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# **Enhancement of carrier mobility along with anisotropic transport in non-regiocontrolled poly (3-hexylthiophene) films processed by floating film transfer method**

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## ABSTRACT

A newly developed floating film transfer method (FTM) has been successfully utilized to fabricate oriented thin films of non-regiocontrolled poly (3-hexyl thiophene) (NR-P3HT) followed by the fabrication of organic field effect transistors (OFETs). AFM microstructural investigations demonstrate the facile molecular alignment of NR-P3HT by FTM leading to highly oriented macromolecular assemblies like fibrous domains with considerably enhanced  $\pi$ -conjugation length. FTM thin films of NR-P3HT not only show enhanced optical anisotropy (dichroic ratio >8) but also significantly improved FET characteristics. FTM films in its parallel orientation exhibited a significant improvement (>2 orders) in the FET mobility as compared to its spin-coated device counterparts.

Keywords: Poly(3-hexyl thiophene), Anisotropy, Orientation, floating film transfer

## Introduction

Recent past has witnessed the utilization of  $\pi$ -conjugated polymers as active semiconducting materials for the diverse applications in the fast-growing field of organic electronics owing to their facile processability and performance tunability by suitable processing conditions [1]. Amongst various conjugated polymers (CPs), poly (3-alkylthiophene) (P3AT) has been most extensively investigated towards its application as active semiconducting components for various electronic and optoelectronic applications owing to its solution processability along with the facile carrier transport [2]. Intractability of the electro-polymerized poly(3-hexylthiophene) (P3HT) led to the development of  $\text{FeCl}_3$ -mediated polymerization as solution-processable non-regiocontrolled (NR-P3HTs) (having moderate regioregularity of about 80 %) [3]. In this procedure, NR-P3HT can be synthesized with 3-hexylthiophene monomer and  $\text{FeCl}_3$  as oxidizing agent. Synthetic process is very simple and use very cheap reagents. On the other hand, synthesis of regioregular (RR) P3HT, demands, relatively much costly chemicals like 2,5-dibromo-3-hexylthiophene as monomer, air sensitive Grignard reagent as mediator and Ni-based complex as catalyst along with utilization of inert atmosphere. This leads to incur much higher cost of production as compared simple synthesis of NR-P3HT using oxidative polymerization. However, the lower mobility of NR-P3HT was found to be the stumbling-blocks for practical applications [4]. It was found that uncontrolled growth of polymeric chains along with the mixing of various regio-isomers were responsible for the poor carrier transport and hampered device performances. To circumvent this problem, a regio-controlled synthesis with very high head-to-tail coupling (regioregularity > 98 %) was developed [5] leading to not only improved carrier transport but also higher field effect transistor (FET) mobility as compared to their pure-regiorandom and non-regiocontrolled (NR) counterparts [3, 6]. This could be attributed to the fact that this regioregularity promotes the two and three dimensional ordering of polymeric chains via self-assembly in both of the solution as well as solid-states [7, 8].

Owing to the inherent one-dimensionality of  $\pi$ -CPs, development of polymers with high mobility needs comprehensive understanding of the intricate roles played by the molecular structures, their inter molecular packing and molecular orientations which affect and controls the finally achievable transport properties [9]. Various procedures have been reported to align the main chains of the organic CPs in order to fabricate oriented films leading to the enhanced electronic as well as optoelectronic properties [10]. Keeping these in mind, a number of methods such friction

