Chapter 3

P3HT BASED FIELD EFFECT TRANSISTORS

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3.1 Introduction

Nowadays conducting polymers are playing very essential role in electronics industry to provide unprecedented flexibility. Conducting polymers are classical organic semiconductors which have lot of advantages over the traditional semiconductors, such as, very good solution processibility, mechanical flexibility, and compatibility with a number of flexible substrates. Organic devices can be fabricated at low cost with wide coverage area even at low temperature [Caboni *et al.* (2009), Sokolov *et al.* (2009)]. Active layer of organic devices such as organic solar cells, light-emitting diodes, OTFTs, memory devices, smart cards, sensors *etc*. [Singh *et al.* (2006), Bao *et al.* (1996)], is made by depositing the organic semiconductors using several dry and wet thin-film coating techniques. The band gap (E_g) in an organic material mostly depends on the π-conjugate length or quantity of monomer coupled with a polymer chain. Regioregular conducting polymers of high molecular weight shows small band gap, whereas, oligomers, and random polymers of low molecular weight has large energy band gap.

From a variety of solution processable organic semiconductors, poly-3-hexylthiophene (P3HT) is widely studied and applicable p-type active material in various micro and nano organic electronic devices so far. A few excellent properties such as good solubility, processibility, regioregularity, chemical stability, relatively high field-effect mobility, and wide commercial availability make this material (P3HT) very much suitable for organic electronic devices applications [Yan *et al.* (2009), Sun *et al.* (2005), Tusumura *et al.* (1986), Singh *et al.* (2008), Valadares *et al.* (2009), Xue *et al.* (2005), Assadi *et al.* (1988), Cui *et al.* (2003), DeLongchamp, *et al.* (2007)]. P3HT exhibits high mobility due to its self-ordered conjugated lamellar configurations that enhance strong π-π interchain interaction [Liang *et al.* (2010)]. Regioregularity means, each 3-hexylthiophene unit in the polymer chain is oriented such that residue group C_6H_{13} is either head to head or head to tail. Therefore, regioregularity of P3HT enhances the device mobility and other performance due to self-organization and ordering inside the deposited thin-film. High regioregularity in P3HT tend its molecules to stack together which leads to the overlapping of orbitals to form delocalized state along polymer backbone which assists charge transport for current conduction. Due to high oxidation potential, P3HT (doped or undoped) shows better environmental stability compared to various other organic semiconductors [Oosterbaan *et al.* (2009), Cosseddu *et al.* (2012), Tiwari *et al.* (2014)]. Recently, the technique preferred for synthesis of regioregular P3HT is called Kumada catalyst transfer polymerization (KCTP) or also referred to as Grignard metathesis polymerization (GRIM) [McCullough *et al.* (1998), Kiriy *et al.* (2011)]. This technique is preferred due to ready availability of reagents, moderately suitable reaction conditions, and quite fast polymerization. In the first step of the synthesis, Grignard monomer is prepared by the basic reaction between 2,5- dibromo-3-hexylthiophene and alkyl magnesium chloride. After that, polymerization starts while required amount of Ni(II) (catalyst) is added in the monomer solution. This polymerization stops after the consumption of all Grignard monomers. Several research groups [Loewe *et al.* (2001), Yokoyama *et al.* (2004), Senkovskyy *et al.* (2010), Bronstein *et al.* (2009)] reported the controlled polymerization of P3HT along with high molecular weights, by small variation in the general synthesis technique. This synthesis technique provides small quantity of throughput; therefore, for large scale production and also for controlled growth, high molecular weight and regioregularity continuous-flow synthesis method is used [Seyler *et al.* (2013)].

Conduction property in P3HT thin-film depends on the molecular ordering of the film [Komino *et al.* (2008)]. Solution processability of P3HT offers inexpensive, large coverage area and structural flexibility as they permit for screen printing, spin-coating, spray-coating, floating film transfer coating, and ink-jet printing [Berggren *et al.* (2007), Morita *et al.* (2009)]. From a variety of coating techniques, spin-coating is usually preferred due to very easy and inexpensive coating technique. Thickness of spin coated thin-film is very much dependent on many factors such as the solution concentration, rotation speed, coating time and viscosity of the solution. Generally spin coating technique is preferred for fabrication of solution processed organic devices such as organic transistors.

