Imaging conduction pathways in organic crystals as function of strain by voltage-contrast scanning electron microscopy

$Investigator$: Robin Rice, Graduate student

$Contact$: The University of Vermont, Department of Physics

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Abstract

Effective design criteria of flexible organic semiconducting devices require detailed understanding of applied strain on charge transport processes to effectively enter commercial scale.[1][2] It has been shown that strain plays a significant role in charge transport in organic crystalline devices.[2] In the plastic regime, strain induced dislocations and defects can augment carrier trapping processes. Yet, within the elastic regime applied strains to organic crystals have shown increased charge carrier mobility and controllable anisotropy, among other benefits.[3][1][4]

Strain engineering is an established method for increasing carrier mobility in inorganic semiconductors, although only recently has this been translated to that of organics. Likewise, while many studies have investigated the effect grain boundaries (GB) play in polycrystalline organic semiconductors (OSC) on charge transport, we are unaware of any studies to date investigating GB evolution under strain with consequent impact on carrier transport.

Voltage contrast scanning electron microscopy (VC-SEM) was recently used to map electronic percolation pathways in single walled carbon nanotube (SWCNT) networks and characterize electronic defects in single SWCNT. As such this technique may be applied to OSC, and thus offers many advantages over traditional crystalline organic electronic characterization techniques. This project proposes to explore a novel application of voltage contrast scanning electron microscopy (VC-SEM) to image conduction pathways in crystalline OSC. Specifically, conduction pathways via VC-SEM will be studied in polycrystalline organics as a function of applied strain, thereby investigating both intra and inter grain charge transport processes.

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Motivation

Strain and Charge Transport

TIPS-P is a robust air-stable OSC with a high degree of crystallinity, brick-wall packing structure, and room temperature mobility of 1.2 cm^2/Vs [5]. As such, TIPS-P is featured in multiple strain-charge transport studies. Zheng et al. used a multiscale nonequilibrium molecular dynamics Monte Carlo simulation based on tunneling enabled charge hopping model. Elastic moduli of 4.0 GPa in pure shear strain, 6.7 GPa in pure normal strain, and 4.0 GPa in combined shear and normal strain were calculated giving TIPS-P a lower elastic modulus than that of inorganics, by roughly three orders of magnitude (compare graphene (~2.0 TPa), carbon nanotubes (~1.2 TPa), ordinary steels (~100–300 GPa))[3]. Molecular packing and therefore charge transport properties may then be dramatically modified by moderate strain. Zheng et al. concluded TIPS-P crystals with combined shear and normal strains resulted in the highest mobility and lowest charge transport anisotropy. The maximum mobility in the preferred *ab* conduction plane (Figure 1) was 12 cm^2/Vs.[3]

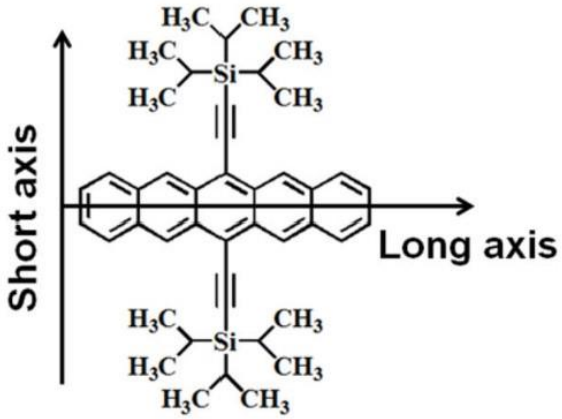

Figure 1Definition of the long and short axes in TIPS-P molecule. Adapted from [3]

The intermolecular transfer integral (TI) is understood to represent electronic coupling strength (i.e. molecular orbital overlap); ergo, it is a common indicator of mobility. Zheng et al. reports TI sensitivity to intermolecular distance and orientation in TIPS-P. Specifically, simulated TIPS-P proved more sensitive to long and short axes intermolecular distance than π–π stacking distance. Concomitant sub Å adjustments of said distances correspond to tens meV TI change. However, Illig et al. indicated the long axis distance was the dominant parameter in strain engineering small molecule OSC [6] overall emphasizing the role of molecular vibrations in device performance.

