Structural ordering in F8T2 polyfluorene thin-film transistors

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ABSTRACT

We have used thermal treatment and rubbed polyimide alignment layers to produce large domains of poly(9,9-dioctylfluorene-co-bithiophene) alternating copolymer (F8T2). The direction of rubbing on the polyimide surface determines the orientation of these domains, allowing us to create thin-film transistors with channel lengths parallel and perpendicular to the liquid crystal polymer director. We showed that thermal annealing at temperatures ranging from 150 to 350°C modifies the polymer structure from an amorphous to ordered phase as observed by x-ray diffraction. Polarized light optical microscopy showed that this ordered phase is associated with very large ordered domains and corresponds to a thermotropic, nematic liquid-crystal phase. We investigated thermal annealing effects on both F8T2 structural ordering and the associated electrical properties of the thin film transistors (TFTs). Enhanced mobility of holes is observed with ordering. Field-effect mobility parallel to the polymer backbone is as much as 6.5 times greater than the perpendicular configuration.

Keywords: organic semiconductor, polymer, liquid crystal, transistor, thiophene, fluorene, absorption

1. INTRODUCTION

The importance of main-chain alignment for enhancement of specific electronic properties of organic polymer thin-film transistors (OP-TFTs) is widely recognized[1-5]. In a single isolated polymer chain, carrier conduction occurs only along the conjugated polymer chain backbone (*intra*molecular transport). For the three-dimensional polymer structure, carrier transport occurs not only along the chains, but also between the neighbor chains (*inter*molecular transport). In a single polymer chain, charges are localized by interference of forward and backward-scattered electron wave functions. If, however, the carrier is transferred to a neighboring molecule before scattering backwards, it is effectively delocalized. It is generally believed that this intermolecular transport occurs via a hopping or tunneling mechanism dependent on molecular separation distances such that better packing of polymer chains enhances interchain transfer rates[6, 7]. Hence, the structural ordering in an intrinsic organic polymer semiconductor can have a pronounced influence on charge transport in OP-TFTs.

To achieve order in solution-deposited polymer films, we rely on the self-aligning nature of polyfluorenes. When heated, poly(9,9-dioctylfluorene-co-bithiophene) alternating copolymer (F8T2) enters a liquid crystalline phase that is retained with quenching. We demonstrate structural effects of heating, identifying phases and transition temperatures, with differential scanning calorimetry (DSC), polarized light microscopy (PLM) and powder x-ray diffraction. Using these results, we establish a thermal treatment resulting in room temperature films with nematic order. To define the orientation of the liquid crystal directors, thermal treatment is not sufficient, so a texturing technique is employed. Polarized UV-vis spectroscopy shows that rubbed polyimide alignment layers used in conjunction with thermal treatment can create well-ordered, textured F8T2 films.

The relationship between the structural ordering of F8T2 and OP-TFT electrical properties is investigated by fabricating transistors on aligned F8T2 films. We observe the highest field-effect mobilities when long polymer molecules are aligned with backbones lying in the direction of current flow. In this orientation, there are more conduction paths, and diffusion of carriers is greatest. In the parallel alignment, field effect mobility values are 2-3 times greater than mobility for as-deposited (amorphous) films, and 4-6 times greater than values obtained for devices with channel lengths perpendicular to polymer chain alignment. Thus, we establish that thermal treatment and texturing of the organic polymer is an effective method for achieving macroscopic ordering and enhanced mobility in F8T2 TFTs.

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2. MATERIALS & METHODOLOGY

Poly(9,9-dioctylfluorene-co-bithiophene) alternating copolymer (F8T2) has several properties which make it convenient for studying electrical characteristics of aligned polymer films: conjugated segments for charge transport, relatively large stability in air, solubility in a wide range of solvents, and thermally induced mesogenic nature which allows better packing via self-assembly. F8T2 is a main-chain liquid crystal polymer of the 'hairy-rod' type. (See Figure 1.) The octyl side chains protruding from the rod-like backbone (hence the name 'hairy-rod') facilitate solvation.
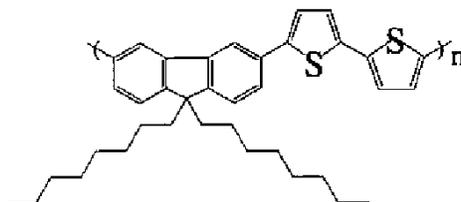

