these systems the differences between experimental observation and the expected behavior of the ideal Luttinger liquid were attributed to the presence of impurities or the interaction between domains is not rate limiting.

![Figure 5.2: Chemical structure (left) of PBTTT, schematic of PBTTT molecular packing (center) and the arrangement of crystalline domains (right). When the polymer is highly doped, each individual chain behaves as a one-dimensional metal with negligible interaction with the neighboring chains. The hopping between domains is not rate limiting.](image)
Figure 5.3: I–V data plotted as \( I_{SD}/T^{1+\alpha} \) versus \( eV_{SD}/k_BT \) for a PBTTT FET (SiO2 as gate dielectric) from 0.26 to 260 K for \( V_G=-150 \) V

Figure 5.4: I–V data plotted as \( I_{SD}/T^{1+\alpha} \) versus \( eV_{SD}/k_BT \) for a PBTTT FET (Si3N4 as gate dielectric) for \( V_G=-160 \) V
between different 1D channels. Until now, no bulk material has been properly described as a Luttinger liquid.

PBTTT is considered one of the most promising semiconducting polymers of the new generation thanks to its tendency to form highly ordered crystalline domains in three dimensions, which improves charge mobility. The work of Yuen and colleagues shows that PBTTT chains seem to behave as 1D wires, even though the chains have non-negligible electronic interactions with their neighbours (Fig. 5.2). The polymer length and the typical length of the crystalline domains are far shorter than the distance between source and drain electrodes, that is, the path followed by the charge carriers between the electrodes must involve hopping between different chains and crossing of the amorphous regions between the crystallites. These disruptions, known as energetic disorder, do not alter the Luttinger liquid behavior, signifying that the tunnelling barrier between liquid-crystalline domains is not rate limiting. These new measurements challenge some common beliefs. It now seems that the Luttinger liquid phenomenon is much more robust than previously thought and it remains mostly unaltered when the charge transport is ‘prevalently one-dimensional’ in strongly anisotropic bulk materials. Moreover, the marginal role of disorder is also quite surprising. The transport characteristics of PBTTT and analogous polymeric materials at low carrier concentrations are well described in terms of variable range hopping between states localized by static disorder. Extrapolation of this model to high charge densities would have suggested a disordered 3D metal more than a Luttinger liquid. The results of Yuen and co-workers indicate that a further generalization of Luttinger liquid theory may be possible, and thus could prompt more work on the characterization of the charge-carrying states in highly doped conjugated polymers, and on the influence of disorder and localization on the behavior of Luttinger liquids. Such generalization could be the key to achieving a coherent description of the electric properties of organic conductors.

After this incredible observation, subsequent low temperature studies on other types of semiconducting organic thin films were performed. The first set of counter examples were reported by Worne et al. [72]. They presented transport measurements in organic field-effect transistors based on poly(3-hexylthiophene) (P3HT) and 6,13-bis(trisopropyl-silylethynyl) pentacene (TIPS-pentacene) with short channels, from room temperature down to 4.2 K. Near 300K, transport in both systems is well described by a model of thermally assisted hopping with Poole-Frenkel-like electric field enhancement of the mobility. The output characteristics show great agreement with Poole-Frenkel model at 100K. At low temperatures and large gate voltages, however, transport in both materials becomes nearly temperature independent, crossing over into a regime described by field-driven tunneling. Moreover, the data from both materials are following the universal curve with the Luttinger liquid fingerprint, i.e. Eq. 5.2. (Fig. 5.5)

They were able to collapse their data onto a single line as temperature is decreased, with choices for \( \alpha \) that are not wildly different from those reported for PBTTT or polyaniline fibers. Note that TIPS-pentacene is a short chain molecule, without the mobility anisotropy found in PBTTT or P3HT. It seems extremely unlikely that TIPS-pentacene can be described by LL theory for a one-dimensional metal, despite the apparent collapse of its I-V curves onto a single master line. With the freedom to adjust \( \alpha \), plotting scaled data as in Fig. 5.5 becomes unwise. As temperature decreases, both P3HT and TIPS-pentacene I-V curves become increasingly non-linear and temperature independent. Plotting the data of Fig. 5.5 turns roughly power law trends over a limited voltage range into a linear segment on such a log-log plot. The freedom to choose \( \alpha \) while plotting allows fine-tuning of the subsequent temperature curves to lie on the same line. Because current and voltage are plotted as \( I_D/T^{\alpha+1} \) and \( eV_{DS}/k_B T \), decreasing \( T \) moves subsequent temperature data sets up and to the right on the graph, even if the data
Figure 5.5: I–V data plotted as $I_{SD}/T^{1+\alpha}$ versus $eV_{SD}/k_B T$ for a PBTTT FET (Si3N4 as gate dielectric) for $V_G=-160$ V
Figure 5.6: Scaling of electrical transport. The scaled current density as a function of the dimensionless parameter $eV/kT$. Both dc measurements at low bias and pulse measurements at high applied bias are included.

Themselves do not change with temperature at all [72]. They argued that the data collapse with this plotting is not sufficient to demonstrate Luttinger liquid physics. They instead proposed the classical field emission hopping for this nonlinearity and weak temperature dependence.

