*Chapter 6*

# TCNQ DOPED P3HT BASED FIELD EFFECT TRANSISTORS

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## 6.1 Introduction

π-conjugated organic semiconductors are enormously used as active layers in the design of usually all kinds of microelectronic and polymer electronic devices in recent days. Compared to traditional inorganic semiconductors, organic semiconductors possess many unique-advantages like, low cost, solution-processable, synthesizable in large-scale, flexible and are compatible with plastic substrates, processable at low temperatures and provide large coverage area. The conductivity of the organic semiconductors can be modulated from insulator to conductor generally by introducing the dopants, but also by modulating the polymeric factors such as the backbone, regularity, nanometric-structure and polymer composites [Tiwari *et al.* (2014), Tiwari *et al.* (2012), Liu *et al.* (2009), Briseno *et al.* (2008)].

In a variety of organic semiconductors, poly-3-hexylthiophen (P3HT) is broadly studied due to its special features [Briseno *et al.* (2008), Urien *et al.* (2007), Saragi *et al.* (2005), Chang *et al.* (2011), Xue *et al.* (2005), Bielecka *et al.* (2011), Scavia *et al.* (2008), Grigorian *et al.* (2011)], and its high semiconductor-performance in a number of organic electronic devices. P3HT exhibits self-organizing property due to the joining of head-to-tail hexyl chains, and also due to the fine π-π interchain stacking nature [Bielecka *et al.* (2011)]. Such interaction amongst P3HT molecules in a deposited thin-film results in a lamella structure of two distinct orientations with mobility variation in the order of more than 100 [Liang *et al.* (2010)]. The electrical conductivity and microstructure of the P3HT thin-film can be influenced by a range of issues such as

polymer purity, regioregularity, doping, and film deposition techniques [Kline *et al.* (2003), Zen *et al.* (2004), Majewski *et al.* (2006)].

Doping of P3HT with a number of electron acceptor components is a suitable and widely used technique to enhance the conductivity as well as air stability of P3HT [Sainova *et al.* (2007)]. Charge injection by molecular doping is a key approach to improve the performance of various electronic devices such as organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs). Molecular doping of P3HT (act as donor) with a very good electron acceptor 7,7,8,8 tetracyanoquinodimethane (TCNQ, molecular formula $C_{12}H_4N_4$) has been extensively studied in the applications of advance organic electronic devices due to its high conductivity. Soluble P3HT and TCNQ form charge transfer complexes which enhance the electrical property of TCNQ/P3HT thin-film. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of charge transfer complexes are formed due to the hybridization of donor's (P3HT) HOMO and acceptor's (TCNQ) LUMO levels [Pingel *et al.* (2012)]. These complexes exhibit non-metallic characteristics owing to the finite energy band gap between their HOMO and LUMO levels [Pingel *et al.* (2012)]. A lot of distinct local conformations in P3HT/TCNQ charge transfer complexes are anticipated owing to the flexibility and various inter-chain interactions in the polymers. This results in change of the electronic structure of the doped film; and therefore, transport properties of the TCNQ doped P3HT thin-film gets improved. A strong charge transfer mechanism occurs amongst the P3HT and TCNQ which leads to change in the molecular conformation to enhance the conductivity. The hole density increases linearly with increasing doping concentration of TCNQ in P3HT, and hence, the conductivity of the doped P3HT film improves with doping concentration.

Organic field-film transistors (OFETs) are very attractive and gaining great deal of attention due to their cost-effective, low-weight, and flexible fabrication properties with promising applications in integrated circuits, digital switches, electronic barcodes and papers, radio-frequency identification tags, and chemical sensors, however; they have low mobility [Chao *et al.* (2010), Sengez *et al.* (2013), Surya *et al.* (2013), Li *et al.* (2013), Chen *et al.* (2013), Ma *et al.* (2008)]. The OFETs' performance is characterized by the parameters such as threshold voltage, field-effect mobility, sub-threshold slope, and ON/OFF current ratio. These parameters are strongly dependent on the channel materials, film deposition techniques as well as the degree of crystalline and molecular ordering in the microstructure of semiconducting polymer film coated at channel.

