Charge Transport Anisotropy Due to Grain Boundaries in Directionally Crystallized Thin Films of Regio-Regular Poly(3-hexylthiophene)

Semicrystalline polymers, such as polythiophenes, hold much promise as active layers in printable electronic devices such as photovoltaic cells, sensors, and thin film transistors. As organic semiconductors approach commercialization, there is a need to better understand the relationship between charge transport and microstructure, in particular, to identify the inherent bottlenecks to charge transport. In semicrystalline and polycrystalline materials, charge transport is most likely dominated by grain-boundary effects, although the exact mechanism is not well understood. Unfortunately, grain boundaries in semicrystalline thin films are difficult to characterize: the grains are too small to allow for measurements across individual grain boundaries (as is often done for polycrystalline films of small molecules) and bulk measurements are complicated by the unknown orientation of polymer chains within the grain. To better understand the effect of chain orientation on grain boundaries, we use anisotropic thin films of poly(3-hexylthiophene) (P3HT) - one of the most well-studied polymeric semiconductors, as a tool to study charge transport.

We characterized the film microstructure and made thin film transistors with the anisotropic film as the active layer. This allowed us to quantitatively extract the effect of different grain boundary structures on charge transport and showed for certain low-angle grain boundaries, charge transport is due to bridging polymer molecules. Our study shows that optimization of the microstructure in semicrystalline electronic devices should include efforts to control grain boundary structure and orientation.

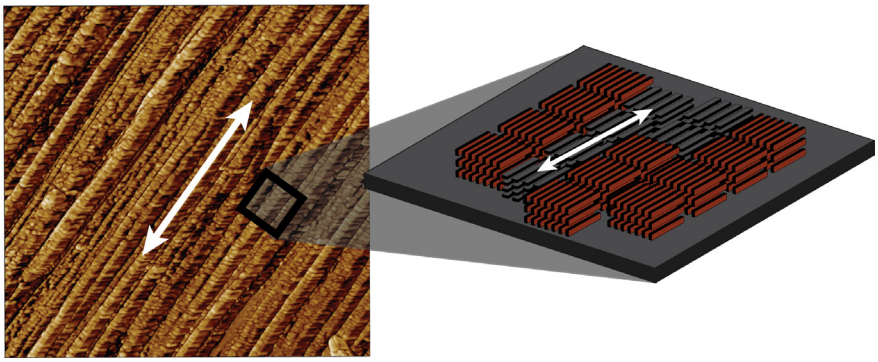

Figure 1: Phase mode AFM image of directionally crystallized P3HT, revealing the unique grain structure. The white arrow indicates the direction of the fiber axis and polymer chain axis. The scan is 4 by 4 μm. (Left) The cartoon shows a possible orientation of crystallites within the directionally crystallized film, as derived from XRD. Red crystallites are "edge-on" with their pi-pi stacking repeat in the plane of the substrate. Grey crystallites are termed "face-on," with their pi-pi stacking repeat out of the plane of the substrate. In this cartoon of the grains, the longest axis is long the polymer chain backbone (001), the next longest along the alkyl-stacking direction (100) and the shortest along the pi-pi stacking direction (010), see Figure 2b for reference. (Right)

Anisotropic thin films of P3HT are fabricated by a directional crystallization technique adapted from Brinkmann and Wittmann (see reference for fabrication details). The behavior of the films under polarized light suggests widespread alignment of the polymer chains, with the chain axes parallel to the fiber axis. Atomic Force microscopy reveals areas of continuous, aligned films, and suggests the presence of grains along the fibers (Figure 1, left). X-ray diffraction experiments at SSRL Beam Lines 11-3 and 7-2 were used to characterize the semicrystalline microstructure of the anisotropic films more directly. Two-dimensional grazing incidence X-ray scattering (2D GIXS) survey patterns (Figure 2a) reveal the unique texture of these P3HT films. Typical spin-cast thin

films of P3HT are highly textured out of plane, with the alkyl-stacking repeat direction lying out of the plane of the substrate and the resulting (h00) peaks appearing along the q_z axis. In the directionally crystallized films, the peak corresponding to the pi-pi stacking appears out-of-plane, along with weaker (h00) peaks (see Figure 2b for reference). The presence of both of these Bragg peaks along the q_z axis indicates that there is a distribution of crystallites present in our films, "face-on" and "edge-on," as shown in the right hand side of Figure 1. High-resolution GIXS experiments were performed at two different substrate orientations, probing repeat distances both along the fibers and across the fibers. The difference in these diffraction patterns confirms significant in-plane crystalline anisotropy. The Bragg peaks that are present in the GIXS patterns also confirm the orientation of the chain axis along the fiber axis, and two different crystallite orientations, as suggested above.