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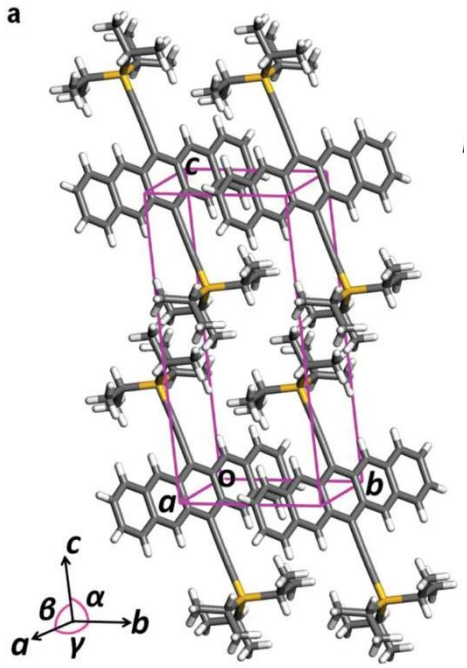

Figure 2: a) Unit cell of TIPS-P crystal with a = 7.80 Å, b = 7.82 Å, c = 17.00 Å, α = 103.3°, β = 88.1°, γ = 98.7°. For brick wall TIPS-P packing, the ab plane represents the preferred charge carrier conduction plane. Adapted from [3]

Further, the transfer integral shows periodicity of 2.5 Å in both the long (heteroacene) and short axes indicating interference of and strong TI dependence on TIPS-P bonding / anti-bonding molecular nodes. Overall, a more oblique unit-cell (increase in γ), and resultant molecular packing, favored charge transport in the ab plane.[3]

Zheng et al. have clearly demonstrated successful application of strain engineering to TIPS-P thin films, showing magnitude order increases in charge carrier mobility as well as decreased charge transport anisotropy, vastly improving the performance of TIPS-P OSC. Clearly, the complete function of strain engineered mobility requires many parameters of which not all have been thoroughly investigated. As such, further study into strain engineering of OSC using novel characterization techniques is necessary.

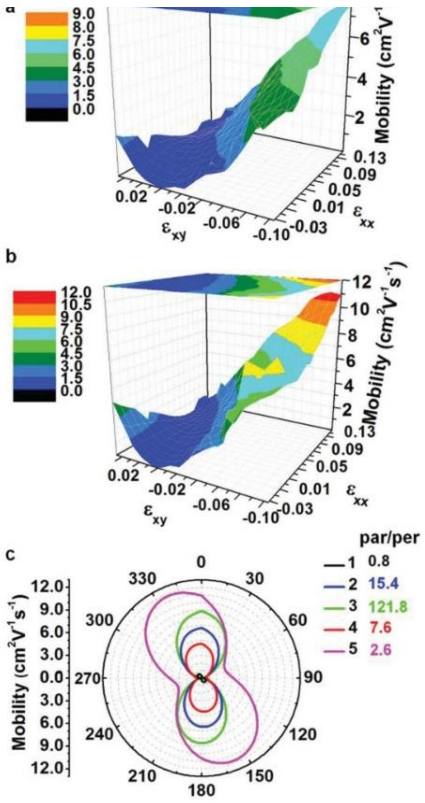

Figure 3: 3D plot of a) in-plane average mobility μ avg and b) mobility along the b -axis μ b for all 272 lattice-strained TIPS-P crystals as a function of ε xx and ε xy . c) Angular-resolved charge carrier mobilities in the ab plane of the unstrained and four lattice-strained TIPS-P crystals. The angle 0° represents the direction along the b -axis. The dotted circles correspond to mobilities between 0 and 12 cm 2 V −1 s −1 at an interval of 1 cm 2 V −1 s −1 . 1 black: unstrained TIPS-P from the NPT simulation; 2 blue: pure shear-strained TIPS-P with ε xy = −0.09; 3 green: pure shear-strained TIPS-P with ε xy = 0.09; 4 red: pure tensile-strained TIPS-P with ε xx = 0.13; 5 magenta: combined lattice-strained TIPS-P with ε xx = 0.13 and ε xy = −0.1. The par/ per denotes ratio of mobilities parallel to and perpendicular to the b -axis, shearing direction in the experiment, for TIPS-P crystals. Adapted from [3]