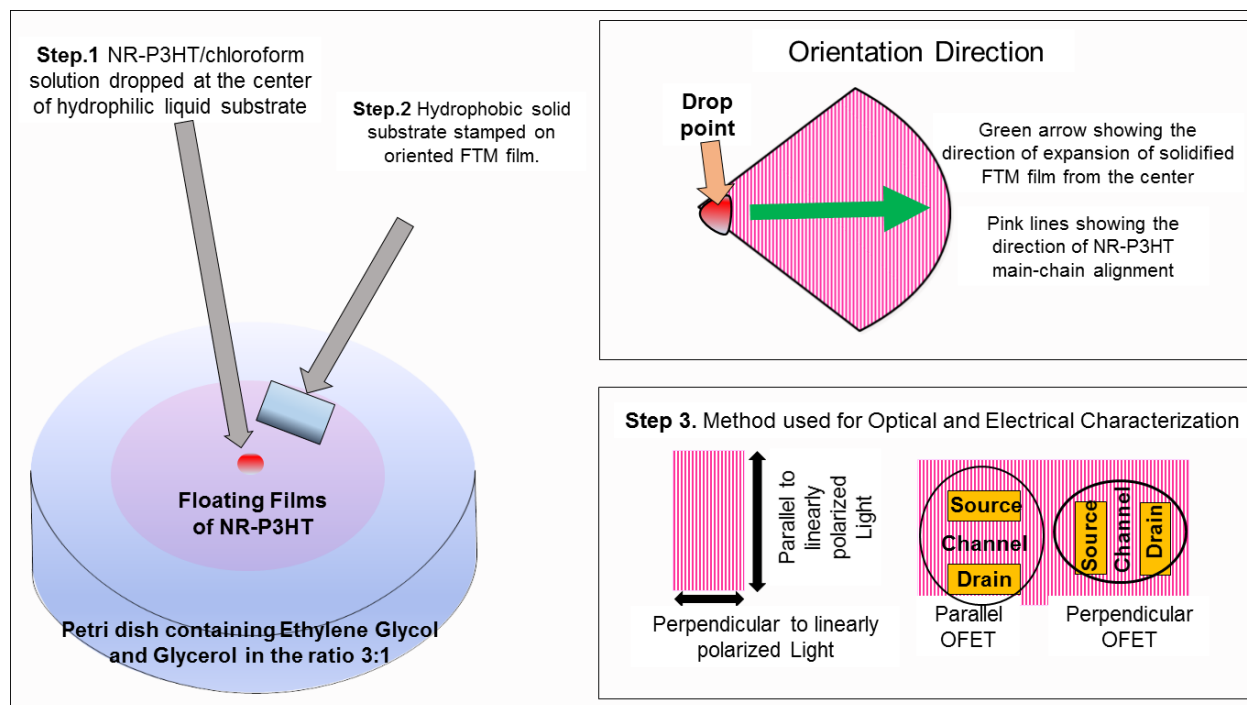
transfer [11], mechanical rubbing [10], high temperature rubbing [12], drawing [13] and solution flow [14] etc. have been attempted for the orientation of  $\pi$ -CPs aiming towards investigation of their implication on transport characteristics in organic FETs. Material wastage, chemo-mechanical damages to the underlying layers and possibility of multilayer coatings are still remaining bottle-necks in the currently employed orientation methods of CPs. Attainment of the facile coating of oriented and multilayer films is desired for the practical realization of highly anisotropic charge transport in electronic devices. In order to provide an amicable solution for such problems, we have proposed a simple and quick film fabrication method known as floating film transfer method (FTM) to prepare the oriented thin-film with minimal material wastage [15-16]. In this method, an oriented floating film is first casted on to an orthogonal liquid substrate followed by its transfer to a desired substrate by stamping.

In this article, we would like to report about the fabrication of OFETs utilizing NR-P3HT as active semiconducting material which is currently considered to be an abandoned conjugated polymer after the discovery of RR-P3HT and our novel dynamic-FTM for thin film fabrication. It has been demonstrated that NR-P3HT films fabricated by dynamic FTM not only exhibits the very high degree of molecular ordering but also leads to the tremendous enhancement (more than two order of magnitude) in the FET mobility as compared to its most commonly utilized spin-coated film counterparts.