Recently, many doped OFETs have been studied [Ma *et al.* (2008), Abe *et al.* (2005), Rikitake *et al.* (2003), Samitsu *et al.* (2010)]. Doping of active layer of an OFET causes a shift in Fermi-level such that efficient free charge carrier injection takes place between metal/polymer interfaces which improves the conductivity of the channel film. Recently, L. Ma *et al*. [Ma *et al.* (2008)] reported that the mobility of F4TCNQ doped P3HT FET was increased approximately thirty folds compared to pristine P3HT FET; however, the threshold voltage can be controlled by varying the doping concentrations. Similarly threshold voltage of a pentacene FET can also be controlled by putting a additional thin-film of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) on top of the pentacene channel [Abe *et al.* (2005)].

It is well known that the organic semiconductor shows diode characteristics with gold (Au) and aluminum (Al) as anode and cathode. The Al/P3HT interface is a typical example of schottky junction. Oxidative metals supply electrons to the p-type organic semiconductor which results in a depletion layer build up in the p-type semiconductor. The depletion layer formed at Al/polymer interface is responsible to generate

rectification characteristics. In this region, all the acceptor levels in the polymer are filled by electrons supplied from Al layer. It is demonstrated that the conductance of pi-conjugated polymer thin-film is reduced by over-coating of a thin (less than 10 nm) Al film [Rikitake *et al.* (2003)]. An extra-thin Al may not form a uniform thin film but forms particles, which will provide electrons to build depletion region but not conductive.

In this chapter, we have fabricated top-contact "Normally-ON" type TCNQ doped P3HT field-effect transistors and studied the effect of molecular doping concentrations on the electrical performance of OFETs. Here, we have also studied the effect of Al thin-film coating on the highly doped OFET performance. The microstructures of doped and undoped P3HT films were also compared.

## 6.2 Experimental Details

Regioregular poly-3-hexylthiophene (P3HT) was synthesized and purified in the lab [Tiwari *et al.* (2014)] and doped with 7,7,8,8-tetracyanoquinodimethane (TCNQ) (purchased from Tokyo Kasei Co). A range of TCNQ doped P3HT solutions (1%, 5%, 10%, and 20% in the number of TCNQ/unit of P3HT) were prepared by mixing 0.2 wt% P3HT/chloroform and 0.1 wt% TCNQ/acetone solutions. In order to prepare several molecular doping concentrations (1%, 5%, 10%, and 20%) of TCNQ in P3HT, initially a P3HT solution of 0.2 wt% concentration was prepared in chloroform which appeared orange in color. Similarly, a TCNQ solution of concentration 1 mg/ml (0.1 wt%) was prepared in acetone which appeared light greenish. TCNQ doped P3HT solution of lower doping concentrations (1% and 5%) were obtained by adding 10 mg and 50 mg TCNQ solution in each of the 400 mg P3HT solution, respectively. However; to get higher doping concentrations (10% and 20%) of TCNQ in P3HT, another TCNQ solution of 1 wt% concentration was prepared. To get 10% and 20% TCNQ doped P3HT solutions, 10

mg and 20 mg of TCNQ solution (1 wt%) was added in each of the 400 mg P3HT solutions, respectively. As P3HT solution was doped with TCNQ, immediately the color of the doped P3HT solution got changed from orange to blackish. Before spin coating, each doped P3HT solution was heated till the colour of the solution changed to orange. Thin-films of these prepared solutions were coated on several $p^+$-Si/$SiO_2$ substrates with coating speed of 1000 rpm for 10 s followed by 3000 rpm for 50 s. These spin coated samples were further annealed at 80 °C for 1 h and thereafter, the film thickness was measured by using DEKTAK 6M Profiler and was found to be 50-60 nm. Two electrodes (source and drain) of gold (40 nm) were deposited on top of the coated thin-films by using Ni-shadow mask. Thermal vapor deposition technique was used for the electrodes (source and drain) deposition, and the pressure inside the deposition chamber during deposition was maintained at $2\times10^{-6}$ Torr. The channel length and the width of the fabricated OFETs were kept 20 μm and 2 mm, respectively.