Figure 1: Chemical structure of F8T2

The F8T2 supplied by Dow Chemical (polymers A, B, and C) vary in molecular weight and polydispersity (PDI). These properties can influence mobility, morphology, transition temperatures, and degree of alignment[8]. Weight average and number average molecular weights (M_w and M_n, respectively) were determined from tetrahydrofuran solutions by gel permeation chromatography (GPC) using polystyrene equivalents. PDI = M_w/M_n is calculated from these values. Thermogravimetric analysis (TGA) shows that polymers decompose at high temperatures (> 400°C). The main characteristics are summarized in Table I.

Table I. Materials Characterization

Analysis	Copolymer	A	B	C
GPC	M_W (kg/mol)	151.5	39.3	31.3
	M_n (kg/mol)	28.2	8.1	14.9
	Polydispersity	5.38	4.86	2.1
TGA	Decomposition Onset (°C)	420.8	422.1	---

Thin films were deposited from 10mg/mL (1%) xylenes solutions using spin- or drop-casting techniques and immediately vacuum annealed at 110°C to remove solvents. Further annealing to the liquid crystal transition temperatures between 216°C and 275°C and subsequent quenching to room temperature were performed under nitrogen purge. It has been shown that long-range ordering of F8T2 can be attained using polyimide alignment layers on substrate surfaces prior to F8T2 deposition[9, 10]. Diluted polyimides from Nissan Chemical were spun onto substrates, baked to imidization and either hand-rubbed (for formation of aligned films) or left without grooves for comparison. Atomic force microscopy (AFM) shows the polyimide surface before and after rubbing (Figure 2). F8T2 is cast on top of these (un)rubbed polyimide layers. Polyimide thickness is 40nm as determined by ellipsometry and Dektak Profilometer.
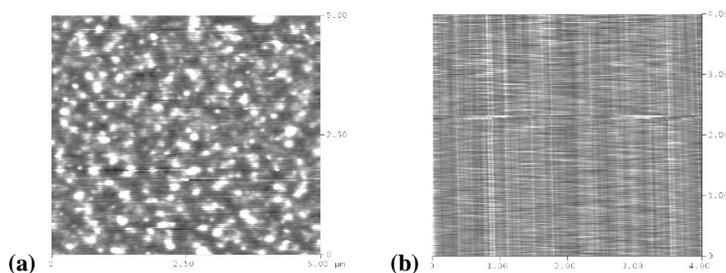

(a)   **(b)**

Figure 2: 5x5μm AFM scans of polyimide surfaces: (a) before and (b) after rubbing.

Electrical analysis is done with the transistor structure shown in Figure 3. The schematic shows that a heavily n+ doped silicon substrate serves as a common back gate. A defined gate structure would be preferred since capacitive charging occurs between the source and drain electrodes and the gate terminal. The gate dielectric layer is composed of a thermal SiO_2 (200nm) layer in series with the rubbed polyimide alignment layer. Gold source and drain contacts are defined by photolithography on top of the F8T2 with a mask allowing for fabrication of devices with parallel and perpendicular channel lengths to be formed on the same sample (Fig. 3b). Channels have length (L) of 5-40μm and width (W) of 500 or 1000μm.
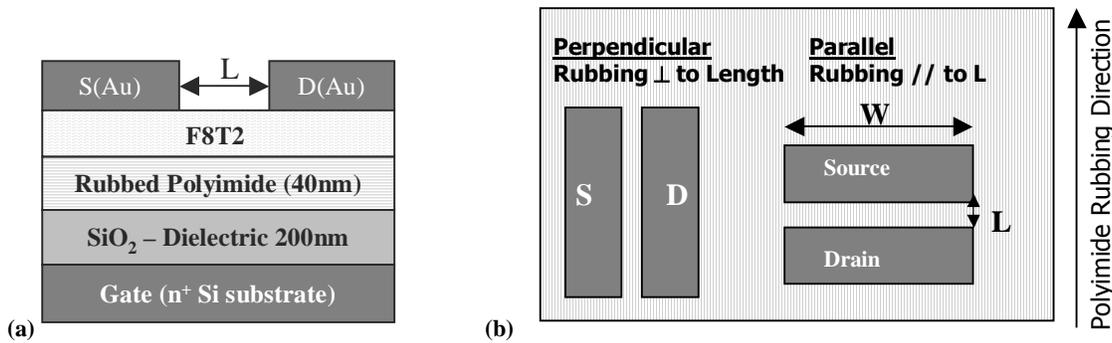