Another counter example was found in the poly-3,4-ethylenedioxythiophene stabilized with poly-4-styrenesulphonic acid (PEDOT:PSS) [73]. The transport transversal through PEDOT:PSS thin films fabricated in so-called large-area molecular junctions. The transport also shows universal power-law scaling with both bias and temperature. All measurements constitute a single universal curve, and the complete $J(V,T)$ characteristics are described by a single equation. (Fig. 5.6) However, PEDOT:PSS is a disordered conducting polymer; the microstructure of thin films consists of spherical amorphous grains. Furthermore, the conjugation of PEDOT chains is too short to form a semi-infinite one-dimensional lattice needed for a Luttinger liquid. Hence, PEDOT:PSS is effectively a three-dimensional electronic system and can therefore not be regarded as a Luttinger liquid. They also argued that the Eq. 5.2 holds for a Luttinger liquid but the reverse is not necessarily true. The I-V characteristics described by Eq. 5.2 does not automatically imply that one is dealing with a Luttinger liquid. They instead attribute this scaling behavior to dissipative tunneling such as environmental Coulomb blockade.

At the same time, other research groups attempted to show the universal curve can be built on the other basis. Rodin et al. argued that the conventional mechanism of transport, which is the variable range hopping (VRH) in quasi-1D systems can also lead to Eq. 5.2 [74]. This is because at low enough temperature, the hopping length is not much smaller than the length of the wires. In this case, the VRH conductance deviated from the usual formula. The hopping is dominated by hopping paths that consist of a few approximately equidistant hops. Although rare, such configurations can always be found in a
Figure 5.7: Collapse on the universal curve (solid line) obtained by plotting the numerical results.

Figure 5.8: Calculated data for different temperatures presented with colored points. Black line denotes the universal function.
Figure 5.9: Scaling of the current-voltage characteristics of rr-P3HT FEFET
Figure 5.10: Scaling of the current-voltage characteristics of rr-P3HT and PTAA FeFETs, chemically doped rr-P3HT and OC$_1$OC$_1$0-PPV in-plane diodes, and a PEDOT:PSS vertical diode sample if the number of channels is large enough. Hence, despite mesoscopic fluctuations that accompany rare events, the conductance can be a smooth quasi-power-law function. (Fig. 5.7)

Cao et al. also investigated the temperature dependence of electric conductance in one-dimensional (1D) systems with thermally excited electron transport under various bias voltages by using Monte Carlo simulation based on the VRH formula [75]. They found that the temperature dependence of the transport can show a power law behavior as a result of summation over a large number of electron traveling paths although the hopping intensity in every step in the VRH formula is exponentially dependent on the temperature. This can well explain the temperature dependence of conductance measured in various experiments on 1D systems. Without taking the interaction between electrons into account, they can also merge most of their data onto one “universal curve”. (Fig. 5.8)

More recently, Asadi et al. also found the universal curve in the various polymer systems and explain the universal curve with polaron hopping mediated by nuclear tunneling [76]. They presented a uniform description of charge transport in semiconducting polymers, including the existence of absolute-zero ground-state oscillations that allow nuclear tunneling through classical barriers. The resulting expression for the macroscopic current shows a power-law dependence on both temperature and voltage. To suppress the omnipresent disorder, the predictions are experimentally verified in semiconducting polymers at high carrier density using chemically doped in-plane diodes and ferroelectric field-effect transistors. The renormalized current-voltage characteristics of various polymers and devices at all temperatures collapse on a single universal curve, thereby demonstrating the relevance of nuclear tunneling for organic electronic devices. (Fig. 5.9)

They have shown that inclusion of nuclear tunneling in the hopping rate leads to a unified description of the I(V, T) characteristics of semiconducting polymers at high carrier densities. For all polymers investigated, the full I(V, T) showed a power-law dependence on both temperature and voltage. In a
single plot, the renormalized data of all the polymers and devices collapse and a universal curve was obtained. The plot integrates all measurements for different electrode distances, at temperatures between 10 and 300K, with a bias swept over five orders of magnitude. (Fig. 5.10) They argued the universal scaling demonstrates that the charge transport mechanism is similar in all the polymers and occurs via polaron hopping driven by nuclear tunneling. The mechanism is operational in conventional opto-electronic devices such as organic light-emitting diodes and solar cells. However, then the charge carrier density is low, and disorder is not suppressed. As a consequence, charge carriers have to overcome energetic differences between the localized states at the energetic transport level, in addition to the barriers induced by polarization.

5.3 Scent of field emission at low temperatures

We have focused on the lower temperature transport behavior in the highly ordered polymer, poly(5′,5′′-(3,6-dimethylselenopheno[3,2-b]selenophene-2,5-diyl)bis(3-dodecyl-2,2′-bithiophene)) (PmTSe), thin films [77]. Fig. 5.11 shows the chemical structure of the ordered polymer we have used in this project. The structure is quite similar with PBTTT except that selenium atoms were inserted in the fused-ring instead of sulfur atoms to delocalize the charge carriers more. The room temperature mobility was reported to be 0.03 cm²V⁻¹s⁻¹.

The temperature dependence of mobility shows typical behavior of semiconducting polymers. At higher temperatures, the activation energy, i.e. the slope in the mobility-inverse temperature plot, is higher than that at lower temperatures. This indicates that there are two regimes; one where the mobility is strongly dependent on temperature and the other where the mobility is weakly dependent on temperature. Moreover, the output characteristics for each regime can be easily distinguishable. (Fig. 5.12) In the higher temperature regime, the output characteristics show ohmic transport in the linear regime and saturated to a certain value in the saturation regime. However, in the lower temperature regime, non-linearity starts to show up without the saturation regime. Here, we will show the transport mechanisms of these two regimes are different and the lower temperature regime includes more interesting physics.

