Mobility Improvement of P3HT Thin Film by High-Voltage Electrostatic Field-Assisted Crystallization

Soon-Won Lee, Chul-Hyun Kim, Sang-Geul Lee, Jun-Ho Jeong, Jun-Hyuk Choi, and Eung-Sug Lee

1Department of Nanomechanical System, Korea Institute of Machinery & Materials, Daejeon, Korea
2Korea Basic Science Institute, Daegu Center, Daegu 702-701, Korea

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High-temperature annealing, assisted by the in-plane application of a high-voltage electric field, was used to form thin films of poly(3-hexylthiophene) (P3HT), boasting increased crystallite size and enhanced charge mobility. In-plane crystallite growth and surface morphology were characterized by atomic force microscopy. X-ray diffraction analyses showed that the application of an electric field decreased film thickness and increased the dimensions of the crystalline domains by 25.6% during subsequent high-temperature annealing. Crystalline domains were 13.4% larger, and exhibited 70% higher mobility, than those obtained with thermal annealing in the absence of an electric field.

Keywords: hole mobility, P3HT, electric field-induced crystallization, molecular chain orientation

1. INTRODUCTION

Regioregular poly(3-hexylthiophene) (rr-P3HT) is characterized by the coexistence of highly ordered crystalline regions and disordered amorphous regions in such a way that densely packed lamellar planes are linked through self-organized, inter-chain \( \pi-\pi \) stacking. Inter-chain networking in the conjugated lamellar regions results in relatively high level mobilities of 0.01 - 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\). It has also been used as an electron-donor layer in organic solar cells. In order to facilitate progress toward the commercial use of both organic FETs (OFETs) and organic solar cells, increasing the mobility yet further has been a long-standing goal in the field of organic electronics. Several previous studies have shown that the mobility of organic electronic materials, including P3HT, depends on several factors, including molecular weight, length and functionality of the side chains, film morphology associated with the degree of regioregularity and crystallinity, and the conformation and alignment of the molecular chains, all of which are in turn affected by various conditions associated with material synthesis and film processing.

Since charge transport occurs mainly along the polymer chains, longer molecular chains with nanowire-like morphologies tend to generate high mobility. Such structures have been achieved by slowing the rate of solvent evaporation and optimization of annealing conditions. Meanwhile, increasing annealing and crystallization times affects inter-chain distances as well as the orientation and conformation of the chains themselves, resulting in improved mobility. Higher degrees of crystallinity with chains stacking parallel to the substrate result from extended annealing, leading to a straight-chain conformation with extended \( \pi \)-conjugation and increased packing efficiency. Chain conformation can be modified by controlling the annealing temperature or the molecular regioregularity using a self-assembled monolayer (SAM) to drive molecular ordering and by applying a high-voltage electric field.

The majority of research toward increasing the mobility of conducting polymer films has focused on material synthesis or device design, while a few studies have attempted to modify the annealing process itself. The latter method is preferred since it is inexpensive and does not require complex transistor designs.

This study presents an advanced film deposition method (which can irreversibly enhance the field-effect mobility in P3HT films by restructuring their molecular formation with the application of a high-voltage electric field. An electric field applied across spin-coated P3HT in its wet state resulted in low levels of crystallization even at room temperature; it promoted further crystallization during thermal annealing. The operating field in OFETs is widely recognized to significantly affect charge mobility through its interaction with molecular dipole moments and correlated effects with the randomly distributed dipole energies of nearby sites. The long-term operational effects of an applied electric field...
on mobility were recently investigated with respect to the chain structure of pentacene and rr-P3HT\cite{29,30}. Those studies implied that the application of an electric field can have a crucial impact on mobility in organic electronic materials. This study is the first to apply an electric field during in situ film formation as a means of obtaining permanent enhancement in charge mobility.

2. EXPERIMENTAL PROCEDURE

The illustration given in the middle of Fig. 1 shows the self-alignment of polymer chains by a torsional moment induced by the external electric field. In the primary process, denoted ‘HVHT’ (high voltage, high temperature), a high-voltage electric field was applied to a spin-coated P3HT film across an open space while film was drying at room temperature. This was followed by an optimized thermal annealing process to complete crystallization. Figure 1 also shows three other process conditions that were included as comparative references; these are referred to as the ‘RT’ (room temperature), the ‘HT’ method, and the ‘HV’ method.

For mobility measurements and analyses of P3HT films, staggered-gate FETs were designed and fabricated on highly doped silicon substrates. The P3HT films were spin-coated onto an oxide layer, followed by the deposition of gold source and drain contacts by sputtering. As-purchased rr-P3HT (Nieke Metal, Inc.) was first dissolved in dichlorobenzene and diluted to a concentration of 3 wt. % after magnetic stirring at 20°C for 48 h. The mixture was then filtered through a 0.2-\(\mu\)m microporous filter using a manual syringe. The highly doped Si substrate was used as the gate electrode, onto which a 300-nm-thick SiO\(_2\) layer was thermally grown. After the substrate was cleaned in a Piranha solution (H\(_2\)SO\(_4\) : H\(_2\)O\(_2\) = 3 : 1) and deionized water, dried in a vacuum oven at 120°C, and exposed to an oxygen plasma, the 80-nm-thick P3HT film was spun-coated onto the substrate at 1000 rpm for 30 s. Each coated substrate was then cured in accordance with one of the four processes outlined in Fig. 1.

An electric field from 1 to 3 kV/cm was applied for 10 minutes during room-temperature solvent drying in an argon-filled enclosure. No further changes were observed when the field was applied for longer than 10 minutes, presumably because the viscosity of the P3HT solution increased during drying, thereby preventing further reconfiguration of the molecular chains.

A 5-nm-thick Ti adhesion layer and source-drain gold electrodes were deposited onto the P3HT film using an electron-beam evaporator (KVET-C500200, Korea Vacuum, Inc.). The electrodes were designed to have a length of 100 nm, a width of 400 \(\mu\)m, and a channel length of 40 \(\mu\)m. The electrical properties of the samples were measured at various gate voltages using a high-speed source monitor unit (E5264A, Agilent Technologies). X-ray diffraction (XRD) analyses were performed using a high-resolution x-ray diffractometer (HR-XRD, Philips X’pert Pro MRD) with Cu K\(_\alpha\) radiation (\(\lambda = 0.15406\) nm).

3. RESULTS AND DISCUSSION

Figure 2(a) shows the source-drain current, \(I_{DS}\), as a function of the source-drain voltage, \(V_{DS}\), at various gate biases, \(V_{GS}\), for the sample HV (shown in Fig. 1). Figure 2(b) shows the relationship between \(I_{DS}\) and \(V_{GS}\) for all process conditions measured at \(V_{DS} = -80\) V. The field-effect mobility, \(\mu\), was calculated from

\[
I_{DS} = \frac{WC_i\mu(V_{GS} - V_{TH})^2}{2L} \tag{1}
\]

where \(W\) is the channel width, \(C_i\) is the gate capacitance, and \(L\) is the channel length. As summarized in the electrical

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Fig. 1. The effects of applying a high-voltage electric field prior to crystallization are illustrated, showing the realignment of molecular chains. Four different process routes were evaluated.