Figure 3: Thin-film transistor structure (a) cross-section and (b) top view.

3. STRUCTURAL ANALYSIS

Liquid crystal phase identification

Thermotropic transitions in large molecular weight main chain polymers are difficult to identify due to the rarity of monotropic mesomorphism and decreased definition of the mesophase texture under the optical microscope. Generally, a combination of techniques is employed for phase identification. Here we use differential scanning calorimetry (DSC) as a primary method to detect transitions. We confirm the DSC analysis with powder x-ray diffraction and polarized optical light microscopy (PLM) methods. Transition temperatures are shown in Table II.

Table II. Transition temperatures from DSC, PLM, and X-ray techniques.

Copolymer	A	B	C
Glass Transition (T_g) [ºC]	164	125	128
Liquid Crystal Transition (T_{XL-N}) [°C]	252/275	216/252	221/259
Isotropic Transition (T_{N-I}) [°C]	330	315	314
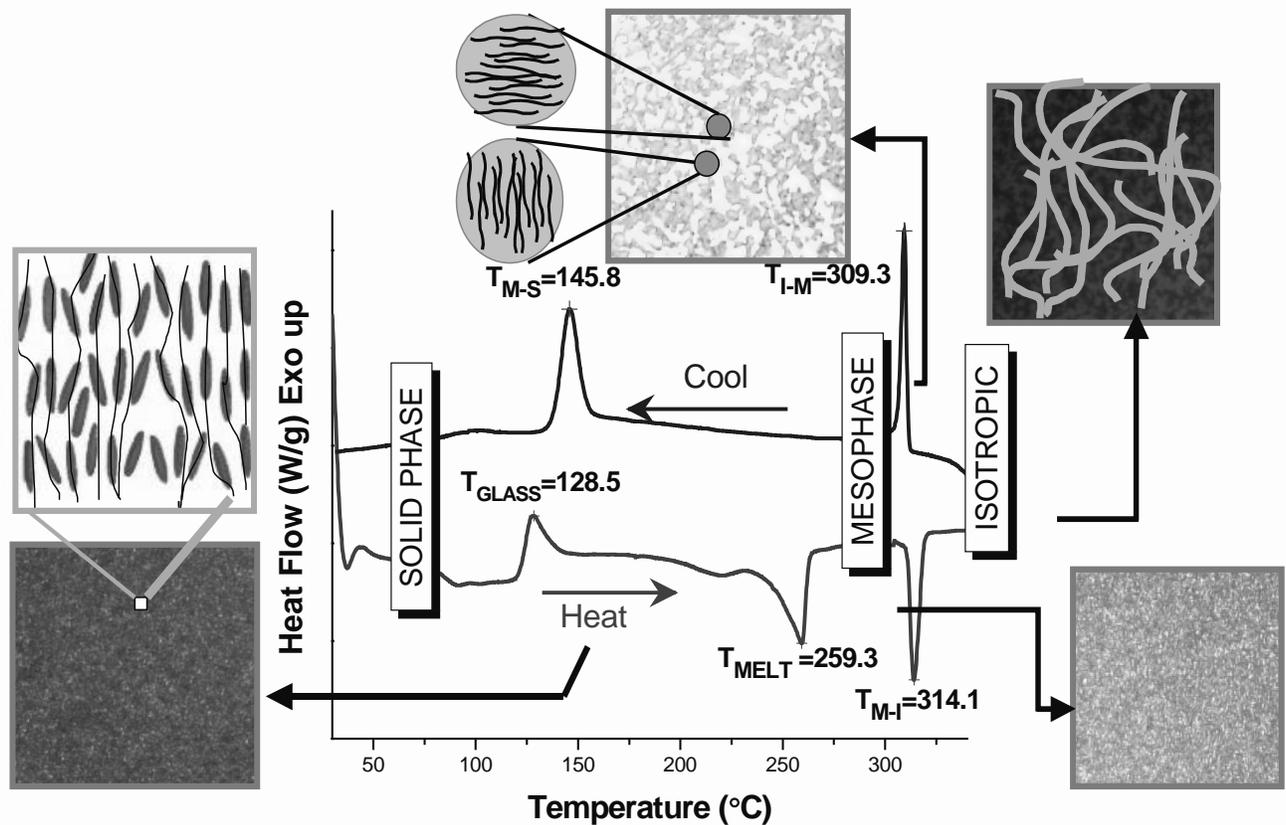
Figure 4: DSC of F8T2-C; Polarized light micrographs (100μm x 100μm) of thin F8T2 films are shown at corresponding temperatures. Illustrations depict the proposed structural transitions.