The microstructure of the films and the electrical characteristics of the OFETs were measured in the same way as described in the previous chapters.

### 6.3 Results and Discussion

Thin-film surface morphology of pristine P3HT and TCNQ doped P3HT films are shown in Fig. 6.1 (a-f). For P3HT film, a flat surface was observed, however, some particles like nanostructures were observed for all TCNQ doped P3HT films. In particular, a few particles got self-assembled and appeared as nanofibers with increasing TCNQ doping concentration in P3HT, as shown in Fig 6.1 (d) and Fig. 6.1 (e). It is already reported that in a comparative poor solvent, P3HT has a tendency to form nanofibers structure [Samitsu *et al.* (2010), Oosterbaan *et al.* (2009)]. Probably mixing process of P3HT/chloroform with TCNQ/acetone also supports these nano-structure formations. The morphology of the Al-coated TCNQ doped P3HT (Fig. 6.1 (f)) film was

very different from the others films microstructures. The whole surface was filled by the well-grown Al particles of diameter range 125-150 nm.

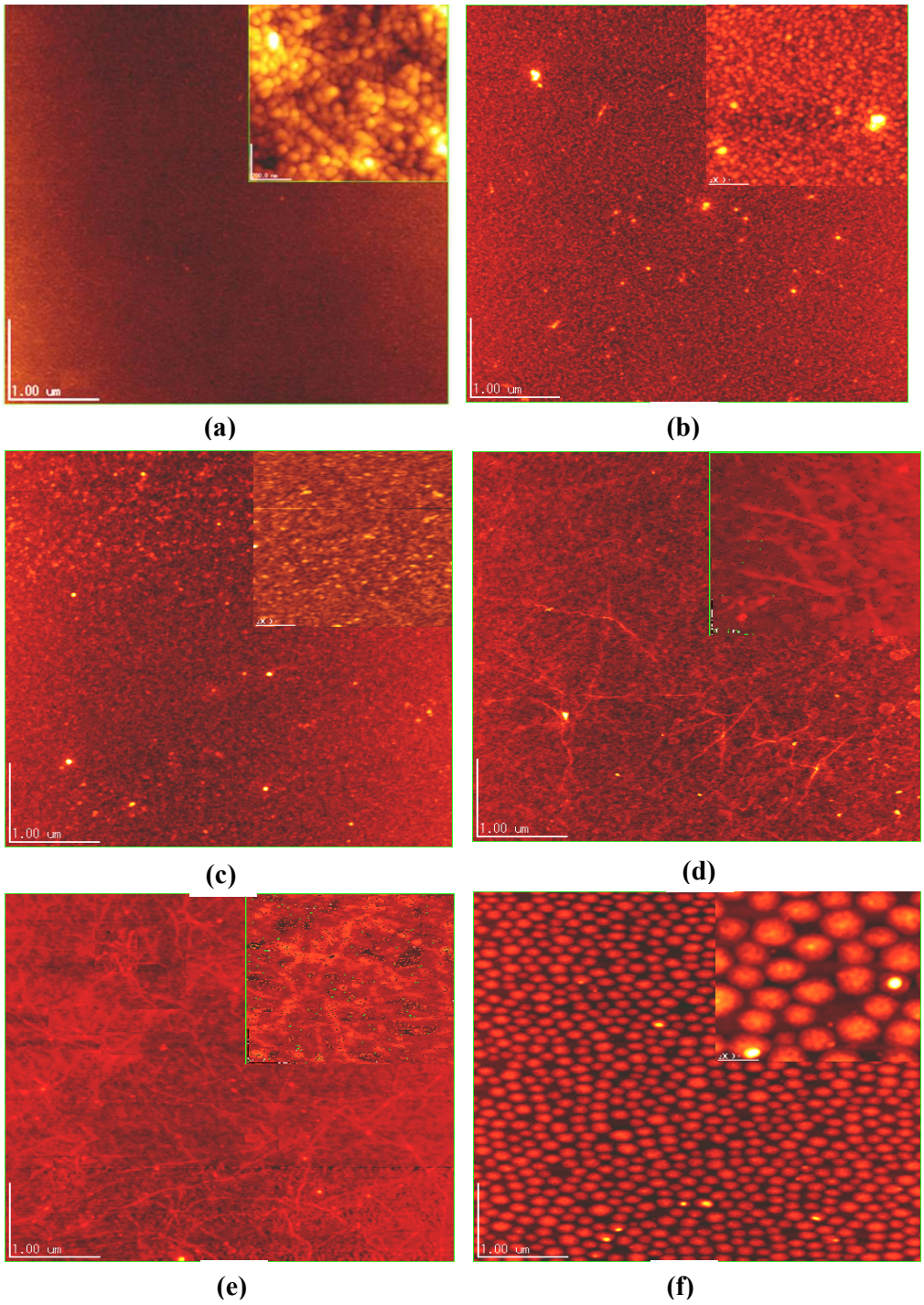


**Fig. 6.1** AFM images of P3HT and TCNQ doped P3HT films **(a)** P3HT, **(b)** 1% TCNQ, **(c)** 5% TCNQ, **(d)** 10% TCNQ, **(e)** 20% TCNQ and **(f)** 20% TCNQ with thin-Al coating. The scale bar represents 1μm (200 nm in the insets)

Figure 6.2 (a-d) shows the combined current-voltage (*I-V*) characteristics of the undoped and TCNQ doped P3HT FETs, and the 3D structure of optimized doped OFET. The output characteristics ($I_{DS}$ *versus* $V_{DS,}$ at fixed $V_{GS}$ = -60 *V*) for various concentrations (0 to 20%) of TCNQ doped P3HT FETs is shown in Fig. 6.2 (a). Similarly, a combined transfer characteristics ($I_{DS}^{1/2}$ *versus* $V_{GS,}$ at fixed $V_{DS}$ = -60 *V*) is shown in Fig. 6.2 (b).