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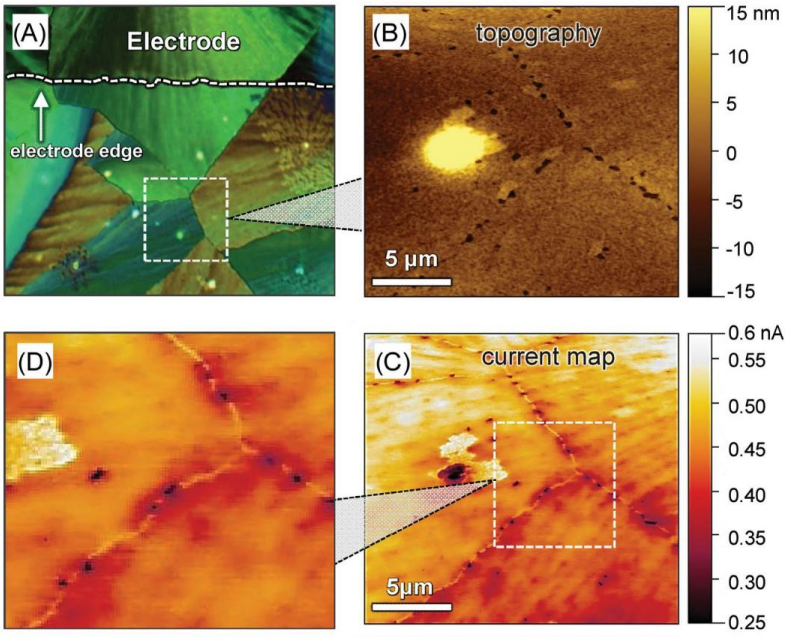

Figure 4: (A) Polarized light optical microscopy image of a diF-TES ADT:PTAA blend film deposited on glass and dried at room temperature for 5 minutes in nitrogen. (B) AFM surface topography image of the highlighted region in A (white square) showing the location of grain boundaries and the presence of periodic perforations between different crystalline domains. (C) Lateral-transport current map of the same film region revealing the orientation of internal crystallites present within adjacent crystals (also visible in microscopy image in A). The image also reveals the presence of electrically interconnected grain boundaries with the exception of crystal perforations, which appear as low-current dark spots. (D) Magnifi ed section of the current map section highlighted in C. The latter image reveals the presence of high current at the grain boundaries that appear as conductive "filament" most likely due to enhanced electrical connectivity of the grain boundaries with the crystalline domains. Adapted from [10]

OSC Grain Boundaries and Charge Transport

OSC offer air stable, room temperature solution deposition processing for low cost high production mass manufacturing. Crystallization by solvent evaporation in general produces unavoidable polycrystalline thin films. [7] Within polycrystalline OSC, GB are largely considered as purely detrimental to OSC performance.[8] Many studies which address the effects of GB on charge transport conclude similarly, and simply avoid polycrystals for the favorable properties of single crystals.[7][9] While demonstrated for rubrene and recently C8-BTBT, large single crystal fabrication is not feasible for all OSC in all applications. Moreover, such advice references a thin body of research detailing GB electrical properties.

Hunter et al. observed crystalline domain size distribution independent hole transport in small molecule 2,8-difluoro-5,11-triethylsily-lethynyl anthradithiophene (diF-TES ADT): amorphous semiconducting polymer poly(triarylamine) (PTAA) blends (diF-TES ADT:PTAA). Further, particularly high GB conductivities of 2.5 ± 0.5 GΩ were found, compared to 10 and 25 GΩ found previously in evaporated OSC films. Hunter et al. suggests this high GB conductivity is responsible for morphology independent device performance in blend films.[10]

Imaging conduction pathways in organic crystals as function of strain by voltage-contrast scanning electron microscopy

Polarized light optical imaging presents GB as obstructive boundaries, shown here as narrow dark regions between crystals (Figure 4A). Current mapping suggests these blend film GB have open (dark low current) and closed regions (light high current) of sub-nm roughness (Figure 4C,D). Further, high current was exhibited along the GB ridges. This phenomena is also common to TIPS-P:PTAA blend films.