## **Material and Methods**

NR-P3HT used in this work was chemically synthesized and purified as per our earlier publication using  $\text{FeCl}_3$  catalyst [17]. Regioregularity of the synthesized NR-P3HT was calculated by ratio of the peak area integration of  $^1\text{H-NMR}$  spectrum and was found to be about 80% as reported in our earlier publication [18]. 10 mg of NR-P3HT was dissolved in 1g of dehydrated chloroform to obtain 1 % (w/w) solution. As shown in diagrammatic representation of FTM (Fig.1), about 25  $\mu\text{l}$  of NR-P3HT solution was dropped on the optimum hydrophilic liquid mixture of ethylene glycol and glycerol in the ratio of 3:1 resulting in to the formation of oriented floating film on the hydrophilic liquid substrate after the natural evaporation of chloroform under ambient atmospheric conditions [18]. The orientation of the main chains of NR-P3HT was found to be perpendicular to the direction of film expansion from the center. This oriented floating film having thickness of

about 20 nm was then transferred on to the glass and SiO<sub>2</sub> substrates for investigation of optical properties and surface morphology, respectively. Films were washed thoroughly with methanol to remove any residual hydrophilic liquid adhered with the hydrophobic substrate prior to the characterization. As a reference, spin-coated films were also prepared from the 0.5 % (w/w) solution of NR-P3HT in chloroform by spin-coating at 3000 rpm for 120 seconds. Bottom gated top contact (BG-TC) OFETs were fabricated by using a highly p-doped silicon having 300 nm of SiO<sub>2</sub> as gate dielectric insulator (capacitance = 10 nF/cm<sup>2</sup>). For FTM deposited OFETs, substrates were spin coated with CYTOP at 3000 rpm for 120 seconds followed by annealing at 150 °C for 1 hour, resulting in to highly stable hydrophobic surface (capacitance = 8 nF/cm<sup>2</sup>). Owing to the existing fabrication problem of spin coating on CYTOP substrates, it was not possible to fabricate BG-TC by spin coating NR-P3HT solution in chloroform on CYTOP [19]. All the films were annealed at 60°C for 1 hour in argon chamber prior to electrode deposition. Source and drain electrodes were prepared by thermal evaporation of gold (50 nm) at a base pressure of 10<sup>-6</sup> Torr using a nickel shadow mask providing the length (*L*) and width (*W*) of the channel to be 20 μm and 2 mm, respectively. Output and transfer characteristics were measured in vacuum. Field effect mobility ( $\mu$ ) and threshold voltages ( $V_{th}$ ) were calculated from the transfer characteristics [20]. Transparent white glass and hexamethyldisilazane treated bare Silicon substrates were used for measurements pertaining to the normal/polarized electronic absorption spectra and atomic force microscopy (AFM), respectively. Polarized absorption spectra were measured using spectrophotometer (JASCO V-570) with Glan Thomson polarizing prism. Atomic force microscopic (AFM) images were taken under tapping mode by JEOL SPM5200 with Olympus probe (OMCL-AC200TS-C3). Sample thickness were measured by Interference Microscopy (Nikon Eclipse LV150). Optical dichroic ratio (DR) was used as a quantitative index for expressing the orientation characteristic and was calculated as per our earlier publication [16].