We also constructed the Luttinger Liquid plot with our data obtained at various temperatures with our highest gate bias (-100 V). In Fig. 5.13, even though the I-V curves obtained with low drain-source voltage has a tail deviated from the universal curve, the high drain-source voltage values show pretty good agreement with the universal curve. This tail deviation was also presented in Yuen’s unpublished qualifying exam presentation. In Fig. 5.14, the Luttinger Liquid plot for PBTTT with same gate bias (-100 V) as ours. This deviation indicates that the transport mechanism at high electric field and

![Chemical structure of PmTSe](image_url)

PTmSe \( \mu \sim 0.03 \text{ cm}^2/\text{Vs} \)

Figure 5.11: Chemical structure of PmTSe.
Figure 5.12: Linear/nonlinear transport at high/low temperature in PmTSe thin film.
Figure 5.13: Luttinger Liquid plot for PmTSe with moderate gate bias (-100 V).

Figure 5.14: Luttinger Liquid plot for PBTTT with moderate gate bias (-100 V). The data are obtained from the qualifying presentation of J. Yuen.
that at low electric field are different to each other. Moreover, the universal curve can be constructed only when sufficient electric field and gate bias is applied. Therefore, the studies to looking for the transport mechanism that leads to the universal curve collapse, or furthermore, one-dimensional transport is necessary.

When there is a barrier for the charge carriers, charge carriers can pass the barrier via various transport mechanisms. (Fig. 5.15) First mechanism is the thermally activated hopping. At high enough temperatures, charge can hop the barrier assisted by thermal vibration energy (phonons). The high temperature transport results are well-explained by this thermally activated hopping. In the linear regime, we can easily derive the current-voltage relation from the thin-film transistor equations as below.

\[
\ln \left( \frac{I}{V} \right) = \ln \left( \frac{1}{V} \right) + \text{const} \quad (5.3)
\]

At low temperatures, due to the lack of the thermal energy, the hopping rate becomes less probable and other transport become dominant. When charges tunnel the rectangular barrier, the current-voltage relation from the tunneling will be derived as below. This transport mechanism is called direct tunneling [78].

\[
\ln \left( \frac{I}{V} \right) = \ln \left( \frac{1}{V} \right) - \frac{2d\sqrt{2m_e\phi}}{\hbar} \quad (5.4)
\]

When the high electric field was applied across the barrier, the situation become a bit different. If the applied bias is greater than the barrier height, the barrier change the shape from rectangular to triangular and the current-voltage relation accordingly changes as well. The transport mechanism here is called field emission [78]. The current-voltage relation is given as below.

\[
\ln \left( \frac{I}{V} \right) = -\frac{4d\sqrt{2m_e\phi^3}}{3\hbar q} \left( \frac{1}{V} \right) \quad (5.5)
\]

Since each equation for the mechanism has common variables, \(\ln(I/V^2)\) and \(1/V\), on the left and right side of the equation, respectively, the transition between these mechanisms can be easily determined when we plot the data in the \(\ln(I/V^2)\)-\(1/V\) plane, which is called “Fowler-Nordheim plot” [78].

Fowler-Nordheim plots for different gate voltages at various temperatures are delineated in Fig. 5.16. At higher temperatures, only the log dependence is shown, indicating the thermally assisted hopping is dominant. At lower temperatures, there can be seen the transition between log dependence to linear dependence. As we derived the \(\ln(I/V^2)\)-\(1/V\) relation above, this transition is originated from the different transport mechanisms; the log dependence at lower bias is due to the direct tunneling whereas the linear dependence at higher bias is due to the field emission. At the intermediate temperatures, as temperature decreases, the hopping gradually vanishes and tunneling mechanisms slowly appears. Note that hopping always involves the deviation at low voltages. At low enough temperature, the low voltage curves are collapsed, indicating no more thermally activated hopping is possible at that temperature range.

The transition voltage can be assigned as the voltage where the transition occurs. In Fig. 5.17, the transition voltages at various temperatures are denoted. As temperature decreases, the transition voltage increases. Since the transition voltage implies the effective barrier height, effective barrier height increases as temperature decreases. Zero temperature effective barrier height can be estimated to be around 58 V.

So far, although the Fowler-Nordheim plot shows good-looking fitting for the field emission and the direct tunneling in PTmSe thin films, the physical meaning of this phenomena is questionable. First of
Figure 5.15: Transport mechanisms.

