

**Orientation of pentacene films using surface alignment layers and its  
influence on thin film transistor characteristics.**

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There has been great interest in organic semiconductor materials composed of molecules such as sexithiophene derivatives and pentacene for organic thin film transistors (TFTs), due to their high field effect mobilities, which approach that of amorphous silicon. It is thought that the high mobilities observed in these materials are due to intermolecular interactions which lead to larger grain sizes and fewer grain boundaries, facilitating charge transport<sup>[1-4]</sup>.

Liquid crystals(LC) are another class of organic materials in which increased mesoscopic order is technologically desirable. High contrast in liquid crystal displays is achieved through the use of underlying alignment layers such as rubbed or irradiated polymers<sup>[5-7]</sup> and self-assembled monolayers<sup>[8]</sup>. A liquid crystal film without an alignment layer will show locally ordered domains with frequent grain boundaries and discontinuities while an LC film over an alignment layer exhibits enhanced long range order. Some of the more promising organic semiconductor materials, such as dihexylsexithiophene, have striking similarities to liquid crystal materials. Thus it appears promising to investigate the affect of liquid crystal alignment layers on organic semiconductor materials.

In this paper we investigate the use of liquid crystal alignment layers to produce order in thin pentacene films. Both rubbed and photoirradiated layers of polymers and self-assembled monolayers were investigated. Their ability to alter the structure of pentacene films was screened by linear dichroism measurements and grazing-incidence x-ray diffraction. Finally, organic transistors were constructed employing an alignment layer and its influence on the device performance was measured.

Self-assembled monolayer (SAM) photoalignment layers were synthesized by conversion of cimmamic, 4-fluorocinnamic and 4-nitrocinnamic acids to the corresponding acid chlorides and subsequent reaction with aminopropyltriethoxysilane. Films of these materials were prepared

by immersion of the substrates (fused silica) in a 1% solution of xylene for 1 hour<sup>[9]</sup>. To generate alignment, these layers were irradiated with polarized light at 280 nm with an irradiation dose of  $\sim 300 \text{ mJ/cm}^2$ . The photoalignment polyimide (PI) Nissan RN1332 was also used, prepared and irradiated following manufacturer specifications.

For rubbed alignment layers, polyvinylalcohol (PVA, Aldrich) was spun from a 2% solution and baked for two hours at 130 C. Film thickness was found to be  $\sim 500 \text{ \AA}$  by ellipsometry. The commercial alignment polyimides Nissan SE150 and SE12710 were prepared following manufacturer specifications. PVA and PI film surfaces were rubbed on a LCBM buffing machine (Optron Systems, Inc., Bedford MA) having a roller radius of 3 cm. Rayon pile cloth (YA-18-R Yoshikawa Chemical Co.) was used for rubbing, with an average fiber length of  $600 \text{ }\mu\text{m}$ , fiber diameter of  $15 \text{ }\mu\text{m}$  and fiber density of  $32000 \text{ threads / cm}^2$ . Each substrate was translated once at a speed of 1 mm/sec under the roller rotating at a rate of 1.67 revolutions/sec (100 rpm). Alignment was found to be maximal with the roller-substrate spacing set for a vertical impression of  $\sim 500$  microns beyond the point of first contact between cloth and substrate.

Pentacene was purchased from Aldrich and used without any further purification. Films were grown by vacuum sublimation at a pressure of  $10^{-6}$  mbar on fused silica or thermally oxidized silicon wafers treated with alignment layers. The rate of deposition was of the order of  $10 \text{ \AA/sec}$  and the final film thickness was  $500 \text{ \AA}$  as determined by quartz crystal microbalance.

Linear dichroism (LD) spectra were measured on a Jasco J720 spectropolarimeter using a LD324 linear dichroism attachment. In this mode the instrument measures the linear dichroism defined as  $(OD_{\parallel} - OD_{\perp})$ , where  $OD_{\parallel}$  ( $OD_{\perp}$ ) is the optical density parallel (perpendicular) to the direction of irradiation polarization for photoalignment layers or the rubbing direction for rubbed alignment layers.