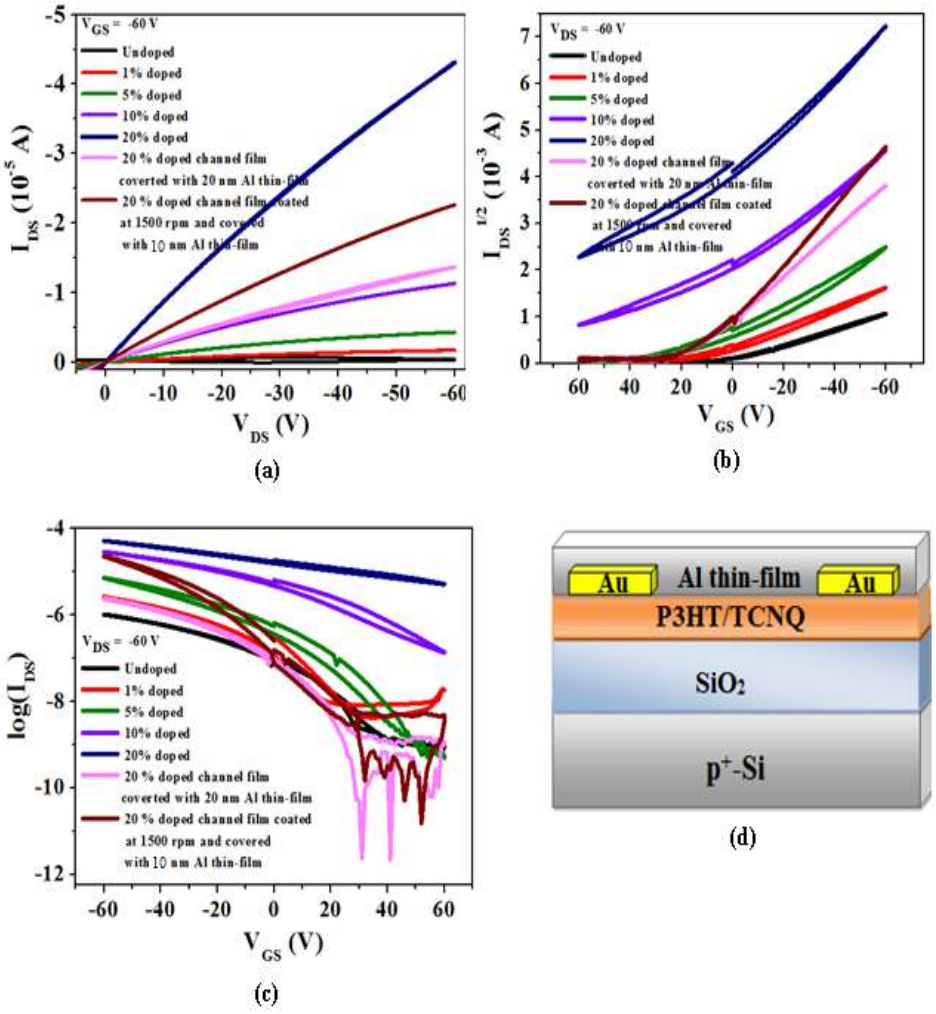


**Fig. 6.2** Combined I-V characteristics for a range (0 to 20 %) of TCNQ doped, and Al coated at highly doped (20 %) P3HT channel film based FETs (a) Output characteristics drawn for $V_{GS}$ = -60, (b) Transfer characteristics $I_{DS}^{1/2}$ versus $V_{GS}$ at $V_{DS}$= -60 *V*, to estimate the $V_{TH}$ for all fabricated OFETs, (c) log($I_{DS}$) versus $V_{GS}$ at $V_{DS}$= -60 *V*, to estimate the value of on/off current ratio for all fabricated OFETs, (d) Schematic structure of top-contact OFET, channel covered with Al thin-film (10 nm)

These characteristics (output and transfer) represent that the drain-source current ($I_{DS}$) of doped P3HT FETs was higher as compared to that for undoped P3HT FET, and $I_{DS}$ was increasing linearly with increasing TCNQ doping concentrations. From the output characteristics it was observed that $I_{DS}$ for each OFET was initially increasing following Ohm's law for lower applied drain-source voltages ($V_{DS}$), but later, got saturated for higher applied $V_{DS}$ values due to pinch off. All the OFETs were prepared under similar conditions in order to compare their performances with respect to the doping concentrations.

The key parameters (field-effect mobility, transconductance, subthreshold slope, ON/OFF ratio and threshold voltage) of OFETs characterize the device performance and these parameters are strongly dependent on several factors such as, polymer processing conditions, coating techniques, nature and quality of the semiconducting polymer coated at FETs channel. These parameters can be estimated from the measured output and transfer characteristics of the OFETs and a few mathematical equations, which are earlier discussed and given in Chapter 3. The calculated values of key parameters for all fabricated devices are summarized in the Table 6.1.