1. Thermally activated hopping:
   \[ I = (V_0 - V_T)V - \frac{V^2}{2} \]
   \[ \ln \left( \frac{I}{V^2} \right) = \ln \left( \frac{1}{V} \right) + \text{const} \]
   Log relation

2. Direct Tunneling:
   (1) Applied bias < the barrier height
   (2) Rectangular barrier
   \[ \ln \left( \frac{I}{V^2} \right) \propto \ln \left( \frac{1}{V} \right) - \frac{2d\sqrt{2m_e\phi}}{\hbar} \]
   Log relation

3. Field emission (Fowler-Nordheim):
   (1) Applied bias > the barrier height
   (2) Triangular barrier
   \[ \ln \left( \frac{I}{V^2} \right) \propto \frac{4d\sqrt{2m_e\phi^3}}{3\hbar q} \frac{1}{V^2} \]
   Linear relation

Figure 5.16: Fowler-Nordheim plot for different gate voltages at various temperatures.
Figure 5.17: Fowler-Nordheim plots for various temperatures. The gate voltage is set to be -100 V.
all, if one regards the barrier as the semiconductor between two electrodes in the field-effect transistor system, then the barrier is too thick for charge to tunnel. Normally, field emission occurs when the barrier is sub-micrometer and the applied voltage is high enough for one-step tunneling. For example, the highest field in this experiment was about 50 kV/cm and the transmission coefficient calculated with the equation below is only $e^{-1000}$, which is too small to be important [79].

$$T_S = \exp \left( -\frac{4\sqrt{2m \Delta^{3/2}}}{3e \hbar F} \right)$$ (5.6)

Consequently, the meaning of zero temperature effective barrier height is vague. If the semiconductor between the two electrodes plays the role of the barrier, the effect barrier height should be the energy level difference between the Fermi level of the metal electrode and the valence band energy level (order of 1eV). However, the number -58 V is too large to be reasonable.

### 5.4 Field emission behavior in PBTTT

#### 5.4.1 Experimental Details

Commercially available PBTTT-C14 (Merck Chemical Co.) was used as purchased. Thin-film fabrication was performed in a glove box filled with N$_2$ gas. A heavily n-doped silicon (Si) wafer with a thermally grown 200 nm silicon dioxide (SiO$_2$) layer was used as a substrate. Before fabrication, substrates were completely dried at 120 °C on a hot plate in the glove box after sonication with acetone followed by isopropyl alcohol. The substrates were treated with octatrichlorosilane (OTS) to make the surface hydrophobic. PBTTT solution was prepared at 0.5 wt% concentration in chlorobenzene. The heated solution (125 °C) was spin cast onto the substrate at 3000 rpm resulting in approximately 30 nm-thick films. Samples were placed on the metal plate and annealed at 150 °C above the liquid crystalline phase transition temperature for 10 min. Slow cooled samples were prepared with cooling rate controlled to be 1 °C/min with the programmable hot plate. Quench cooled samples were prepare with quench cooling on the metal surface with large thermal mass after the annealing.

TFT devices were fabricated with conventional top-contact geometry. The heavily n-doped substrate worked as a gate electrode. Source and drain electrodes were formed on the spin-coated polymer layer by thermal evaporation of 70 nm Au using a patterned shadow mask. Various channel length (L) mask was used from 20 µm to 100 µm. The width (W) was fixed with 2000 µm. All electrical measurements were performed with the Keithley 2636 Dual-Channel System SourceMeter. For temperature dependent transport measurements, samples were mounted on the cold head of a GM refrigerator (130GM, Leybold Cryogenics) where a Si thermometer (LakeShore Cryotronics) was attached. We carefully organized the measurement system with leakage current less than $10^{-11}$ A for all temperature range. Every measurement was performed after full thermal equilibrium was reached.

#### 5.4.2 Weak temperature dependence and nonlinearity

Using the conventional output characteristics, we can derive simple 2-probe conductivities ($=I_{ds}/V_{ds}$) for various gate voltages and drain-source voltages. Fig. 5.18 indicates a transition from strong temperature dependence with conductivity falling below the noise level at low temperatures to finite conductivity as temperature goes to zero as a function of the gate voltages (left) and drain-source voltages (right). As we described in the previous sections, at high temperature regime, the slope in this graph indicates
Figure 5.18: Conductivity as a function of temperature with various gate voltage and drain-source voltage.
the activation energy, i.e. the barrier height, in the conjugated polymer thin films. However, at low temperature, the conductivity becomes almost independent of temperature, the slope no longer means the activation energy. Drain-source voltage dependence shows high nonlinearity; the conductivity increase by orders of magnitude when $V_{ds}$ is increased by only a factor of few. The existence of a weak temperature dependent regime was observed in PBTTT FETs and attributed to a one-dimensional transport [62].

Fig. 5.19 shows this nonlinearity more clearly. As temperature decreases below 50K, the saturation region gradually disappears and the nonlinearity starts to appear. Because of this non-linearity, the conventional method to derive the mobility does not hold anymore: we instead used 2-probe conductivity ($=I_{ds}/V_{ds}$) and I-V curves themselves to analyze the low temperature behavior of PBTTT thin films.

### 5.4.3 Candidates for field-induced transport mechanisms at low temperatures

To explain this low temperature nonlinearity, a variety of models involving the field dependence were investigated. The field-induced transport models we applied are organized in Fig. 5.20. The main difference is the relation between the conductivity and the temperature, and the relation between the conductivity and the applied electric field. For example, Poole-Frenkel hopping is dependent on temperature, and the log conductivity follows $E^{1/2}$ dependence [80, 72]. Other field-induced transport models are temperature independent. Field-assisted hopping [81], Multistep tunneling [79], and Efros-Shklovskii VRH models [82] reveals that the log conductivity has $E^{-1/2}$ dependence. Only field emission shows $E^{-1}$ dependence [78, 83]. Direct tunneling shows ohmic behavior [78].