Grazing incidence x-ray diffraction measurements were performed at the A2 station of the Cornell High Energy Synchrotron Source using 11 keV x-rays with a flux of  $\sim 10^{13}$  photons/sec. The sample was mounted on a custom built<sup>[10]</sup> surface diffraction vacuum chamber, and the intensity of the pentacene (200) reflection was recorded as the sample was rotated about its surface normal while keeping the incident x-ray beam at the critical angle for total external reflection from the pentacene surface. In order to accurately determine the scattering intensity,  $Q_{\parallel}$  scans were recorded at each azimuthal angle, and the integrated intensity of the (200) peak above background was determined.

For the fabrication of the thin film transistors PVA layers were spun on thermally oxidized Si wafers (oxide thickness 4200 Å). The wafers were n-doped and served as the gate electrodes, while the oxide served as the main gate insulator, allowing a higher breakdown threshold. The wafers were introduced into a nitrogen glove box (<1ppm oxygen and moisture), where the devices were completed by the deposition of pentacene and source/drain electrodes through a set of shadow masks, defining TFTs with a channel length of 100  $\mu\text{m}$  and width of 6 mm. Two Keithley source-measure units were used to record the current-voltage characteristics.

Pentacene films exhibited significant LD signal for both photo- and rubbed alignment layers. Rubbed layers were found to be much more effective than photoalignment layers, with rubbed PVA producing the strongest effect. A typical LD spectrum of a pentacene film deposited over a rubbed PVA layer is shown in Fig. 1. The peak at 670 nm corresponds to the maximum of the absorption spectrum of pentacene and indicates a preferential alignment of pentacene molecules along the rubbing direction.

A quantitative measure of the magnitude of optical anisotropy induced in the pentacene film is the dichroic ratio  $D=LD/OD$ , where OD is the optical density measured for a pentacene film deposited without alignment. This parameter should be proportional to the order parameter. The values achieved with the various alignment layers are summarized in Table I. Pentacene aligns along the direction of irradiation polarization for photoalignment layers and the rubbing direction for rubbed alignment layers, with the exception of the nitrocinnamic SAM and the irradiated polyimide, where alignment is perpendicular to the direction of irradiation polarization. While the mechanism of alignment is poorly understood, it appears that pentacene partially aligns along the PVA polymer chains, which are known to be oriented along the direction of rubbing<sup>[11]</sup>. It should be noted that sexithiophene films were not found to show appreciable linear dichroism using either a cinnamic SAM photoalignment layer or rubbed PVA.

<Fig. 1>

<Table I>

In order to gain insight into the morphology of the aligned films we carried out x-ray diffraction studies of pentacene films deposited on rubbed PVA layers. Fig. 2 shows results of grazing-incidence X-ray diffraction measurements for the (200) integrated intensity as a function of rotation about the surface normal<sup>[12]</sup>. The zero of the rotation angle corresponds to alignment of the scattering vector along the rubbing direction. The almost continuous intensity over the 180 degrees is consistent with the pentacene grains having a nearly random distribution around the axis defined by the surface normal of the film. However, the peak centered at about 90 degrees indicates a small degree of ordering with a preference for the [200] crystallographic direction to be perpendicular to the rubbing direction. This is consistent with the LD measurements that indicate preferential alignment of pentacene along the rubbing direction. The degree of ordering may be estimated by noting that about 27 percent of the intensity falls within a 30-degree range near 90 degrees (if there were a complete absence of order, about 17 percent of the intensity would fall within this range).

<Fig. 2>

Fig. 3 shows typical source-drain current vs. source-drain voltage curves from three devices prepared side-by-side, with rubbed and unrubbed PVA layers. The up and down triangles are data from devices with PVA layers rubbed perpendicular and parallel to the direction of current flow in the channel respectively, while the filled circles are data from the control device with the unrubbed PVA layer. The device with the perpendicular rubbing direction shows a saturation current that is over 2.5 times larger than the control device, indicating a higher mobility in the partially oriented pentacene film. This effect was systematic, as all devices with PVA rubbed in this direction showed a 30 to 200% higher current than the respective controls. On the other hand, rubbing of the PVA layer along the direction of current flow was found to have very little influence on the saturation current.