DSC curves of polymer C in heating and then cooling at 10°C/min in N_2 are shown in Figure 4. Phase changes are accompanied by a release or intake of thermal energy represented by peaks and dips in the DSC scan. Using crossed polarizers, optical micrographs of the thin film surface (on glass substrates without the polyimide alignment layer) are taken at corresponding temperatures to illustrate the phase transformations. Each micrograph shows an area of 100x100μm.

The as-deposited material is in a glassy form. Upon heating to around 128°C, the film crystallizes. Double melting peaks, showing the solid to mesophase transition are observed for all polymers with positions between 216°C and 275°C. At these temperatures, thin films of F8T2 become birefringent, brightening the image observed through crossed polarizers as regions of molecules with preferred orientation in the substrate plane rotate the incoming light such that it is not cancelled by the second polarizer. Mesophase to isotropic transitions occur above 300°C, bringing the material to a disordered, liquid phase as illustrated on the dark PLM image. Upon cooling from liquid, the material again enters the mesophase. When held at this temperature in nitrogen environment, the liquid crystalline domains enlarge. Being prone to super-cooling, the material can be frozen in the mesophase by rapid quenching.

Powder x-ray diffraction shows structural changes at temperatures corresponding to those determined by DSC analysis (Table II). X-ray scans were performed in reflection on thin films using a Philips XPERT MPD Diffractometer at angles $2\theta = 4°$ to $30°$ and power of 40kV/30mA. Scans at elevated temperatures were obtained by heating to temperature with a Pt hot stage and holding temperature during data collection. All heating and scanning was performed in N_2 environment. Results at temperatures of 30-340°C from polymer B deposited on glass coverslips without alignment layers are shown in Figure 5.