The electrons are generally trapped in localized states (loosely speaking, they are “stuck” to a single atom, and not free to move around the crystal). Occasionally, random thermal fluctuations will give that electron enough energy to get out of its localized state, and move to the conduction band. Once there, the electron can move through the crystal, for a brief amount of time, before relaxing into another localized state (in other words, “sticking” to a different atom). The Poole–Frenkel effect describes how, in a large electric field, the electron doesn’t need as much thermal energy to get into the conduction band (because part of this energy comes from being pulled by the electric field), so it does not need as large a thermal fluctuation and will be able to move more frequently. According to the Poole-Frenkel model, the conductivity shows the following relation with external electric field.

$$\sigma \propto \exp (-\gamma \sqrt{E})$$

where $\gamma = B \left( \frac{1}{k_BT} - \frac{1}{k_BT_0} \right)$

We plotted the output characteristics with the ln $\sigma$ and $\sqrt{E}$ axes. (Fig. 5.21) At high temperatures, the plot clearly shows linear relation, indicating the transport mechanism is Poole-Frenkel hopping. On the other hand, the I-V curves at low temperatures starts to deviate from the linear relation below 50K, reflecting that otherwise transport mechanism is dominant at low temperatures.

To determine the dependence on electric field, we plotted the same output characteristics with different axes. (Fig. 5.22) Under modest field, $1/E$ and $1/E^{1/2}$ plot doesn’t show clear difference. However, under high field region, the I-V curves starts to deviate from the linear relation in $1/E^{1/2}$ plot, whereas linear relation is preserved even under high field in $1/E$ plot. Therefore we can exclude the transport mechanisms resulting in $1/E^{1/2}$ dependence of conductivity, such as field-assisted hopping [81], multiple tunneling (MUST) [79] and Efros-Shklovski VRH [82].
Figure 5.19: Output characteristics for low temperatures.

<table>
<thead>
<tr>
<th>Poole-Frenkel hopping</th>
<th>Equations</th>
<th>Relations</th>
<th>References</th>
</tr>
</thead>
</table>
| $\sigma \propto \exp \left(-\sqrt{\frac{E}{E_0}}\right)$ | $\sigma \propto \exp \left[-\frac{E}{E_0}^{1/2}\right]$ | $T$-dependent | Worne, APL (2010)  

| Field-assisted hopping | $\sigma = \sigma_0 \exp \left[-\frac{E}{E_0}^{1/2}\right]$ | $T$-dependent | Bourgie, APL (2011)  
Prigodin, PRL (2007) |

| Multistep tunneling | $\sigma \propto \exp \left[-\frac{E}{E_0}^{1/2}\right]$ | $T$-dependent | Worne, APL (2010) |

| Efros-Shklovskii VRH | $\sigma \propto \exp \left[-\frac{E}{E_0}^{1/2}\right]$ | $T$-dependent | Dhoot, PRL (2006)  

| Field emission | $\ln \left(\frac{T}{\mu}\right) \propto 4d\sqrt{2m\phi}^{3/2} \frac{1}{T}$ | $T$-dependent | Rahimi, JAP (2011)  
Beebe, PRL (2006) |

| Direct tunneling | $\ln \left(\frac{T}{\mu}\right) \propto \ln \left(\frac{1}{\mu} \right) - \frac{2d\sqrt{2m\phi}}{k}$ | $T$-dependent | Beebe, PRL (2006) |

Figure 5.20: Field-induced transport mechanisms at low temperatures.
Figure 5.21: Poole-frenkel plot for I-V curves at various temperatures

Figure 5.22: Comparison between 1/E dependence and $1/E^{1/2}$ dependence
5.4.4 Field emission

The last transport mechanism with $1/E$ dependence is the field emission [78]. As described with PTmSe in the previous section, the best way to check whether the transport mechanism is following field emission or not is to construct the Fowler-Nordheim plot ($\ln(1/V^2)$ vs. $1/V$). In Fig. 5.23, the output characteristic curves are reconstructed in the Fowler-Nordheim plot. Each curve is obtained from different gate biases. At higher temperatures, only the log dependence between $\ln(1/V^2)$ and $1/V$ is shown, indicating the thermally assisted hopping is dominant. Note that thermally assisted hopping always accompanies the separation between the curves obtained with different gate bias at low field region. At lower temperatures, on the other hand, there can be seen a transition between log dependence to linear dependence. As we derived the $\ln(I/V^2)-1/V$ relation in the previous section, this transition indicated the transition between two different transport mechanisms; the log dependence at lower bias is due to the direct tunneling whereas the linear dependence at higher bias is due to the field emission. Note that field emission only takes place when sufficiently high electric field and gate bias are applied. At the intermediate temperatures, as temperature decreases, the hopping gradually vanishes and tunneling mechanisms slowly appears and becomes dominant.

There are two physically meaningful parameters we can obtain from the Fowler-Nordheim plot; the transition voltage ($V_T$) and the slope of the linear relation. The former is the drain-source bias when the field emission starts to appear. Here, let’s remind that the field emission is the transport mechanism for the triangular barrier. This triangular barrier is made by the electric field across the common rectangular barrier. As the electric field increases, the rectangular barrier starts to transformed into trapezoidal shape. Under a certain amount of bias, the barrier turns into perfect triangular shape. This bias when the triangular shape appears is the same bias when the field emission starts, which is the transition voltage. Thus, the transition voltage automatically indicates the barrier height. (Fig. 5.23: Fowler-Nordheim plot for I-V curves at various temperatures.)