<Fig. 3>

Mobilities were calculated from the square root of the saturation current vs. gate voltage plots<sup>[4]</sup> and were found to be of the order of  $0.01 \text{ cm}^2/\text{V}\cdot\text{sec}$ , which is typical for pentacene deposited on room temperature substrates<sup>[4]</sup>. The mobility in these films is limited by charge trapping at grain boundaries<sup>[13]</sup>, rather than transport inside the grains. The exact mechanism of trapping and its dependence on the mutual orientation of the grains is not understood at present. However, it is conceivable that by inducing some degree of preferential alignment in the pentacene film, some of the grain boundaries will be eliminated as two neighboring grains can have the same orientation. Accordingly, partial orientation of pentacene film perpendicular to the channel length will result in elimination of some grain boundaries that are perpendicular to the direction of current flow, resulting in a higher mobility. This will not be the case in the film that is partially aligned along the channel, in which grain boundaries are eliminated parallel to the direction of current flow. We are currently conducting a detailed study of the growth of pentacene on PVA in order to verify this hypothesis.

In conclusion, we studied the influence of alignment layers on the orientation of pentacene films. We found that rubbed polyvinylalcohol layers induce preferential orientation of pentacene grains along the rubbing direction, with approximately 27% of the grains aligned within a 30° range. This can be used to lead to an enhancement of the pentacene mobility, which we attribute to partial elimination of grain boundaries.

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## Table and Figure Captions

Table I: Dichroic ratio  $D$  at 670 nm for the various alignment layers. A negative sign signifies alignment of pentacene perpendicular to the irradiation polarization direction.

Fig. 1: Linear dichroism spectrum of a pentacene film deposited on a rubbed PVA layer.

Fig. 2: Grazing-incidence X-ray diffraction measurements from a pentacene film deposited on a rubbed PVA layer. The data shown are for the (200) integrated intensity as a function of rotation about the surface normal. The zero of the rotation angle corresponds to alignment of the scattering vector along the rubbing direction.

Fig 3: Current voltage characteristics of three TFTs with PVA layers. The up and down triangles are data from devices with PVA layers rubbed perpendicular and parallel to the direction of current flow in the channel respectively, while the filled circles are data from the control device with the unrubbed PVA layer.

	<i>Alignment layer</i>	<i>Dichroic Ratio</i>
Irradiated	Cinnamic SAM	0.001
	Fluorocinnamic SAM	0.001
	Nitrocinnamic SAM	-0.0065
	RN1332 Polyimide	-0.0065
Rubbed	SE150 Polyimide	0.15
	SE2710 Polyimide	0.15
	Polyvinylalcohol	0.3

Table 1. Swiggers et. al.