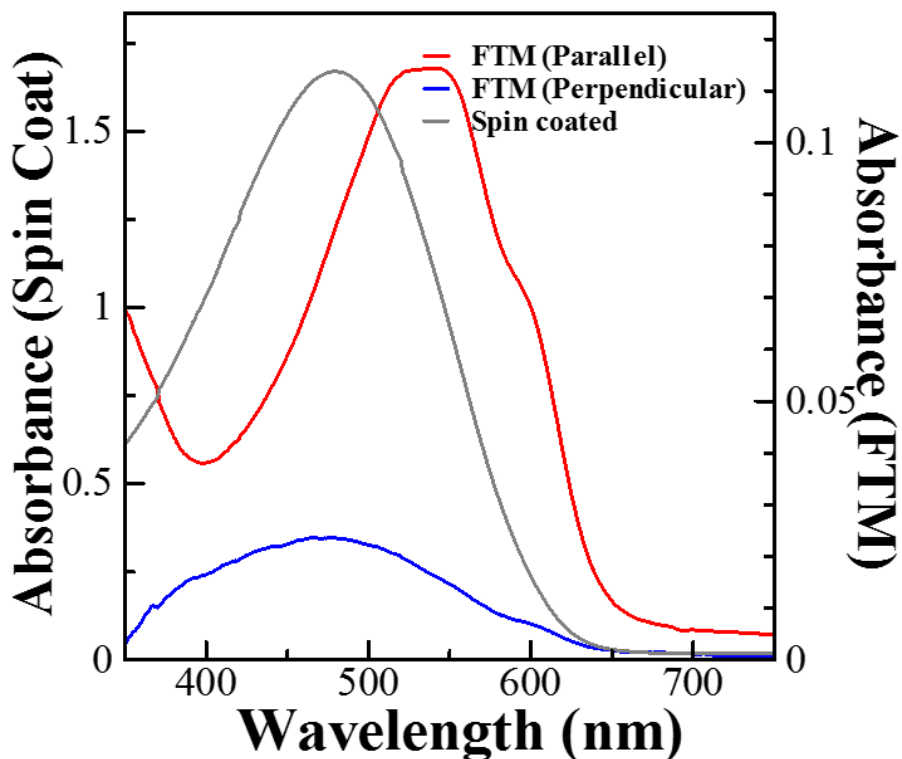


**FIG. 1.** Schematic diagram showing the FTM and selection of film direction for parallel/perpendicular orientation for optical and electrical characterization

## Results and Discussion

Figure 2 shows solid-state electronic absorption spectra of spin coated and FTM processed thin films. This figure indicates that spin-coated thin film exhibits a feature-less absorption spectrum with absorption maximum ( $\lambda_{\max}$ ) at 480 nm [21]. Although this peak has been attributed to  $\pi$ - $\pi^*$  electronic transition, it is reasonable to be assigned as 0-4 transition of P3HT based on Frank-Condon theory by the spectral analysis [7, 22]. Chen et al have reported that the main-peak wavelength of P3HT film exhibits a red-shift with the increase in the regioregularity of main-chain [6]. In the P3HT prepared by oxidative polymerization using  $\text{FeCl}_3$  [23], vibronic shoulders are very weak and sometime do not appear in the thin film-absorption spectra [24]. In contrast, regioregular (RR-) P3HT (regioregularity > 90 %) clearly shows vibronic modes along with the main  $\pi$ - $\pi^*$  peak in the absorption spectra [6, 25, 26]. The relative height of the vibronic shoulder absorption with respect to the main peak changes with the preparation procedure of the film [26]. This is attributed to the Huang-Rhys parameter varying with the conformational states of macromolecules [22]. On the contrary, FTM processed thin films of NR-P3HT shown in Fig. 2 exhibits two absorption peaks around 510 nm and 550 nm along with clear vibronic shoulder at

610 nm. This spectral profile is quite similar to those observed in RR-P3HT films prepared by spin-coating [26]. These findings indicate that only employment of NR-P3HT film formation by dynamic FTM instead of spin-coating provides a film with well-defined vibronic features having optical properties very similar to RR-P3HT.