![Fowler-Nordheim plot for I-V curves at various temperatures.](image)
Figure 5.24: Transition voltage and slope at 10K

Figure 5.25: Transition voltage is the voltage that separates the direct tunneling and field emission regime.

\[ V_{\text{trans}} = \text{barrier height} \]

i) \( V_{\text{ds}} = 0 \)

Direct tunneling is dominant.

ii) \( V_{\text{ds}} = V_{\text{trans}} \)

Field emission starts.

iii) \( V_{\text{ds}} > V_{\text{trans}} \)

Field emission is dominant.
5.25) The latter is also related to the unreduced barrier height. From the field emission equation, if the effective mass of charge carrier and the barrier width is given, we can readily calculate the barrier height.

As gate voltage increases, the transition voltage tends to decrease. The transition voltages as a function of gate voltage in devices with various gap-sizes are described in Fig. 5.26. This behavior is well delineated in Fig. 5.27 As gate voltage increases, the charge concentration in the channel increases. Thus, the effective barrier also decreases. Consequently, the transition voltage, which is the necessary bias to change the shape of the barrier, decreases. Note that this whole field emission picture is consistent with the data.

Moreover, we compared the I-V curves in the Fowler-Nordheim plot with gate voltage fixed at -120 V at various temperatures. (Fig. 5.28) Each colored curve is obtained at a different temperature. The transition voltage decreases as temperature increases, and the slope decreases as temperature increases as well. This indicate the temperature increase leads to the lowering the effective barrier height. The temperature dependence of transition voltage and the slope is very similar, reflecting both parameters are closely related, as argued above. Note that above 25 K, the low field data start to deviate from the low temperature data. This means thermal effect starts to play a role. Therefore, we only choose the data obtained at the temperatures below 25 K.

When the transition voltages and the slope is expressed as a function of temperature, we can see the clear linear fits for both data sets. (Fig. 5.29) Moreover, one can extrapolate the zero temperature value for transition voltage and the slope. The zero temperature transition voltage is calculated to be around 40V. From the slope extrapolation, we can also derive the unreduced barrier height $\phi$ at zero
Figure 5.28: Fowler-Nordheim plot with gate voltage -120V for various temperatures.

Figure 5.29: Transition voltage and slope as a function of temperatures.
Assume identical domains/boundaries between electrodes.

\[
\begin{align*}
\text{d1: boundary size} \\
\text{d2: domain size} \\
L: \text{channel length} \\
N: \# \text{ of domains}
\end{align*}
\]

Figure 5.30: AFM image of slow-cooled PBTTT thin film (left) and the schematic description for the microstructure in PBTTT thin films (right).

Figure 5.31: PBTTT film cast on OTS-treated SiO\textsubscript{2} and subsequently delaminated (left) The edge region of the same film (right) depicts the nanostructured nature of the film. To enhance contrast the images are approximately 500 nm out of focus. A focal series was recorded to rule out imaging artifacts.

temperature, which is 64 meV. Here, we assumed the effective mass of the charge carrier is same as \(m_e\). Note that, as mentioned above, if the system consists of a single barrier, then this two barrier height should be equal. However, the real values here shows discrepancy of three orders of magnitude. In our system, a more practical model to remove this discrepancy is necessary.

Fig. 5.30 (left) shows the AFM images for the PBTTT thin film structure. The PBTTT thin film is composed of large size domains (around sub-micrometer) and domain boundaries. The domains are composed of aligned small grain flakes, which were confirmed with the TEM images, as shown in Fig. 5.31 [46]. The charge transport direction in field-effect transistor is parallel to the substrate, so that charge departed from one electrode need to propagate through many domains to reach the another electrode. According to Street et al. [84], at sufficiently low temperatures, due to the lack of thermal assistance, one-dimensional percolation along the low-angle domain boundaries is dominant. (Fig. 5.32) Therefore, the bottleneck for the charge transport would be the domain boundaries along the one-dimensional path. (Fig. 5.30 (right)) Assuming the same barrier height and width with \(\phi\) and \(d_1\), respectively, and equidistance \(d_2\) between adjacent domain boundaries, we could get new relations between the single barrier height (obtained from the slope in the Fowler-Nordheim plot) and the total barrier height (obtained from the transition voltage).

When there applied the bias \(V\) between the electrodes, one single barrier feels the reduced bias, which would be \(V/N\). Then the transition voltage can be defined as \(N\phi\), where \(N = \frac{L}{d_1 + d_2}\) is the number of grain boundary barriers between two electrodes.
Figure 5.32: Schematic illustration of the proposed transport path along preferential directions with low-angle grain boundaries, forming a high-mobility percolation path.

Table 5.1: Barrier heights and domain sizes.