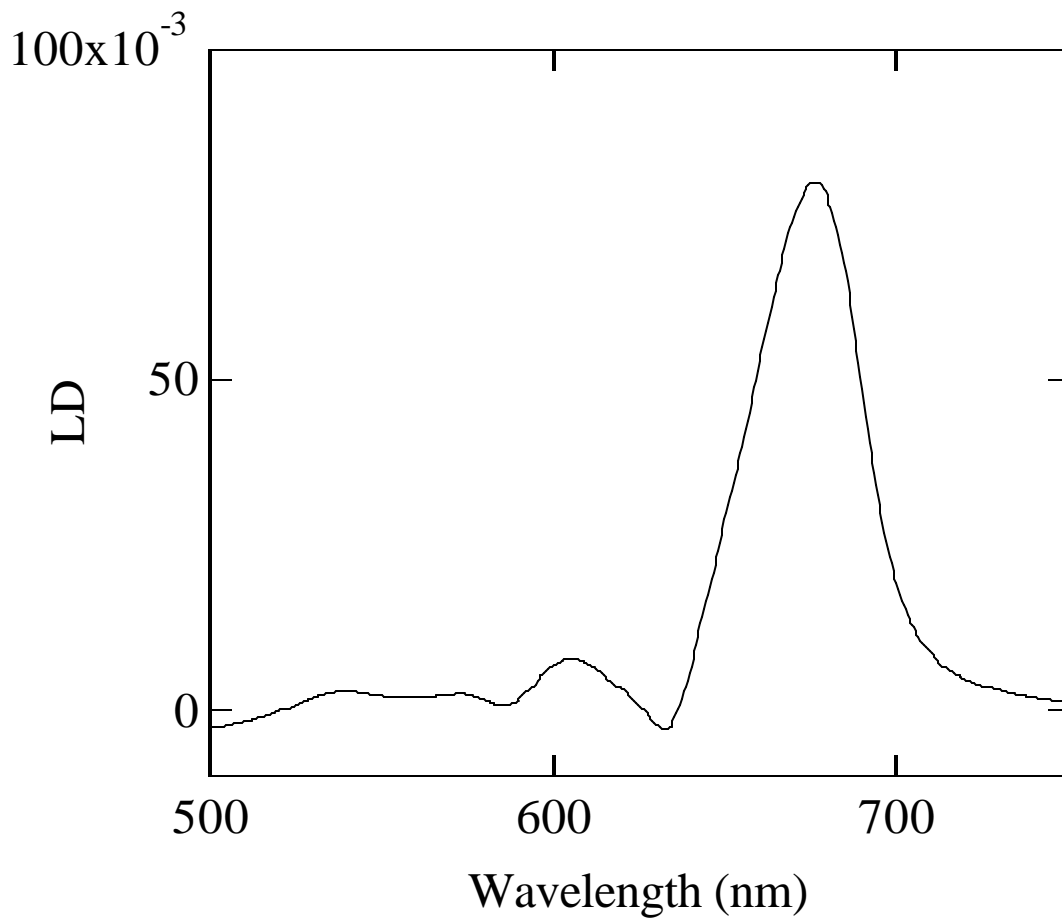


Fig. 1. Swiggers at. al.