From the last twenty five years, OFETs are receiving very much curiosity owing to their low cost, easy processing, and flexibility for the potential application in the domain of electronic papers flat-panel displays, electronic nose and tongue, electronic identification tags, smart card, large-area display devices, and many other flexible electronic devices. In addition, low processing temperature and batch fabrication technique are also very useful to encourage the numerous advantages of the OFETs. Recently, it has been reported [Sirringhaus *et al.* (1998), Sirringhaus *et al.* (1999), Wang *et al.* (2003)]. that the field-effect mobility and ON/OFF ratio of OFETs based on regioregular P3HT are comparable to the mobilities and ON/OFF ratio of amorphous silicon FETs in which field-effect mobilities and ON/OFF ratio range are from 0.1 to 1 cm^2/Vs and from 10^6 to 10^8, respectively. The performance of an OFETs is highly dependent on the value of their performance parameters, which is influenced by the device configuration, organic solvent used to coat the OFET channel with organic semiconductor and the film morphology of deposited thin-film. P3HT based OFETs can be fabricated with novel approaches for moderately stable performance. The particular curiosity of P3HT with higher molecular weight and regioregularity for the active channel material in OFETs are generally due to their self-organizing properties in forming microcrystalline structures which support proficient charge carrier movement through the film. Therefore, P3HT of higher molecular weight and regioregularity exhibits good field effect mobility amongst various known solution processable p-type organic semiconductors. It has been reported [Bao *et al.* (1996), Kline *et al.* (2005), Sirringhaus *et al.* (1999)]. that the charge carrier mobility of RR-P3HT depends drastically on the factors such as thin-film preparation method, solvents used, gate insulator materials, and pretreatment of the gate insulator. The stable functionality of this polymer (P3HT) makes it more suitable for development of organic thin film transistors.

3.2 Experimental Details

Organic field effect transistors were fabricated in bottom-gate, top-contact configuration as shown in Fig. 3.1. The square substrates (p^+-Si/SiO_2) of defined dimensions of area 1 cm^2 were prepared from a circular wafer (p^+-Si/SiO_2) disc, and were treated in a number of wet processes to make them suitable for OFET fabrication. Firstly, the substrates were cleaned in a mixer of aqueous solution of distilled water, hydrogen peroxide, and aqueous ammonia of defined amount (2:1:1). This treatment was done for approximately 1:30 h at temperature 100 ^oC to make SiO_2 surface smooth, dust free, and to minimize the organic impurities present at the surface. This treatment also was to make the surface hydrophilic, which meant that OH group was present at the surface [Tiwari *et al.* (2014)].]. After cooling, substrates were removed from the solution and further washed with distilled water followed by drying them through blower. Finally, the substrates were kept for 12 to 18 h in a closed glass vessel containing a solution of dehydrated toluene and octyltrichlorosilane (2-3 drops). This treatment provided hydrophobic surface of substrates (p^+-Si/SiO_2) which was very much compatible with organic solution. Later, after removal from this solution, these substrates were again washed with dehydrated toluene, and dried at 100 ^{o}C for 15 min. These were the substrates ready for OFET fabrication. Further, a P3HT solution of concentration 0.2 wt% was prepared in dehydrated chloroform which is a very good solvent for P3HT. This solution was deposited at the top of the substrates to form a semiconducting film. Spin coating technique was used to deposit the thin-film. The solution was coated with 1000 rpm for 10 s followed by 3000 rpm for 50 s. In total, eight samples were prepared successfully for OFETs fabrication. These spin coated samples were further annealed at 80 °C for 1 h in ambient condition in order to remove the residual solvent through the thin film and also to boost the interaction among the substrate surface and active thin film. The thickness of the film was measured in the range of 45~50 nm by using DEKTAK 6M Profiler. The thin-film morphology of spin coated P3HT film was studied using Atomic Force Microscopy (AFM). Further, the gold electrodes (source, and drain) of thickness 40 nm were deposited at the top of the coated thin-film using Ni-shadow mask by thermal vapour deposition method in high vacuum (2×10^{-6} torr). Theoretically these two gold electrodes offer sufficient charge carriers to the respective energy bands for proficient flow of drain-source current in the deposited organic semiconductor thin-film. The terminals (source, drain, and gate) for electrical connections were made by using thin copper wire of diameter 0.1 mm, and silver paste. Electrical characteristics of the fabricated OFETs were measured through Semiconductor Parameter Analyzer at a vacuum of 4×10^{-6} torr. The microstructure of P3HT thin-films were studied by using AFM.

3.3 Results and Discussion

The schematic 3-D structure of bottom-gate top-contact OFET is shown below in Fig. 3.1.