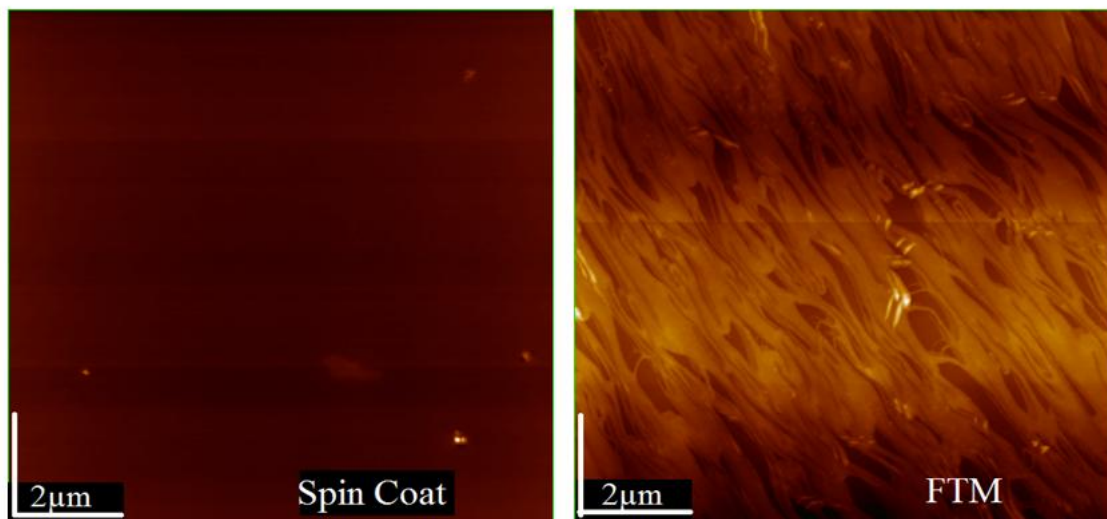


**FIG. 2.** Electronic absorption of spectra of spin-coated and FTM (parallel and perpendicular) thin films.

Fig. 2 also exhibits very good molecular orientation of NR-P3HT having high DR of 8.3. The spectral profile in perpendicular polarization is different from that in parallel polarization. Although similar characteristics were reported in the literatures for P3HT, but there is no clear explanation for this difference [8]. In the case of NR-P3HT, in accordance with the assignment of 480 nm peak in spin-coat film, the absorption spectrum of perpendicular-FTM film can be assigned to non-oriented part present in the film. Strong shrinking or bending form of macromolecules is possibly present in this part which is difficult to align like spin-coated film. To verify the high degree of molecular ordering in the FTM films of the NR-P3HT, AFM surface microstructural imaging was also conducted and results are shown in the Fig. 3. Tapping mode AFM image of the



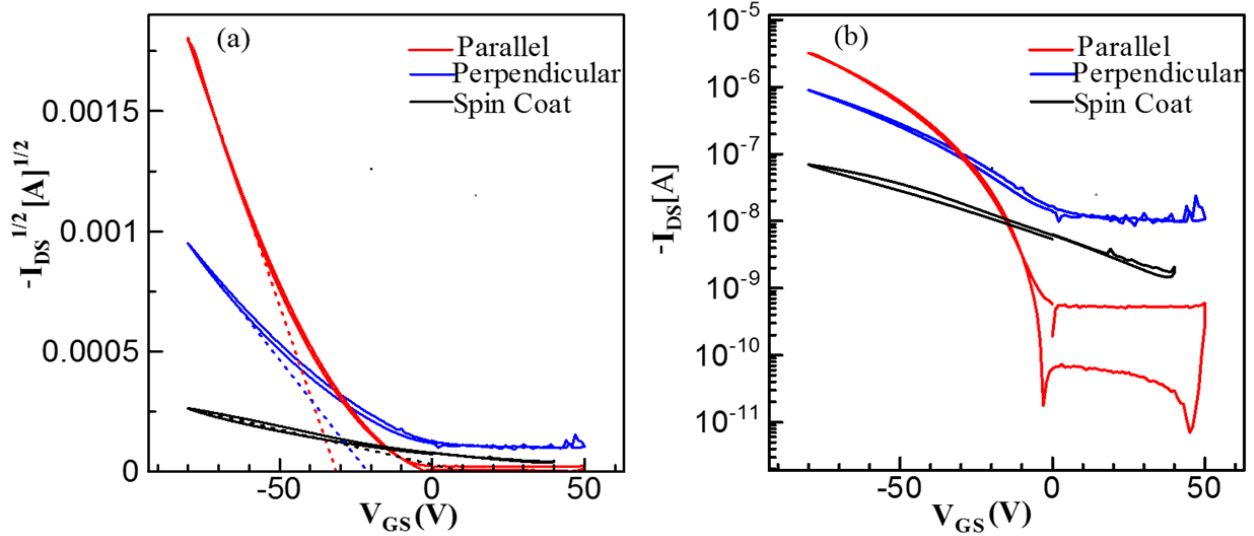
spin coated film exhibits highly smooth surface without having any distinguishable surface microstructure. On the other hand, AFM image of the oriented FTM film clearly exhibits highly aligned polymeric assemblies like fibrous domains which might be responsible for not only to the optical anisotropy but also to the highly aligned polymeric chains with extended  $\pi$ -conjugation and is in the well agreement with the optical absorption spectrum.