Supporting the PLM and DSC results, Figure 5 shows that as-deposited F8T2 films are amorphous and that structural ordering is achieved through thermal treatment. X-ray scans at elevated temperatures (150°-300°C) show 2θ peaks at ~5.5°, revealing a periodicity of $\cong 16$Å normal to the surface. As temperature is increased, this peak decays and finally disappears as the material undergoes transitions between the crystal, liquid crystal, and isotropic phases. Observation of birefringence in PLM implies that F8T2 backbones lie in the plane of the substrate. This leads us to believe that the 16Å periodicity is associated with the layering distance between sheets of F8T2 chains. This layered structure appears due to the segregation of main chain backbones from aggregated alkyl side chains. Smaller, broader peaks corresponding to spacings of 4.7 and 5.6Å could be due to the lateral distance between polymer chains within the layer. Similar coplanar arrangement of aromatic backbones within layers is observed for polyesters and polyamides with alkyl chains[11, 12]. Alternatively, these small peaks could arise from side chain crystallization[13]. Cycling the sample temperature shows that crystallization is reversible and that with rapid cooling, we can freeze the sample in the liquid crystalline or crystalline phase.
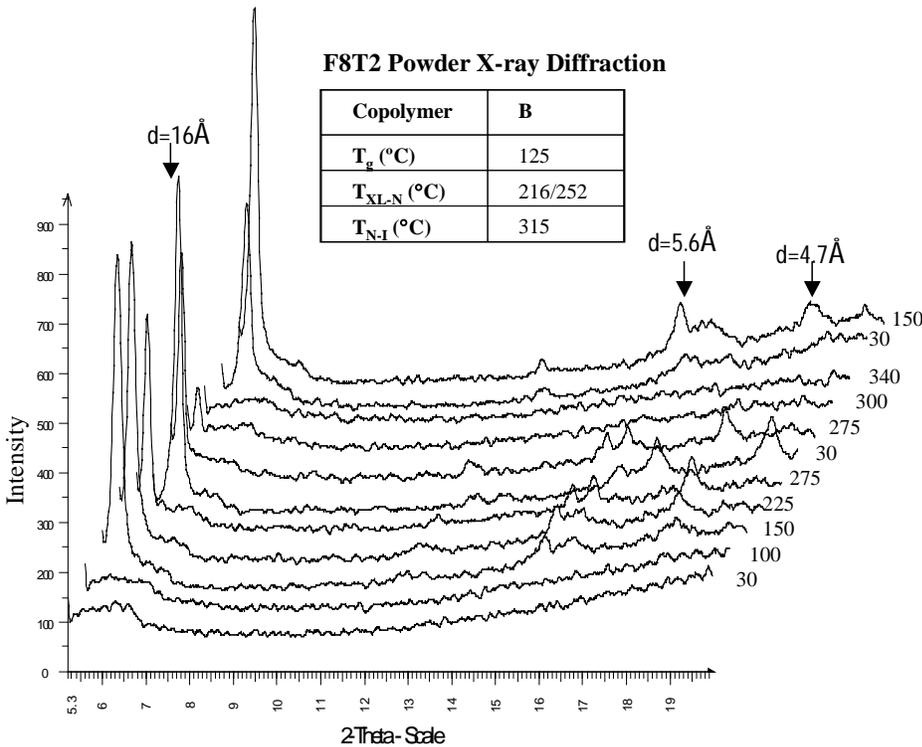
F8T2 Powder X-ray Diffraction

Copolymer	B
T_g (°C)	125
T_{XL-N} (°C)	216/252
T_{N-I} (°C)	315

Figure 5: X-ray scans of polymer B at temperatures (30-340°C) indicated for each scan. Plots are offset to show development of 2θ peaks.

Orientation of liquid crystal phase

X-ray and PLM results discussed above are obtained from F8T2 films deposited on glass or unrubbed polyimide surfaces. Annealing these samples creates liquid crystalline domains, but films lack long-range ordering since individual domains are not all oriented in a specific direction. When F8T2 is deposited on rubbed polyimide surfaces, well-ordered, monodomain films can be made. F8T2 molecules close to the interface lie with their long axes along the rubbing direction. Neighboring molecules align with these underlying molecules when heated to the mesophase. Figure 6 shows a polymer C film on a glass substrate coated with rubbed polyimide alignment layers. We see that before heat treatment, the material shows no signs of ordering – it is not birefringent and UV-vis spectroscopy shows that light polarized parallel to the rubbing direction is as strongly absorbed as perpendicularly polarized light. When this sample is heated to 280°C, nematic domains and threadlike defects appear in PLM images (Fig. 7a). Holding this temperature