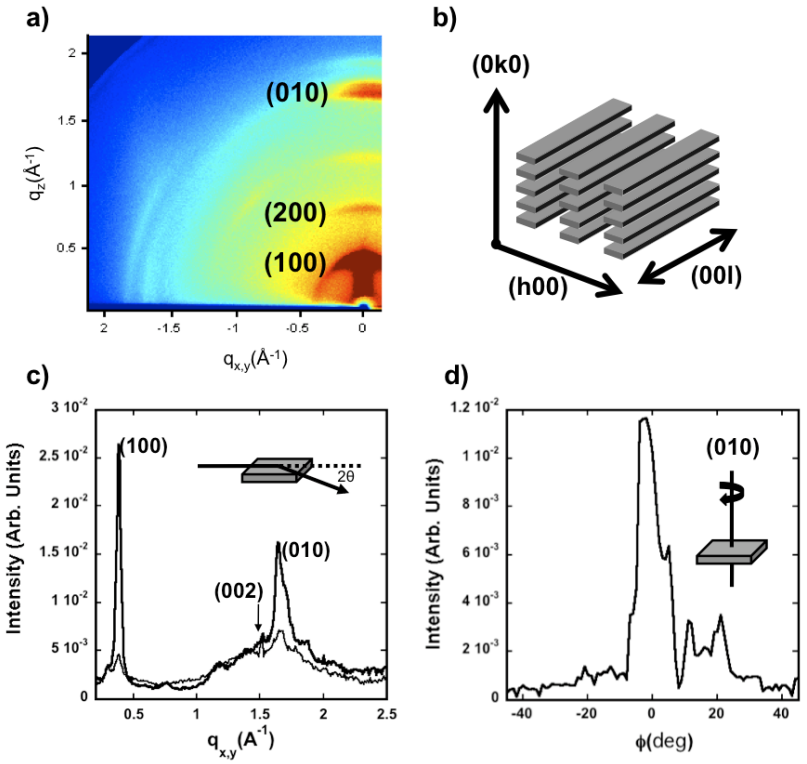

Figure 2: a) Grazing Incidence X-Ray Diffraction (GIXD) survey pattern of directionally crystallized P3HT, revealing the unique thin film texture. b) A representative crystallite of P3HT, for reference. c) High resolution grazing incidence X-ray diffraction, taken in two different sample orientations (phi). The thick black line corresponds to a scattering vector oriented across the fibers. The thin black line corresponds to a scattering vector oriented along the fibers. d) A phi scan of the (010) peak, quantifying in-plane film anisotropy.

From our diffraction experiments, we were able to develop a model of the film microstructure, shown in Figure 1, right. By collecting diffraction data from only the crystalline regions, we have obtained indirect information about the structure at the grain boundaries. It has been previously suggested that in polymeric semiconductor films, grain boundaries separating two grains with a small orientation mismatch, known as "low-angle" grain boundaries, can contain bridging polymer chains that create favorable paths for intergrain charge transport. Our films are comprised entirely of low-angle boundaries, but due to the orientation of the polymer axis, boundaries along the fibers, or "in-line" boundaries, are more likely to have bridging polymer chains than boundaries between fibers. To test the effect of these boundaries on charge transport, we made thin film transistors (TFTs) using the anisotropic film in two different orientations, one with fibers parallel to the channel length along which the current flows (parallel devices) and the other with fibers perpendicular to the channel length (perpendicular devices.) The mobility values for the two types of devices revealed a significant mobility anisotropy: parallel devices had mobilities approximately 20 times higher than perpendicular devices (Figure 3). In fine-grained materials such as the directionally crystallized films of P3HT, the effective device mobility is

dominated by the mobility in the grain boundaries. Thus, the mobility anisotropy in the semicrystalline films studied here is attributed to different microstructure at the grain boundaries. Transport across grain boundaries along the fiber, with the potential for bridging polymer chains, is easier than transport across the fibers. Additionally, similar activation energies, extracted from temperature dependent mobility measurements (Figure 3, inset), indicate that despite mobility anisotropy, charge transport in the two types of devices is governed by the same transport bottleneck. We believe that due to film imperfections, grain boundaries between fibers play a role in both types of devices, serving as the rate limiting step.