**FIG. 3.** Tapping mode AFM images of the NR-P3HT film fabricated by spin-coating (left) and FTM (right).

Excited by very good molecular alignment and high optical anisotropy in the FTM films of NR-P3HT, efforts were directed to investigate the implication of this striking structural morphology on the electronic characteristics by fabricating the OFETs. Fig. 4(a) shows the transfer curve of different OFETs prepared by FTM as well as spin coating. Various device parameters of the fabricated OFETs estimated from the out-put and transfer curves are summarized in the Table 1. It can be clearly seen that in the operational regime of the OFETs, there is very low hysteresis in the transfer characteristics. The field effect mobility ( $\mu$ ), in the parallel orientation of FTM films based FETs was  $3.4 \times 10^{-3} \text{ cm}^2 \text{v}^{-1} \text{s}^{-1}$  and higher than the FETs having perpendicular oriented films ( $6.5 \times 10^{-4} \text{ cm}^2 \text{v}^{-1} \text{s}^{-1}$ ) reflecting the anisotropic transport in the NR-P3HT. Interestingly, measured  $\mu$  in both of the orientations of FTM films exhibited more than two orders of magnitude increase as compared to the films fabricated by the conventional spin-coating. It can be seen from the Fig. 4(b) that FTM not only improves the mobility by  $>2$  orders of magnitude but also it

sharpens some other features like a clear ON voltage and increase in ON/OFF ratio which was almost unclear in the spin-coated OFETs.



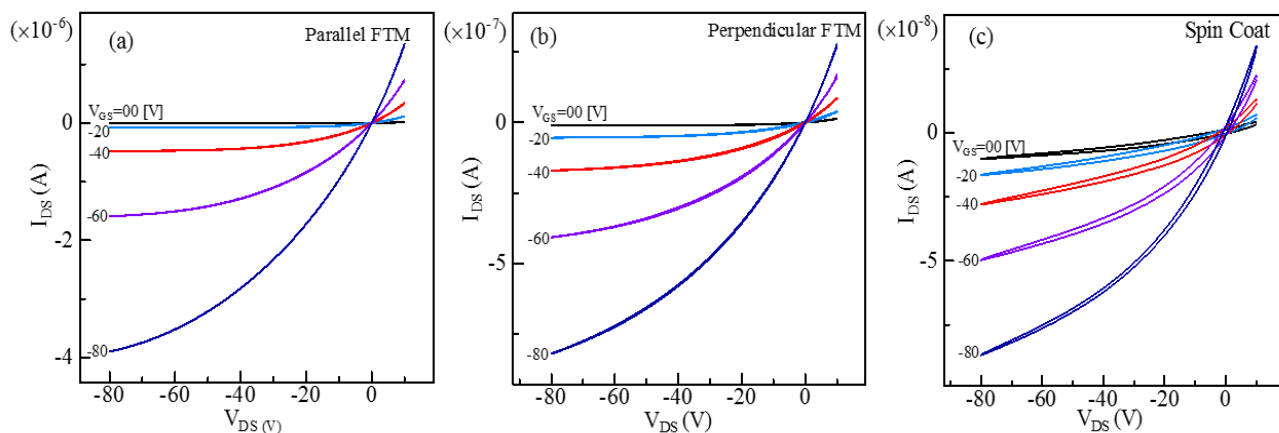
**FIG. 4.** Transfer characteristics (a), semi logarithmic plots (b) for the NR-P3HT based field effect transistors fabricated using thin films by spin coating and FTM (at  $V_{DS} = 80V$ ).