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Channel length L (µm)</th>
<th>Single barrier height φ (eV)</th>
<th>Domain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>slow</td>
<td>20</td>
<td>1.727</td>
<td>1.17</td>
</tr>
<tr>
<td>slow</td>
<td>30</td>
<td>1.467</td>
<td>1.101</td>
</tr>
<tr>
<td>slow</td>
<td>40</td>
<td>0.944</td>
<td>0.55</td>
</tr>
<tr>
<td>quench</td>
<td>30</td>
<td>1.19</td>
<td>0.46</td>
</tr>
<tr>
<td>quench</td>
<td>40</td>
<td>0.587</td>
<td>0.238</td>
</tr>
</tbody>
</table>

\[ V_{\text{trans}|T\to0} = N\phi = \left( \frac{L}{d_1 + d_2} \right)\phi \quad (5.8) \]

\[ \phi = \left( \frac{d_1 + d_2}{L} \right)V_{\text{trans}|T\to0} \quad (5.9) \]

From the field emission equation (Eq. 5.5), when we focus on a single barrier, we can replace \( d \) with \( d_1 \) and \( V \) with \( V/N \). Now the new slope can be expressed as below.

\[(\text{slope}) = \frac{4L\sqrt{2m_e\phi^3}}{3hq} \cdot \frac{d_1}{d_1 + d_2} \]

\[ \phi = \left[ \frac{3hq}{4L\sqrt{2m_e\phi^3}} \cdot \frac{d_1 + d_2}{d_1} (\text{slope}) \right]^{2/3} \quad (5.11) \]

There are three variables \( (d_1, d_2, \phi) \) and two equations (Eq. 5.9, Eq. 5.11). However, we can estimate one variable and check the other values are reasonable. The TEM studies on PBT TT thin films shows the domain is composed of small grain flakes with size of around 10 nm. (Fig. 5.30) Since the small grain flakes are the building blocks for the large domains, the grain misalignment would be a source of the domain boundaries. Therefore, we can fix the \( d_1 \) to be 10 nm. Now that we have two
variables and two equations, we can calculate the variables. The values are calculated and shown in the Table 5.1. In slow-cooled PBTTT thin films, the domain size is known to be sub-micrometer from the AFM images. The domain size and the barrier height is reasonable in spatial and energetic sense, respectively. Note that even though the transition voltage and the slope from different gap samples show no significant tendency, the resulting domain size and the single barrier height are in similar ranges, guaranteeing that the model is suitable to be applied. For quench cooled samples, the domain size decreases by more than half. This result is consistent with the AFM images, where the domain size is much smaller in the quench-cooled thin film. Since gate voltage was set to be -120 V, the domain sizes might be overestimated.
Chapter 6. Conclusion

In this thesis, we describe the low-temperature transport characteristics for high mobility polymers. Amorphous dithienylcyclopentadienone-carbazole copolymer, thiophene-based polymer, and selenium-based polymer were investigated. Well-functioning thin-film transistors with high mobility (> $10^2$ cm$^2$V$^{-1}$s$^{-1}$) were prepared for low temperature experiments.

From the systematic low temperature measurements, we tried to explain the origin of the high mobility for each system. In the amorphous polymer system, the resulting high mobility at room temperature was originated from the relatively low activation energy and low characteristic temperature, reflecting that the localization of the charge carrier is not substantial in the film. Moreover, the ordering of the highly ordered polymer films was controlled by various cooling rates after thermal annealing. Not only the domain size but also the connectivity and the 3D ordering between the domains are important for high mobility. The activation energy obtained from the temperature dependent transport measurement showed that the charge transport obstruction tends to reduce as the cooling rate reaches the critical value. The smaller activation energy observed in the sufficiently slow cooled sample is attributed to the improved microstructure of the thin film.

We have focused on the lower temperature transport behavior in the highly ordered polymer thin films. At low temperatures, temperature dependence of transport become much weaker than that at high temperatures. At the same time, the I-V characteristics evolves from typical saturation curves to nonlinear curves. To determine the precise transport mechanism responsible to this phenomena, we systematically excluded all the other candidates for transport mechanism. Finally, Fowler-Nordheim plot clearly shows a linear dependence, meaning that the field emission is dominant at low temperatures under high electric field and with high charge-carrier concentration. The detailed discussion showed probable microstructural origin for field emission and the calculated parameters are reasonable both energetically and spatially. This field emission process is thought to be following the one-dimensional path formed by the percolation in polymer networks. These series of results might provide the answer for the recent fundamental debate on the charge transport in the semiconducting polymers: “Is the transport one-dimensional or two-dimensional?”

![Figure 6.1: Schematic states of my works in the frame of temperature and electric field.](image-url)
In conclusion, we could construct the transport mechanism map with temperature and electric field axes. (Fig. 6.1) For high temperature and low field, the transport was well described by thermally assisted hopping with the mobility edge model. For high temperature and high field, Poole-Frenkel hopping is dominant. At low temperatures, field emission and direct tunneling become the main transport mechanisms. The transition is depending on the barrier height of the disordered domain boundaries.
Summary

LOW TEMPERATURE TRANSPORT IN SEMICONDUCTING POLYMER THIN FILMS

1977년, 헤거(Heeger), 매퍼미드(MacDiarmid), 사라카와(Shirakawa)에 의해 폴라스틱에서도 전기가 흐를 수 있다는 것이 보고되면서 전도성 고분자의 시대가 시작되었다. 전기가 통할 수 있다는 전기적인 장점과, 구부릴 수 있고 대량생산이 가능한 폴라스틱의 물질적인 장점이 공존하는 전도성 고분자의 특성 덕분에 그 응용가능성이 나날이 증가하고 있다. 전도성 고분자를 이용한 향후 미래 장치들은 접계나, 흐름 방향으로 작동하게 될 것이고, 이런 특징은 스마트폰, 태블릿, e-book 등의 휴대용 장치(portable device)에의 전달이라는 새로운 시대를 열 것이다. 또한 대면적을 프린트 하듯이 대량생산 할 수 있다는 장점은 디스플레이 산업에서는 사용시 퍼져 나올 수 있는 대화면, 에너지 산업에서는 대면적 대량 전지나 대용량 배터리를 통한 비용으로 구현해 볼 것이다. 그 밖에도 각종 화변, 센서, 논리 회로 등을 접에서 A4용지에 프린팅 해서 쓰는 시대를 현실화 시킬 것이다. 그러나 무궁무진한 응용가능성을 가지고 여러가지 장치들에 적용되는 현재 동향에 비해, 실제 전도성 고분자 내에서 일어나는 전하 이동(transport)이 어떤 방식으로 되는지를 위해서는 아직도 많은 연구가 가치있다. 본 연구는 물리학자들의 시각에서 전기 실험을 통해 전도성 고분자 박막(film, 필름) 내에서 일어나는 전하 이동 메커니즘을 규명하고자 하는 큰 투자를 가하고 수행되었다.