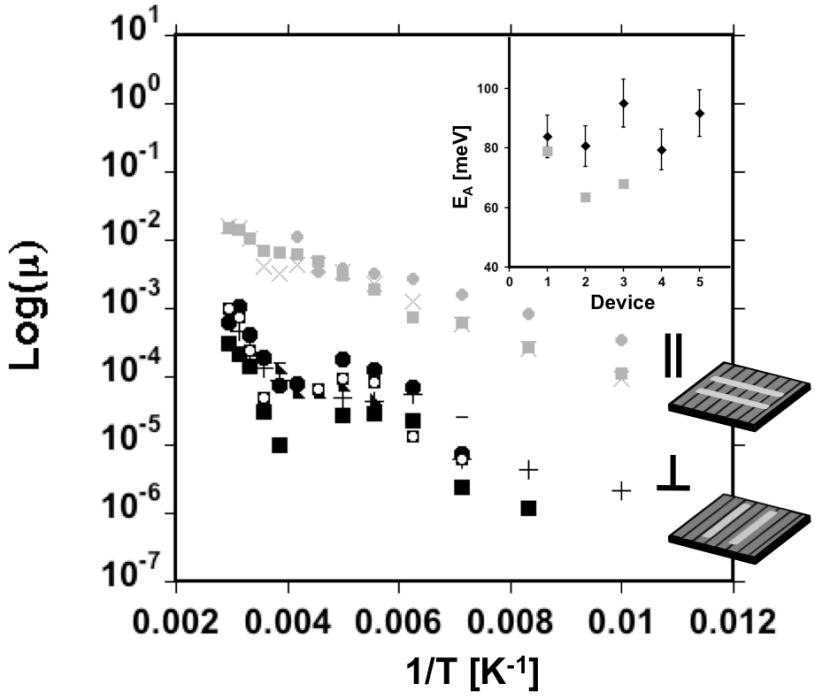

Figure 3: Temperature dependent mobilities for perpendicular (black) and parallel (grey) devices. The different symbols correspond to different devices. Inset: Activation energies extracted from the temperature dependent mobilities. Error bars for the parallel devices are smaller than the symbols.

In summary, we have created anisotropic films of P3HT via directional crystallization and used them as a tool to study the effect of grain boundary structure on charge transport. Film microstructure was largely characterized using X-ray diffraction at SSRL, and charge transport was investigated by making thin film transistors with the anisotropic films as the active layer. This work helps to solidify the hypothesis that in low-angle grain boundaries, transport is easier only in the direction parallel to the polymer backbone, due to bridging polymer molecules. Optimization of the microstructure in electronic devices should therefore not focus solely on the elimination of grain boundaries, but also include efforts to control grain boundary placement and relative grain orientation.

Further Reading

"Charge Transport Anisotropy Due to Grain Boundaries in Directionally Crystallized Thin Films of Regio-Regular Poly(3-hexylthiophene)", L.H. Jimison, M.F. Toney, I. McCulloch, M. Heeney, A. Salleo. Adv. Mater. **21**, 1568-1572 (2009).

Primary Citations

"Orientation of Regioregular Poly(3-hexylthiophene) by Directional Solidification: A Simple Method to Reveal the Semicrystalline Structure of a Conjugated Polymer" M. Brinkmann, J. Wittmann. Adv. Mater **18**, 860 (2006).

"Transport in polycrystalline polymer thin-film transistors" R. Street, J. Northrup, A. Salleo. Phys. Rev. B. **71**, 13 (2005).

SSRL is primarily supported by the DOE Offices of Basic Energy Sciences and Biological and Environmental Research, with additional support from the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and the National Institute of General Medical Sciences.