**Table 1** Device parameters in OFETs consisted of parallel and perpendicular oriented FTM along with the spin-coated NR-P3HT films.

	$\mu$ ( $\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ )	$V_{th}$ [V]	$V_{on-set}^*$ [V]	$I_{on}$ [A]	$I_{off}$ [A]	On/Off ratio
<b>Parallel</b>	$3.4 \times 10^{-3}$	-31	0	$3.23 \times 10^{-6}$	$1.91 \times 10^{-10}$	$1.69 \times 10^4$
<b>Perpendicular</b>	$6.5 \times 10^{-4}$	-21	10	$9.00 \times 10^{-7}$	$1.26 \times 10^{-8}$	$7.14 \times 10^1$
<b>Spin Coat</b>	$2.1 \times 10^{-5}$	7	unclear	$6.99 \times 10^{-8}$	$1.77 \times 10^{-9}$	$3.94 \times 10^1$

\*on-set voltage was defined as per the reference [27].

$I$ - $V$  characteristics of OFETs of all the configurations have been compared in Fig. 5(a)-5(c). Although every configuration have shown clear p-type transport characteristics but larger currents were observed in case of parallel FTM films as compared to perpendicular FTM and Spin-coated films. These results are in well agreement with the improvement observed in the transfer characteristics of each individual configurations.



**FIG. 5** Output Characteristics of NR-P3HT OFETs (a) parallel FTM, (b) perpendicular FTM and (c) Spin-coated films.

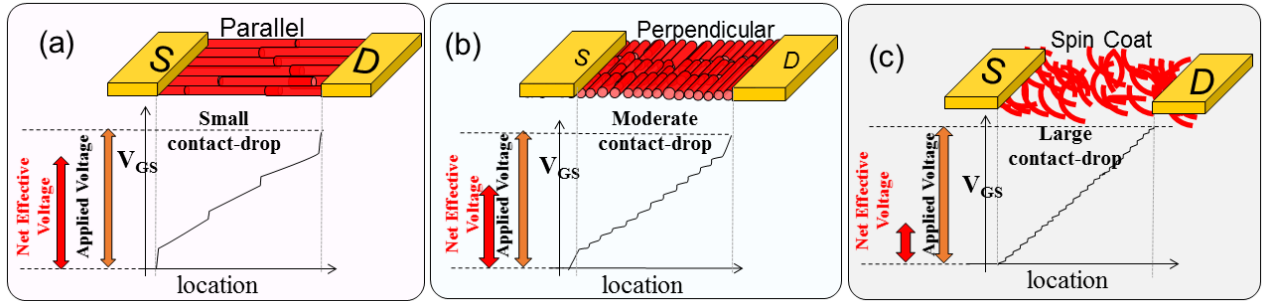
Considering the drastic difference in the spectra and the surface morphology of the films by casting methods, uniaxial extended fibrous-domains were formed in the oriented FTM films. In these oriented domains, NR-P3HT macromolecules are expected to be arranged in well-stretched conformation [22]. Charge carriers travel in these domains swiftly, the total carrier flow is limited by the hopping transport at neighboring domain boundaries or amorphous region. This causes relatively larger inter-domain resistance as compared to that at intra-domain region along with electric field. Thus, the electric potential strongly drops at inter-domain and remaining potential contributes to modulate the transport characteristics by the field-effect. This inter-domain number between source and drain, therefore, plays a key-role in the potential ratio of  $V_{GS}$  to drive FET.

