

Thin Film Morphology of Organic Electronic Materials

X. Zhang¹, S. D. Hudson¹, D. M. Delongchamp¹, and D. J. Gundlach²

National Institute of Standards and Technology, Organic Electronics and Photovoltaics Project, ¹Polymers Division and ²Semiconductor Electronics Division, Gaithersburg, MD 20899 ^a

INTRODUCTION

Organic electronic materials are desired for low cost printed circuits. As expected, the microstructure of these materials is crucial for their performance, such as charge-carrier mobility. These materials typically comprise anisotropic molecules, and the molecular packing, crystallization, texture (orientation), interfacial structure and grain boundaries all may play a role. As part of an effort to develop and use measurement methods to relate microstructure with chemical structure, processing and performance, we report here transmission electron microscopy (TEM) analyses of the crystal orientation and morphology of two high-performance organic semiconductors.

In the first instance, we use diffraction and imaging to evaluate the crystallization process, illustrating how crystal growth modes govern the orientation and device performance. In the second, we explore an image analysis method coupled with dark-field microscopy to generate nanoscale two-dimensional maps of crystal orientation and grain boundaries. The device performance in this instance does not depend on grain size; we therefore point to two other features of the semicrystalline morphology that seem to be responsible for this behavior.

EXPERIMENTAL

Two semiconductors were examined. The first was fluorinated 5,11-bis(triethylsilylethynyl) anthradithiophene,¹ diFTES ADT, which is an analog of pentacene.² The second was poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene,³ pBTTT-C₁₄. These are soluble in high-boiling-point chlorinated solvents. These materials were spun-cast onto silicon-wafer substrates with various surface treatments (native oxide, hexamethyldisilazane (HMDS), gold, or pentafluorobenzene thiol (PFBT) treated gold) and electrode patterns. To remove the solvent, the diFTES ADT films were placed in a vacuum oven at 30 °C and the pBTTT-C₁₄ films were heated to 180 °C for 10 min and then cooled at approximately 5 °C/min to room temperature. Both of these materials are p-type semiconductors, and the hole mobility was measured from electrical current-voltage characterization of bottom-contact thin-film transistors.

To prepare TEM samples of each material, a drop of poly(acrylic acid) (PAA) in aqueous solution was deposited on the film, dried at 55 °C overnight, and detached, removing the film from the substrate. After rinsing the PAA thoroughly with water, the film was mounted on a blank copper grid. The films were then examined by electron diffraction, bright-field and dark-field TEM using a Philips EM400T^b operated at 120 kV. Images and diffraction patterns were recorded with an SIS Cantega 2k CCD camera.

^a Official contribution of NIST; not subject to copyright in the United States.

^b Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.

RESULTS AND CONCLUSIONS

Substrate Effects on the Crystal Orientation and Thin Film Morphology of diFTES ADT.

This molecule crystallizes in a triclinic, nearly monoclinic unit cell, and conjugation and π - π stacking directions lie in the conductive a-b plane. The material exhibits poor conductivity along c. Hole charge-carrier mobility spans from approximately 0.001 cm²/Vs to 0.4 cm²/Vs, depending on surface treatment and gate length.⁴ When the surface is uniform, grazing incidence x-ray diffraction (GIXD) indicates that the [001] zone axis is essentially normal to the surface (i.e., the molecules are upright) on PFBT treated surfaces, and that on all other surfaces, the molecules lie mostly flat with the (111) planes nearly parallel to the surface.⁴

In addition to examining the morphology of those uniform films, TEM was also suitable for examining the morphology of actual transistors. The morphology near, and in between, the gold (source and drain) contacts was of particular interest. On the PFBT treated gold contact, the [001] zone axis orientation was confirmed and large crystals spanning several micrometers were observed. Their largest dimension was generally normal to the (010) planes, indicating that this is the direction of fastest growth. Such behavior is expected since this direction is closely aligned to that of π - π stacking. The largest crystals were observed at the edge of the gold contacts, where crystals of this same orientation extended tens of micrometers over the oxide surface, highly elongated normal to (010). Their larger size indicates that the nucleation rate over the oxide is slower. Further from the gold contact (approximately 100 μ m away), crystals characteristic of nucleation on oxide are observed. These are much smaller and found in aggregates with mixed [001] and [331] zone axis orientations, which are epitaxially related, sharing the [110] growth axis.

Crystal orientation and morphology are therefore determined by substrate interactions and nucleation and growth kinetics. The PFBT surface promotes nucleation, and does so in the orientation favorable for rapid charge transport.

Direct Mapping of Crystalline Grain Orientation in High Performance Thienothiophene Copolymer Thin Films.

Electron diffraction of semicrystalline pBTTT-C₁₄ thin films indicate orientation of the [100] zone axis normal to the film, with an equal uniaxial distribution about this axis. To map the local orientation within the plane, series of 8 dark-field images were obtained for a given area and their relative intensities were compared pixel-by-pixel. In this image series, the magnitude of beam tilt away from the surface normal was essentially constant (so that in each image the high intensity (010) reflection was collected), and only its azimuthal orientation (0°, 45°, 90°, 135°, etc.) differed from image to image. This image analysis revealed grains, several hundred nm in size, in which the orientation is nearly uniform. Within these domains, the material comprises nanocrystals, as indicated by speckles in the dark-field images, and smooth arcing in selected area diffraction patterns.

We show that solution casting and annealing conditions have a significant effect on the morphology of pBTTT, and correlations between film surface step morphology and crystal orientation are determined. Comparable hole hopping activation energies are obtained from two pBTTT-C₁₄ films with distinctly different grain size, due to the presence of nanocrystals and a gradient transition of nanocrystal orientation between domains.

ACKNOWLEDGEMENTS

We gratefully acknowledge Dr. Andrew J. Lovinger's leadership and mentorship, and we applaud his selection for the 2010 Applied Polymer Science Award. We also thank Prof. S. Z. D. Cheng for organizing the symposium in Dr. Lovinger's honor.

REFERENCES

1. Dickey, K. C.; Anthony, J. E.; Loo, Y. L. *Adv. Mater.* **2006**, *18*(13), 1721.
2. Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *JACS* **2005**, *127*(14), 4986.
3. Tierney, S.; Heeney, M.; McCulloch, I. *Syn. Metals* **2005**, *148*(2), 195.
4. Gundlach, D. J., et al. *Nature Materials* **2008**, *7*(3), 216.