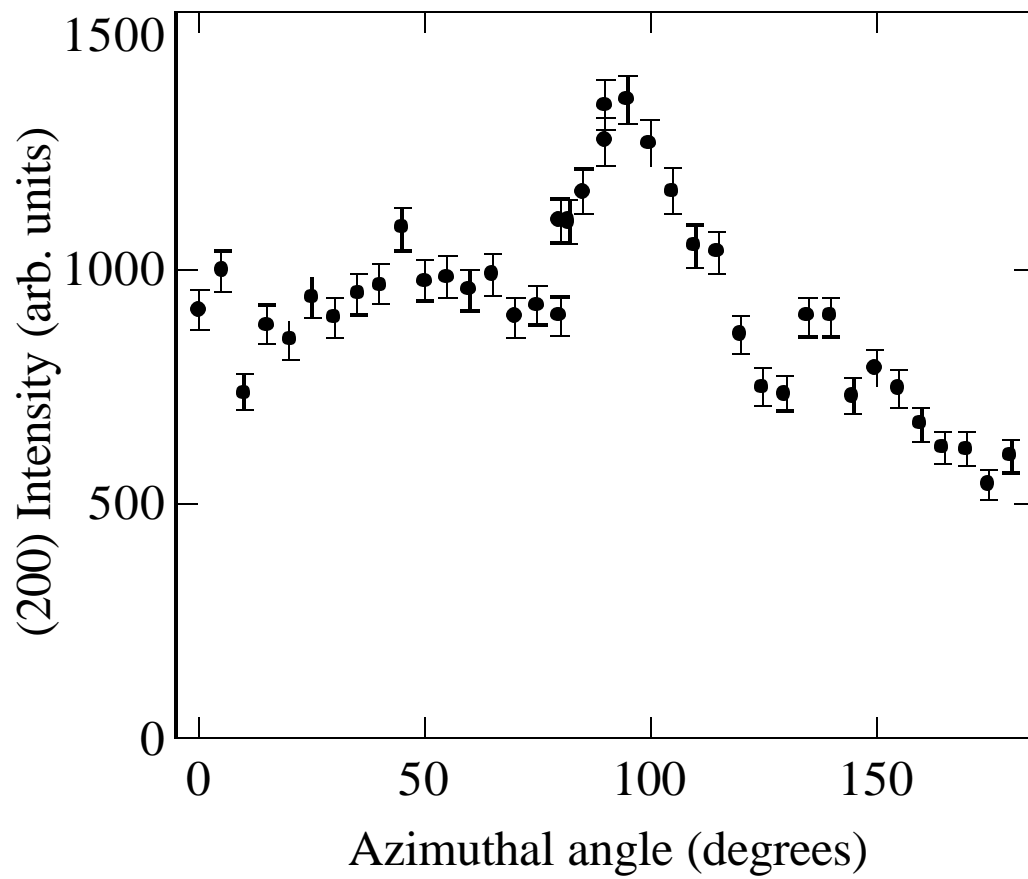


Fig. 2. Swiggers et. al.

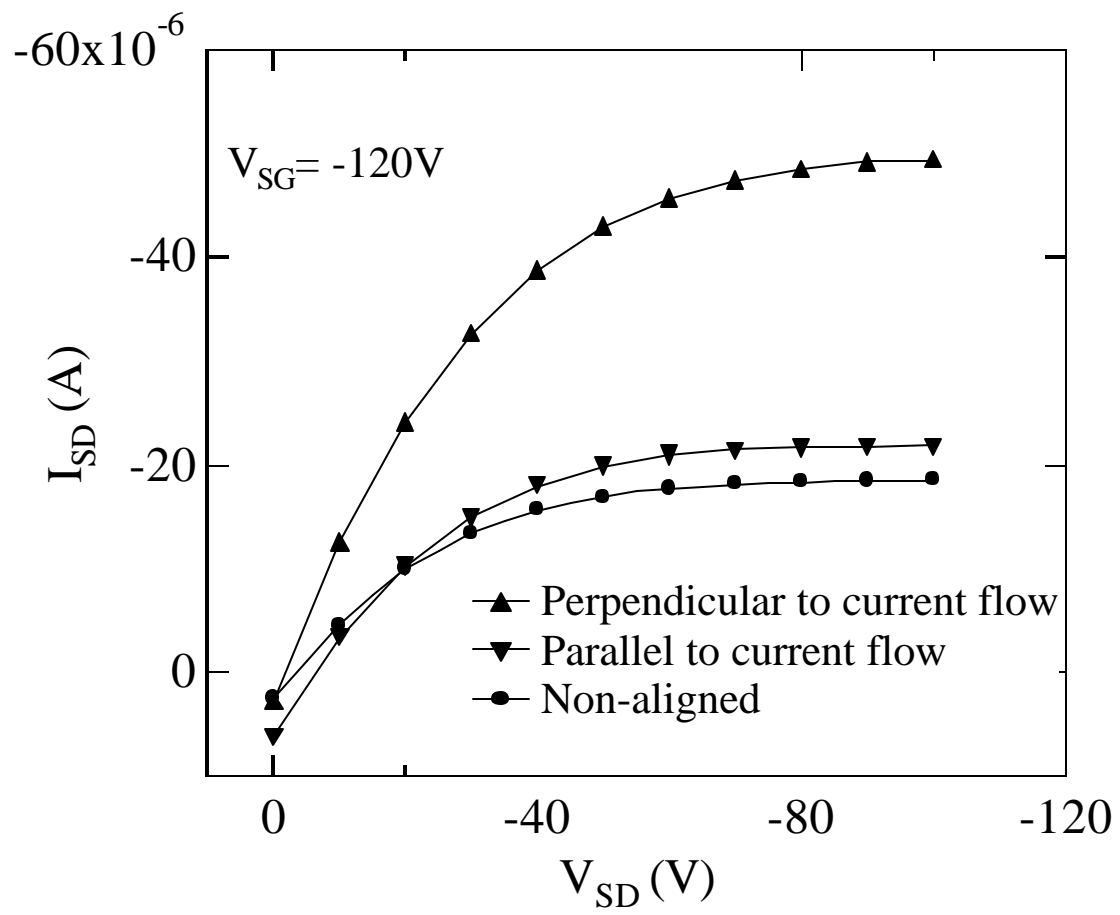


Fig. 3. Swiggers et. al.