This phenomena has been schematically shown in the Fig.6. The effective electric potential to drive FET largely applies to the channel of parallel FTM-film. In contrast, the FET with perpendicular FTM-film is consisted of rather more inter-domain rich channels. Since the higher ratio of applied potential is consumed at the inter-domains, the driving potential are reduced in the perpendicular FET. In the case of spin-coated films, domain size is thought to be very small owing to relatively shorter  $\pi$ -conjugation length as indicated by blue-shifted absorption maximum. In other words, macromolecules are expected to shrink or bend, thus fail to form large domains. In this case, the inter-domain characteristics are likely to be inter-molecular type, resulting in large potential drops while intermolecular hopping. This reduces the effective drive-potential for spin-coated FET. Such difference in  $V_{GS}$  distribution for each FET is the cause of different slopes in

transfer characteristics, i.e. the field-effect mobility, as listed in Table 1 even in the same potential region. The off-state also characterizes the field-effect modulation of carrier number in the channels. As found in Table 1 as well as in Fig. 4 (b), a very small off-current was obtained in the parallel-FET. This directly contributes to improve the on-off ratio of FET. Against this, for the perpendicular-FET, relatively large and constant off-current is persistent in the whole off-state (positive) voltage region. This leads to decrease in the on-off switching performance. In addition, a continuous decrease in the transfer current was observed in the entire gate-voltage region for spin-coated FET, which fails to show any clear off-state region unlike the FTM-based FETs.

One can argue that  $\mu$ , should also change with the field-effect but extent of this modulation in  $\mu$  is relative small as compared to the change in carrier numbers (therefore, we can obtain  $\mu$  as a value of the field-effect mobility). Thus, the modulation of channel conductance in FET is represented by the change in carrier number by the field-effect. Some carriers are stationary and the others are induced/depleted by the field-effect. Whole the carriers are consisted of the sum of the static carriers,  $n_s$ , and the field-induced carriers,  $n_{fe}(V_{GS})$ . Since the field-induced carriers are completely depleted at the ideal off-state region as  $n_{fe}(V_{GS\_off}) = 0$ , the on-off ratio can be simply represented by the ratio of carrier number as  $\{n_{fe}(V_{GS\_on}) + n_s\} / n_s$ . The very low off-current observed in parallel-FET indicates that the positive  $V_{GS}$  is effectively applied in the whole channel region to deplete the carriers. Against this, the observed large off-current in perpendicular-FET suggests that the perpendicular alignment generates some domains to be isolated from the transverse potential ( $V_{GS}$ ) application, in which the carrier number is stationary or insensitive to  $V_{GS}$  modulation. The former consists of the static conduction and the later relates to the subthreshold traps. These characteristics are in accordance with the drain current in transfer characteristics of perpendicular-FET. Relatively large off-current relates to the static conduction and the large subthreshold swing relates to the existence of various traps in perpendicular-FTM channel as shown in Fig.4. A clear on-set characteristic in parallel-FET indicates the sharp carrier injections in the whole channel at the same  $V_{GS}$ . This is probably due to the well-controlled  $V_{GS}$  application into many domains and facilitated by reduced potential drop at inter-domains. These characteristics are still observed but the sharpness of the injection is relatively weak with shifting positive potential of  $V_{on-set}$  due to increased inter-domain potentials [27]. For spin-coat film, huge and a variety small domains are responsible for carrier transport. The carrier number modulated

by a certain  $V_{GS}$  also depends upon the carrier path. Such variations in possible carrier path diversify the transport characteristics [26], which provides indefinite behaviors to switch between on- and off-states along with the negative shift of  $V_{th}$ . As a result, a clear on-set voltage is failed to appear in transfer characteristics for spin-coat film.



**FIG. 5.** Schematic representation showing possible transport mechanism in different orientations of NR-P3HT OFETs and respective voltage distribution for (a) parallel, (b) perpendicular and (c) Spin-coated films.

## Conclusion

In summary, FTM has been used as a novel thin film fabrication method for the preparation of highly oriented thin film of NR-P3HT towards its application as active material for OFET. Implementing this method has resulted in the formation of highly oriented domains of NR-P3HT having high optical dichroic ratio of 8.3. NR-P3HT based OFETs with FTM processed film exhibited a pronounced enhancement in the field effect mobility along with the anisotropic carrier transport as compared to that of spin-coated film. The anisotropic behavior and highly facile carrier transport in FTM films is attributed to both of the well-organized inter-domain and intra-domain transport characteristics along the FET channel.

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