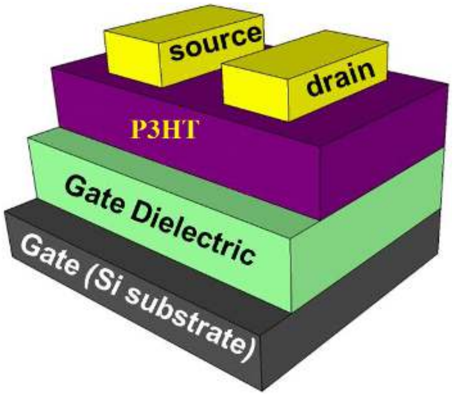
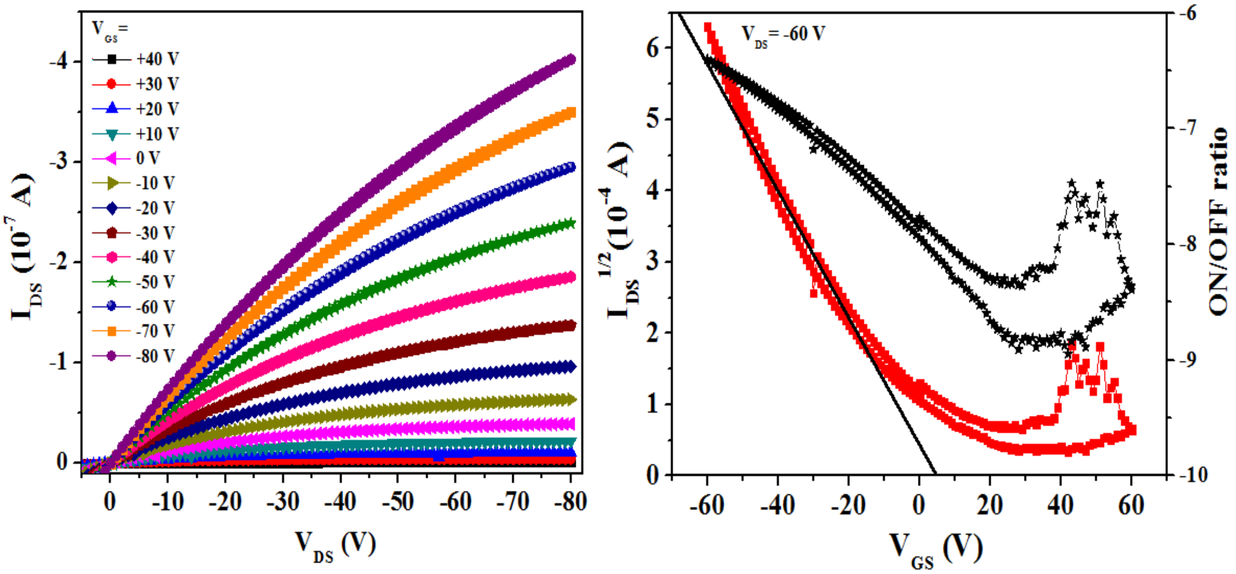


Fig. 3.1 Schematic 3-D structure of bottom-gate top-contact OFET

Fabricated OFET was operated in accumulation mode for negative applied gate-source voltages (V_{GS}) and in depletion mode for positive applied gate-source voltages. Therefore, it is clear from the I-V characteristics that device configuration is “normally on” type p-channel OFET. The output and transfer characteristics of the device were shown, respectively, in Fig. 3.2 (a) & (b). As the negative V_{GS} was applied across the electrode terminals, positive carriers get induced at the interface of organic layer and insulating layer, and if the Fermi level of electrodes would match with the HOMO level of organic material then carriers would start to move from the channel while appropriate drain-source voltage was applied. Measured I-V characteristics were used to extract the various device performance parameters like carrier mobility (μ) in saturation region, ON/OFF current ratio, threshold voltage (V_{TH}), subthreshold slope (SS) and transconductance (g_m). The thin-film morphology of spin coated P3HT film was measured using AFM, shown in Fig. 3.3. The AFM measurement was done for the scanning area of 5×5 μm^2 and 1×1 μm^2. The inset of Fig. 3.3 corresponds to the measurement for the area 1×1 μm^2. A flat and uniform surface was observed for the scanning film area of 5×5 μm^2. Spherical P3HT molecules of diameter 8~10 nm were observed for the zoom scanning as shown in the inset of Fig. 3.3.



(a) **(b)**

Fig. 3.2 The I-V characteristics of P3HT based OFET (a) output, (b) transfer characteristics

