

Origins of Anisotropic Hole Mobility in a Disordered Conjugated Polymer

Hole mobility in spin coated films of poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV) has been found to be highly anisotropic with measured mobilities parallel to the substrate being up to four orders of magnitude larger than measured perpendicular to the substrate. Previously this has been thought to be solely as result of a strong dependence of the mobility on charge carrier density. Through the use of grazing incidence wide angle X-ray scattering and X-ray reflection measurements, we show that this anisotropy structural in origin, being primarily due to an interfacial layer of several nanometers at the film-substrate interface formed during spin-coating. This layer has a higher electron density than the bulk facilitating hole transport.

Flexible plastic devices such as cell phone displays and smart tags comprised of thin film light emitting diodes (LEDs) or field effect transistors (FETs) as well as photovoltaics based on amorphous conjugated polymers promise low-cost fabrication and low energy consumption due to solution processing. While carrier type and mobility (μ) are key parameters in describing such semiconducting materials, these quantities are not necessarily directionally independent in devices based on thin films. Indeed, charge transport anisotropy in crystalline and liquid-crystalline semiconductors is a well established phenomenon. In this work we investigated a more glassy polymer. In particular we investigated thin films of low polydispersity, high molecular weight polymers of poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV), a derivative of the well studied polymer poly(phenylenevinylene) (PPV).

Charge mobility perpendicular to the substrate was measured using the transient electroluminescence (TrEL) technique for the spin-coated films and the time-of-flight (TOF) technique for drop cast films while mobility parallel to the substrate was measured using the bottom contact FET geometry. [Figure 1](#) summarizes our mobility measurements as a function of electric field for all devices. While for the drop cast film, mobility was relatively anisotropic, the mobilities reported for the spin cast films was highly anisotropic -- the degree of anisotropy being solvent dependent. The solvent dependence suggests that this effect is structural rather than a charge density effect. (If the higher mobilities observed in the FET configuration relative to the diode configuration in spin-coated films was primarily a charge carrier effect, one would expect that the anisotropy factor would be similar for the two spin-coated films. One would also expect that the solvent which gives the highest mobility in one configuration would also give the highest mobility in the other configuration, in contrast to the observed experimental data.) The isotropic charge transport in drop-cast films indicates the morphological

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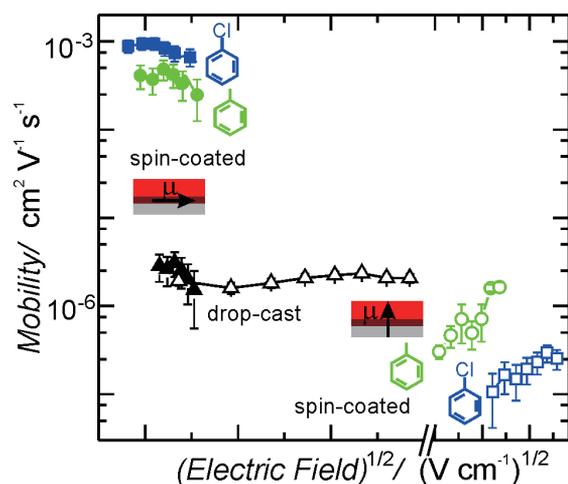


Fig. 1: Summary of the field dependent hole mobilities measured in FET and diode configurations plotted as a function of the square of the electric field for the three films. Films spin coated from toluene (chlorobenzene) are shown in green (blue) while films drop cast from chlorobenzene are shown in black.

anisotropy responsible for this phenomena is weak or absent in drop cast films (i.e. spin speed = 0) suggesting that this anisotropy is induced by the spin-coating process.

Initial characterization using optical techniques (standard far field techniques, confocal microscopy and near-field optical microscopy) revealed that the films were uniform on all optical scales and that the photoluminescence (PL) and absorption properties of the spin-coated films were identical. While the optical properties of the drop cast film indicated the existence of aggregates within the film, the signature of aggregation was absent in all spin coated films. Aggregation was thus ruled out as a possible cause for the transport anisotropy. Atomic Force Measurements indicating that the films were flat (sub nm surface roughness) support this conclusion.

The structure of the three films were next investigated using X-ray techniques. **Figure 2** displays a grazing incidence wide angle X-ray scattering (GI-WAXS) pattern of spin-coated MEH-PPV film prepared from chlorobenzene. The meridional reflection (perpendicular to the substrate) at scattering vector $Q = 15.2 \text{ nm}^{-1}$ suggests a vertical inter-backbone packing with a d-spacing of 0.41 nm, while the backbone chains remain parallel to the substrate. The width of this broad peak ($\Delta Q \sim 4 \text{ nm}^{-1}$) corresponds to an average domain size of 1.4 nm, as derived by the Scherrer formula, and taking into account a resolution of 0.4 nm^{-1} .