To the best of our knowledge, this study represents the most comprehensive electrical characterization of grain boundaries in OSC to date, and despite work by Hunter et al., electrical study of GB remains underdeveloped. At present, we are unaware of any study investigating GB in strained OSC and subsequent effect on charge transport. This project proposal is twofold: equilibrium investigation of GB impact on TIPS-P charge transport to expand on previous studies with VC-SEM, followed by unprecedented investigation of GB evolution under strain impact on TIPS-P charge transport.

VC-SEM Advantages

VC-SEM presents an ideal technique for nano to mesoscale OSC electrical potential characterization. Given the probe can be enlarged (defocused) unlike physical probes, this technique opens the door to rapid mesoscopic electrical potential mapping. One necessary study for flexible electronics is charge transport in OSC under strain. Transport specifically across grain boundaries is difficult using alternative techniques due to slow scan speeds of physical probes which sacrifice resolution for image size. Such techniques include scanning Kelvin probe microscopy (SKPM) and conduction probe-atomic force microscopy (CP-AFM), among others. Enhanced contrast under bias allows lower magnification and higher scan speeds for comparable imaging. Lower magnification is valuable in SEM, especially for volatile OSC easily damaged by the electron beam. [11]

Strain induced defects (i.e. dislocations) can develop at high speeds over a large area. Rapid potential profile imaging can clearly define functional device geometries such as GB and electronic defects. Vijayaraghavan et al. demonstrated rapid failure analysis of semiconducting SWCNT bundles, as

well as electrical defects of individual SWCNT with no paired structural defects.[12] In-situ tungsten nanoprobes within Kleindiek Nanotechnik MM3A-EM micromanipulators equipped with tungsten nanoprobes were be used to precisely bias samples and current-voltage (IV) measurements were taken to corroborate VC-SEM observations.

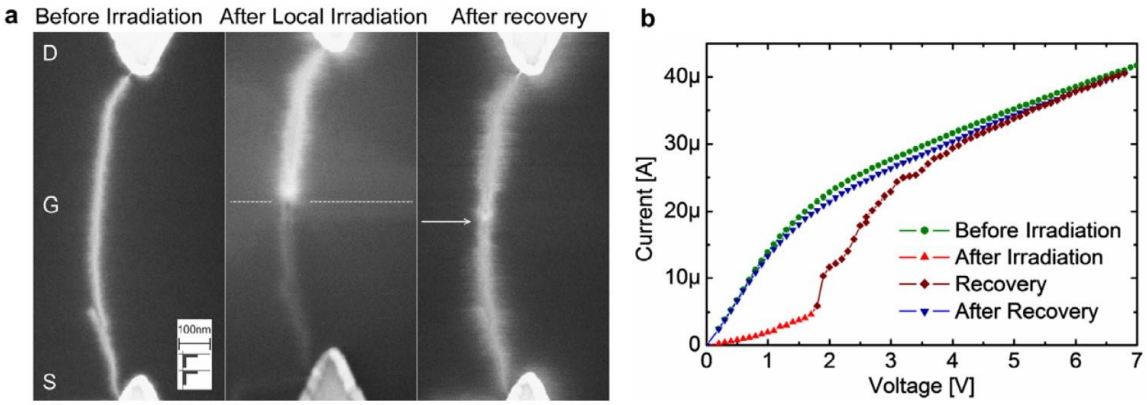

Figure 5: (a) VC-SEM images of a metallic nanotube device before electron irradiation, after line-scan electron irradiation, and after high gate-bias induced device recovery. The line-scan trace is indicated by the dashed-line. The line-scan electron-irradiation produces a local electronic defect (insulating segment), at which the surface potential changes abruptly. Uniform contrast along both nanotube segments indicates that the nanotube retains its metallic nature and ballistic conductivity. Drain (D) is grounded, source (S) is floating, and gate (G) is biased to 20 V in all images. (b) The corresponding IV curves of the nanotube device before irradiation (green) and after recovery (blue) show a typical metallic nanotube device characteristic. After irradiation (red), the current is suppressed due to hopping conduction in the insulating segment. The gate-induced recovery is shown in dark red. Adapted from [12]

Impact of the Study

Robust study into electrical properties of GB will aid choice between single and polycrystalline material applications. Moreover, this study is a necessary antecedent to informed engineered performance gain in polycrystals.