for 10 minutes anneals out the defects, leaving a nematic domain at least as large as the image area (250x250μm) and much larger than the size of a transistor channel (Fig. 7b). After quenching, the sample is analyzed with polarized UV-vis spectroscopy and we observe that the sample has a dichroic ratio (absorption$_{//}$: absorption$_\perp$) of 11, indicating strong alignment in the rubbing direction.
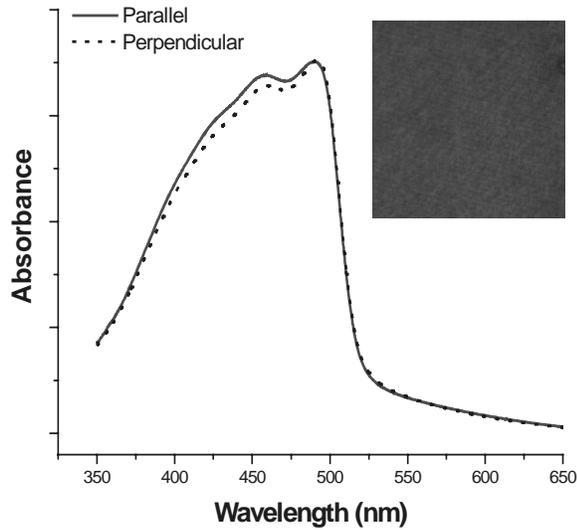
Figure 6: Absorption // and ⊥ to rubbing direction of polymer C before thermal treatment. Inset: Image (250x250μm) of the surface under crossed polarizers.
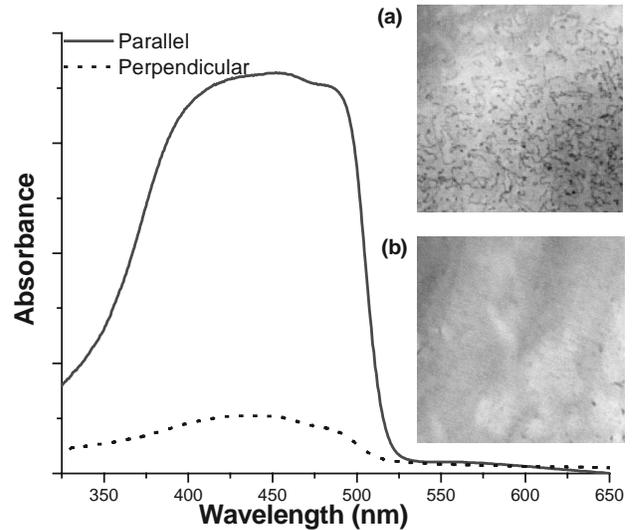
Figure 7: Same sample after thermal treatment. Inset: Image (250x250μm) of surface under crossed polarizers (a) upon reaching 280°C and (b) after 5 minutes anneal at 280°C.

4. ELECTRICAL ANALYSIS

To investigate the relationship between structural and electrical properties in F8T2, we fabricate OP-TFTs. Transistor contacts are oriented such that on the same F8T2 film, current flow parallel and perpendicular to the alignment direction can be probed. Electrical characterization of transistors with semiconducting polymer C (device structure in Figure 3) is discussed below. Figure 8 shows output characteristics for perpendicularly oriented devices. (As in Fig. 3b, // indicates that the device channel length (L) is parallel to the polyimide rubbing direction whereas ⊥ indicates that L is perpendicular to the rubbing.) Negative signs of drain current (I_{ds}) under negative drain voltage (V_{ds}) and gate voltage (V_{gs}) indicate hole transport and a p-type F8T2 semiconductor. These devices operate in the accumulation mode, turning on as gate bias is negatively increased (V_{gs} = 0 to –20V). At low V_{ds}, the drain current I_{ds} increases linearly, indicating good charge injection from the source and drain contacts. There is a clearly defined linear regime at $V_{ds} < V_{gs}$ followed by saturation regime at $V_{ds} > V_{gs}$ for each gate voltage. Output characteristics are sensitive to the chain orientation becuase when polymer backbones align to the flow of current (// configuration), more conduction paths are available to transport charges. Figure 8 shows that the parallel saturation current is 4 times greater than the perpendicular saturation current.
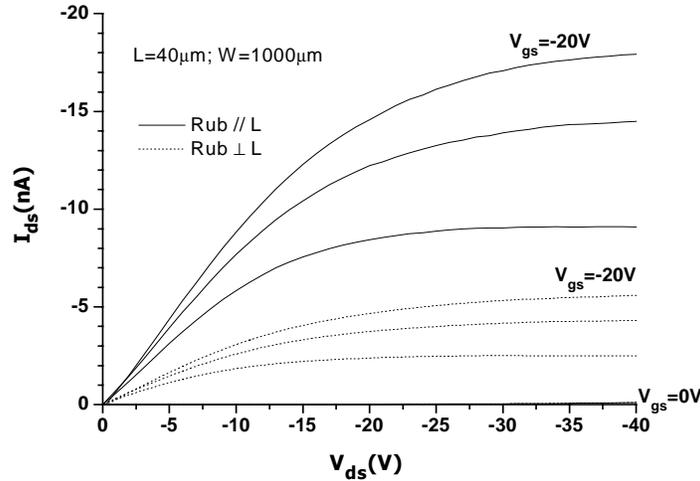
Figure 8: Output characteristics (I_{ds}-V_{ds}) at V_{gs} = 0 to -20V for perpendicularly oriented polymer C devices.