The field-effect mobility in the saturation region and transconductance for all fabricated OFETs were calculated and found that both were increasing with TCNQ doping concentrations. Threshold voltage ($V_{TH}$) at which "ON" current starts flowing through the device channel was calculated by extending the tangent line drawn on the $I_{DS}^{1/2} - V_{GS}$ curve such that it intersects x-axis at a particular vale of $V_{GS}$, and that the intercept value on x-axis where $I_{DS}$=0, was the device threshold voltage. The values of $V_{TH}$ estimated for all doped and undoped P3HT FETs are shown in Fig. 6.2 (b), drawn between $I_{DS}^{1/2}$ and $V_{GS}$ at fixed $V_{DS}$ = -60 *V*. It was found that $V_{TH}$ was shifting towards more positive values with increasing TCNQ doping concentrations in P3HT films. It was

because of the fact that the increased TCNQ doping concentration enhances the hole charge density in doped P3HT film. These dopant-induced mobile charge carriers fill the trap states present at the interface of $SiO_2$/doped P3HT as well as in the bulk of $SiO_2$. Therefore, increasing doping concentrations decreases the number of trap states. Threshold voltage can also be defined using the trap and release model as that voltage at which the entire trap positions get filled with induced mobile carriers and the conduction starts through the film [Horowitz *et al.* (1991)]. Hence increasing doping concentrations decreases the trap states and shifts $V_{TH}$ towards more positive values [Chao *et al.* (2010)].