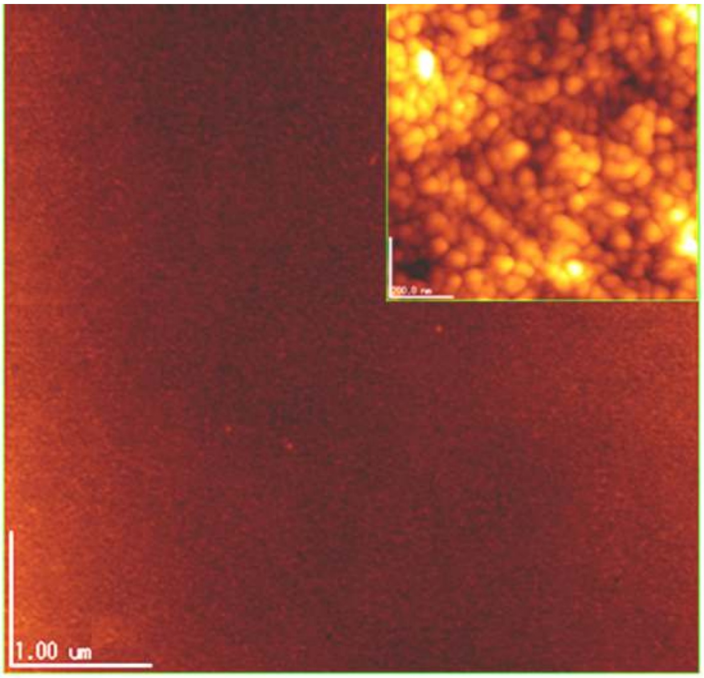


Fig. 3.3 AFM image of the spin-coat P3HT thin-film. The scan area dimension is 5 μm×5 μm; inset scan area dimension is 1 μm×1 μm.

The field-effect mobility in the saturation region [Briseno *et al.* (2008), Saragi *et al.* (2005), Xue *et al.* (2005)] can be calculated by using the formula

$$\sqrt{I_{DS}^{sat}} = \sqrt{\frac{W \mu_{sat} C_{OX}}{2L}} \left(V_{GS} - V_{TH} \right) \quad (1)$$

where, I^{sat}_{DS} is the drain current in the saturation region, L is the channel length, W is the channel width, C_{OX} is the capacitance per unit area (10 nF/cm^2) of the insulating layer. The threshold voltage is the minimum gate voltage required to induce the conducting channel. This value is obtained from the transfer (I_{DS} vs. V_{GS}) characteristics.

Threshold voltage was estimated by the extrapolation of a tangent line drawn on $I_{DS}{}^{1/2}$ versus V_{GS} curve at $V_{DS} = -60$ V, and the value was found to be +5 V as shown in Fig. 3.2(b). Positive threshold voltage shows that the device is “turned on” in depletion mode; therefore, it is clear that the fabricated OFET was “normally ON” type device. The carrier mobility in the saturation region shows the processing speed of a device and this was calculated for our case by determining the slope of the curve $I_{DS}{}^{1/2}$ versus V_{GS} drawn at $V_{DS} = -60$ V, and the measured mobility value was 2.01×10^{-4} cm^2/Vs. Another important key parameter for the OFET is ON/OFF current ratio ($I_{ON/OFF}$). This ratio characterizes the capability of the device to control a signal “ON” and “OFF.” It is calculated by taking the ratio of maximum (“ON”) I_{DS} and minimum (“OFF”) I_{DS} values. Mathematical expression for $I_{ON/OFF}$ [Saragi *et al.* (2005)] is given by

$$I_{ON/OFF} = \frac{I_{DS}\left(V_{DS}, V_{GS\,\max}\right)}{I_{DS}\left(V_{DS}, V_{GS\,\min}\right)} \quad (2)$$

The measured value of ON/OFF ratio for the fabricated device was found to be in the order of $10^{2.5}$. Subthreshold slope (*SS*) is a rate by which I_{DS} in decades varies with V_{GS} for a device operated in the subthreshold region. The value of S*S* is extracted by putting a linear fit to the log(I_{DS}) just as the current starts to increase. Mathematical formula for subthreshold slope is given by [McDowell *et al.* (2006)]

$$SS = \frac{\partial[V_{GS}]}{\partial[\log_{10} I_{DS}]} \tag{3}$$

and its value was found to be 12 V/dec. Transconductance (g_m) of the device for saturation region at a constant V_{DS} was calculated through [Chang *et al.* (2011), Samitsu *et al.* (2010), Kudo *et al.* (2001)]

$$g_m = \frac{\mu C_{OX} W}{L}\left(V_{GS} - V_{TH}\right) \tag{4}$$

and it was found to be 18 nS.

3.4 Conclusion

Poly-3-hexylthiophene of high purity and molecular weight was prepared in the lab and further used for OFET fabrication. The surface morphology of the spin coated P3HT thin-film was examined through AFM. The spin coated P3HT based OFETs were fabricated at room temperature under ambient conditions. The electrical (I-V) characteristics were measured in high vacuum conditions in order to get high accuracy and good performance of the OFET. The various important parameters were calculated by using I-V characteristics and some mathematical equations. Measured parameters showed good performance of an OFET. Further improvement in the performance was obtained by just doping and changing the morphology of P3HT active channel thin-film, which is reported in the coming chapters. .