첫번째 실험은 비결정성(amorphous) 고분자가 가지는 높은 전하 이동도(mobility)에 주목하였다. 일반적으로 비결정성 고분자들은 결정성(crystalline) 고분자에 비해서 높은 무질서(disorder)을 가지고, 따라서 전하 이동도 또한 높다고 알려져 있다. 하지만 이 실험에서 사용한 고분자인 DTCPD-alt-CB의 경우 비결정성 고분자임에도 불구하고 높은 전하 이동도를 갖는 것을 보였다. 저자 실험 결과를 통해 이 고분자의 전하 이동 메커니즘을 규명하고 비슷한 다른 고분자들에 비교해본 결과, 비결정성이면서도 무질서가 적고 전하이동에 방해되는 장벽(barrier) 또한 낮은 것을 알 수 있었다. 이런 점은 기존에 학계에서 당연하다고 생각해온관 비결정성=무질서라는 관계가 형상 성립되지 않음을 보여주는 반례라는 점에서 그 가치를 매길 수 있다.

두번째 실험에서는 결정성 고분자를 이용해 박막 내부의 미세구조(microstructure)를 입으로 바꾸고 그것이 전하 이동에 어떤 영향을 미치는지 알아보았다. 미세구조가 전하 이동 사이에는 큰 상관관계가 있다고 믿어지지만 그것을 직접적으로 확인하기에는 고분자 박막의 미세구조를 통제하는 것이 쉽지 않았다. 이 실험에서는 고분자 박막을 가열 후 냉각하는 과정에서 박막 속도를 조절하여 미세구조를 원하는대로 통제할 수 있었다. 실제로 냉각속도가 늦어질수록 박막 내부의 결정성 영역 (domain)이 더욱 커지는 것을 확인할 수 있었다. 나아가 2차원 엑스-레이 회절(2D XRD)실험을 통해 결정성 영역의 크기를 알아내었다. 이런 미세구조의 차이가 실제로 전하 이동에 영향을 미치는지를 확인하기 위해 저자 실험을 수행했고, 미세구조가 서로 잘 연결될수록 전하 이동에 방해되는 장벽 또한 낮아질 것을 확인하였다. 미세구조를 능동적으로 통제할 수 있었고, 그 결과 미세 구조와 전하 이동 사이의 직접적인 관계를 규명하였다는데 그 의미가 있다.

세번째 실험은 이와 실험보다 더욱 넓은 온도 범위에서, 전기장(electric field)과 전하 밀도(charge carrier concentration)를 바꾸기면서 전하 이동 메커니즘을 규명하는 실험을 수행하였다. 그 결과 극저온에서 높은 전기장과 전하밀도에서는, 기존 트랜지스터 구조에서는 아직 세대로 설명된 적 없는 전기장 방출(field emission)이라는 메커니즘을 따라 전하가 이동하는 것을 관찰하였다. 최근 고분자 박막 내에서 일어날 수 있는 전하 이동이 1차원적인 2차원적인지에 대한 근본적인 논쟁이 계속되고
있는데, 특히 1차원적인 전하 이동을 주장하는 쪽에서는 아직 이를 잊기 쉽게 전하 이동 메커니즘이 명확히 제시되지 않았다. 이 실험 결과로, 높은 전기장과 전하밀도에서는 침투 모델(percolation model)에 의해 형성된 1차원 길이 따른 전기장 방출이 그 메커니즘이 될 수 있다는 것을 보였다.

학위를 받는 동안 수행했던 전하 이동 메커니즘 규명 작업을 요약하면 그림 7과 같이 나타낼 수 있다. 상대적으로 높은 온도에서는 온도에 의해 영향을 많이 받는 메커니즘으로 전하 이동을 설명할 수 있다. 전기장의 세기에 따라 낮은 전기장에서는 모빌리티-엣지 모델(1) mobility edge model, 높은 전기장에서는 풀-프렌켈 모델(2) Poole-Frenkel model이 각각 지배적인 전하 이동 메커니즘을 보였 다. 반면에 더 낮은 온도로 내려가면 온도에 의한 영향이 매우 약한 메커니즘이 더 우세해진다. 즉, 낮은 전기장에서는 직접 터널링(3) direct tunneling, 높은 전기장에서는 전기장 방출(4) field emission 이 각각 지배적인 전하 이동 메커니즘으로 바뀌는 것을 확인하였다.

![그림 7. 온도와 전기장에 따른 전하 이동 메커니즘 연구 결과를 요약한 도식도](image-url)

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References