Figure 9 shows linear regime transfer characteristics of a similar device. The slope of this I_{ds}-V_{gs} curve is used in the following TFT equation[14] to calculate the hole field effect mobility, μ_{FE}. Here g_m is the transconductance and C_i is the capacitance of the dual layer dielectric. This series capacitance is calculated from the dielectric constant and thickness measured from the polyimide and silicon oxide layers.

$$g_m = \left.\frac{dI_{ds}}{dV_g}\right|_{V_{ds}=const} = \frac{W}{L}C_i\mu_{FE}V_{ds}$$

In the linear regime, mobility values of 0.5 x 10^{-4} – 8 x 10^{-4} cm^2/V-s are observed. Devices with parallel alignment consistently out-perform perpendicular devices, showing higher values of μ_{FE} and saturation current. The mobility anisotropy ratio ($\mu_{//}/\mu_{\perp}$) is as large as 6.5. Amorphous devices, which are deposited on rubbed polyimide alignment layers but not thermally treated (Fig. 6), have mobility values in-between those of the ordered films. Enhancement of device performance is observed when interchain charge transport is facilitated by ordering the film in the nematic phase (which improves chain packing and reduces the number of grain boundary defects) and aligning the director of this nematic liquid crystal in the direction of current flow.
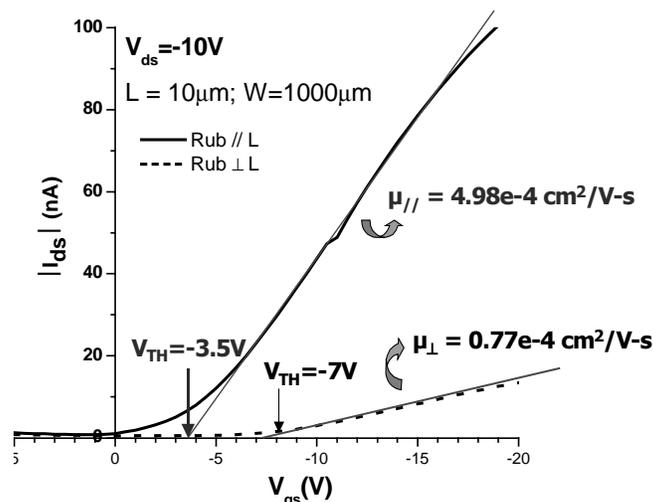

Figure 9: Transfer characteristics of perpendicularly oriented polymer C devices in the linear regime (V_{ds})=-10V.

5. CONCLUSIONS

We have conducted structural and electrical analysis of ordered F8T2 films. Structural analysis, combining DSC, PLM and x-ray diffraction techniques, shows that F8T2 enters a layered liquid crystal phase at elevated temperatures. The transition temperatures and phases for three polymers are identified, and these values are used to define thermal annealing processes to macroscopically order the films. Polarized UV-vis spectroscopy shows that rubbed polyimide alignment layers effectively texture the liquid crystal, and this alignment is preserved upon quenching. We demonstrate that this alignment method is compatible with processing. In fabrication of transistors, photolithography is used to define source and drain contacts on top of the F8T2 film without affecting its alignment capability. OP-TFTs with aligned F8T2 layers show that the hole mobility is anisotropic with ratios, $\mu_{//}/\mu_{\perp}$ up to 6.5. We observe a relationship between structural and electrical properties in F8T2 films, showing that proper processing leads to enhanced mobility.

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