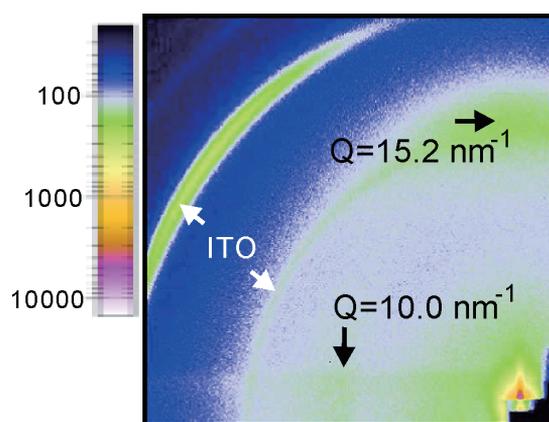


Fig. 2: GI-WAXS pattern of chlorobenzene spin-coated film. All films exhibited a similar pattern.

This suggests that the backbone order extends only over about three lattice constants confirming that the polymer film is essentially amorphous. The weaker equatorial reflection (parallel to the substrate) at scattering vector $Q = 10.0 \text{ nm}^{-1}$ (corresponding to a d-spacing of 0.63 nm) stems from the backbone repeat units of MEH-PPV. The strong arc in the upper-left corner and an adjacent weak scattering ring are due to the ITO substrate layer. The fact that all three films exhibited similar structure, suggests that, although this bulk alignment may play a role in the charge anisotropy, it is likely not the dominate factor.

Figure 3 presents the X-ray reflectivity (XRR) data for the three films cast on the HMDS coated oxide layer of a silicon wafer. The XRR of the spin-coated films are characterized by high frequency fringes modulated by a lower frequency oscillation. The high frequency Kiessig fringes ($\Delta Q'$) reflect the film thickness ($\sim 88 \text{ nm}$ for chlorobenzene, $\sim 90 \text{ nm}$ for toluene). Their extended observability indicates the films are flat and of low roughness. The low frequency modulation (ΔQ) points to an additional structure within the spin-coated films having a thickness of $\sim 5 \text{ nm}$. In comparison, the reflectivity profile of the drop-cast film is smooth and structureless. Kiessig fringes were not resolved due to the large film thickness ($\sim 3400 \text{ nm}$).

For this low frequency modulation there are several possible explanations: alternating layers of high and low electron density, a layer of higher electron density at the film-substrate interface or a layer of higher or lower electron density at the film-air interface. Each of the above density profiles were used as input into Parratt32

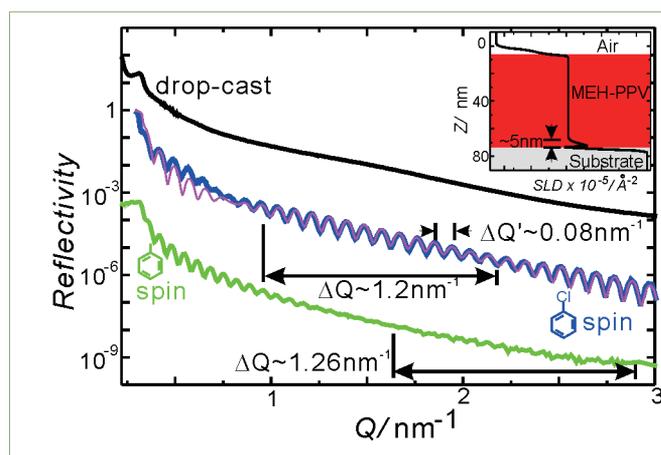


Fig. 3: X-ray reflectivity of the three (free standing) films along with the calculated pattern based on the two layer scattering length density (SLD) profile shown in the inset. $\Delta Q'$ indicates the period of Kiessig fringes and ΔQ their modulation period. (inset) Calculated SLD profile through the film spin coated from chlorobenzene.

XRR simulation software.(see reference). Attempts to fit with alternating layers of high and low density reproduced the modulation, but either predicted the existence of Bragg peaks which were not observed experimentally or required the use of unrealistic values of the electron density. Assuming a thin layer at the film-air interface reproduced the fast thickness oscillations of the reflectivity curve, however, it was not possible to reproduce the low frequency modulation. The best fit was obtained by dividing the 88 nm film into an 83 nm layer with the MEH-PPV bulk density on top of a ~ 5 nm layer of 10% higher density at the film-substrate interface (Fig. 3 magenta line). The inset shows the variation in electron density across the film based on the Parratt32 simulation results. The above results indicate that a thin high electron density layer (~ 5 nm thick) seems to form at the interface between the thin film and the substrate. As can be seen from Fig. 3 the strength of this effect is both solvent and processing dependent (i.e. absent in the drop cast films).

We thus conclude that the origin of the observed charge transport anisotropy in aggregate free, films of the glassy polymer MEH-PPV is a solvent dependent formation of a thin (~ 5 nm) high electron density layer on at the substrate film interface. This finding has crucial implications on the device level as it suggests that by controlling microstructure, mobility in a diode or solar cell geometry could be increased by over 3 orders of magnitude in a nominally amorphous system. For example, in solar cells the rather low hole mobility of the polymer phase as compared to the electron mobility of the fullerene limits both device thickness and energy extraction.

Experimental Station

XRR 8-circle diffractometer

Publications

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