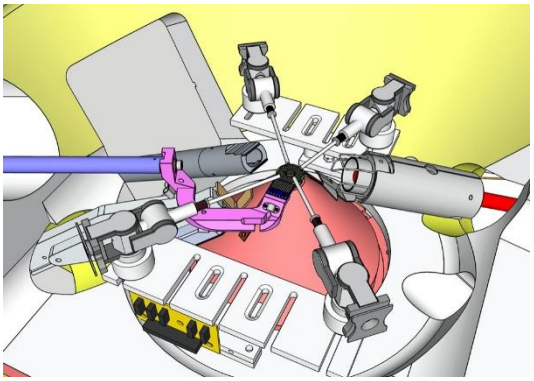

Figure 6: The machined electrical clamps and SEM stage will resemble that of Kleindiek Nanotechnik MM3A-EM micromanipulators will be equipped with tungsten nanoprobes (Picoprobe T4 series) to bias individual samples within the SEM vacuum chamber. Adapted with permission from Kleindiek Nanotechnik.

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Objectives of the Proposed Research

The objectives of the proposal are:

1. Confirm previous strain / equilibrium studies of TIPS-P using VC-SEM
2. Investigate TIPS-P GB evolution under strain using VC-SEM
3. Establish VC-SEM as a robust electrical potential characterization technique.

General Methodology

The project will begin by fabricating thin films of TIPS-P using Dr. White's Thermal Vacuum Evaporation Lithography system. TIPS-P will be used to corroborate previous results using alternative potential mapping techniques (C-AFM, KFM). The project will then investigate TIPS-P charge transport and GB evolution under strain with established VC-SEM technique.

The UVM Physics Department machine shop facility will be tasked to custom design a sample holder and electrical feedthrough for the UVM Physics Department's Zeiss Sigma 300VP FESEM chamber. The clamps will be equipped with tungsten nanoprobes (Picoprobe T-4 series) to bias individual samples, VC-SEM will be used to investigate TIPS-P films in equilibrium. In-situ current-voltage (IV) characterization of individual samples to corroborate VC-SEM observations will be done using Keithley 2461 Sourcemeter. A Kammrath Weiss SEM strain stage will then be used to investigate charge transport and GB evolution of TIPS-P films under strain.

The Zeiss FESEM EBSD will be used to correlate conduction pathways in TIPS-P with crystal axis in unstrained films as the strain stage not EBSD compatible.[13] Future work will make use of an EBSD compatible strain stage. Sets of crystal domains in TIPS-P films will be identified. An XRD will be used to correlate each set of crystal domains with their respective crystal structure (intermolecular spacing, rotation angle, etc.) to correlate conduction pathways with their molecular axis.

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Table 1: Work schedule for the proposed project

Personnel	1st Quarter		2nd Quarter	Mid term report	3rdQuarter	4thquarter	Final Report + HIG meeting
Undergra-duate student + Graduate student + Faculty	HIG meeting	1)Machine shop will fabricate SEM stage and electrical clamps 2) VC-SEM analysis of unstrained TIPS-P will begin	1)Investigate defects within TIPS-P crystals using VC-SEM		Investigate the effect of applied strain on GB evolution and charge transport in TIPS-P films		
Graduate Student + Faculty		VC-SEM analysis of unstrained TIPS-P will begin with IV measurements taken to quantify VC-SEM observations	Prepare tensile stage and perform tensile tests on TIPS-P thin films		Investigate creep mechanisms and fatigue in TIPS-P crystals with applied strain	Wrap up and obtain complete understanding of effect of strain on TIPS-P crystals, both intra and inter grain charge transport properties	

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