**Table 6.1** Performance parameters of all fabricated transistors discussed in this chapter.

| **Channel Conducting Materials** | $V_{TH}$ **(V)** | $\mu_{sat}$ **($cm^2$/Vs)** | **ON/OFF current ratio** | ***SS*** **(V/dec.)** | $g_m$ **(nS)** |
|---|---|---|---|---|---|
| Undoped P3HT (0.2 wt%) | 5 | $2.01\times10^{-4}$ | $10^{2.5}$ | 12 | 18 |
| 1 % TCNQ doped P3HT | 12 | $7.13\times10^{-4}$ | $10^{3}$ | 15 | 58 |
| 5% TCNQ doped P3HT | 15 | $1.62\times10^{-3}$ | $10^{4}$ | 18 | 185 |
| 10 % TCNQ doped P3HT | 35 | $2.85\times10^{-3}$ | $10^{2.3}$ | 24 | 275 |
| 20 % TCNQ doped P3HT | 70 | $4.28\times10^{-3}$ | $10^{1.1}$ | 95 | 595 |
| 20 % TCNQ doped P3HT channel film covered with Al thin-film | 18 | $2.25\times10^{-3}$ | $10^{4}$ | 8 | 200 |
| 20 % TCNQ doped P3HT coated with 1500 rpm at channel and covered with Al thin film | 10 | $1.85\times10^{-2}$ | $10^{5.5}$ | 12 | 1165 |

Another key parameter of OFET is ON/OFF current ratio which characterizes the switching perfotrmance of a transistor. The ON/OFF current ratio was measured by taking the ratio of $I_{DS,sat}$ in the accumulation mode (on state) to the $I_{DS,sat}$ in the depletion mode (off state). Fig. 6.2 (c) is drawn between $\log(I_{DS})$ versus $V_{GS}$ at a fixed $V_{DS} = -60\ V$,

to estimate the values of ON/OFF current ratio for every doped and undoped P3HT FETs.

Subthreshold slope (S*S*) is the rate at which the drain current changes with gate voltage while the FET operates in the subthreshold region. The *SS* value is estimated by putting a linear fit to the log($I_{DS}$) just as the current starts to increase [McDowell *et al.* (2006)]. The S*S* is also associated with the surface trap density. It is well known that the surface trap density increases with TCNQ doping in p-type semiconductor. The calculated values of SS for all TCNQ doped and undoped P3HT FETs are listed in Table 6.1 which indicates that the subthreshold voltage region has increased with increasing TCNQ concentrations in P3HT FET channel. This finding is also supported with the literature [Yamagishi *et al.* (2012)]. The doping of P3HT with TCNQ increases the surface traps in the film which hamper the channel for getting on-set at linear regime. Therefore, in an OFET, doping of a p-type organic semiconductor with some strong acceptor (TCNQ) promotes the ON-state performance such as mobility and transconductance and decreases the on-set performance such as SS in subthreshold region.

From Table 6.1, it can be seen that $\mu_{sat}$, $g_m$, $S$, and $V_{TH}$ of OFETs were increasing with TCNQ doping concentrations (1%, 5%, 10%, and 20%), however ON/OFF current ratio initially increased for smaller doping concentrations in the range of 0 to 5% and then decreased for higher doping concentrations (10%, and 20%) in P3HT. The mobility of TCNQ doped P3HT FETs increased with doping concentration [Pinge *et al.* (2012)] owing to the formation of charge transfer complexes which improve the electrical conductivity of the doped film. Formation of a few nanofibers in the highly doped film as shown in the Fig. 6.1 (d) and (e), also raises the electrical conductivity of the TCNQ doped P3HT film. The doped TCNQ effectively generates a large number of mobile

holes in the P3HT film; therefore, free charge carrier density of TCNQ doped P3HT film increases. Increasing doping concentration also increases the electric-field strength at the interface of electrodes (source, drain) and organic semiconductor, which causes reduction in the ohmic contact (Au/doped P3HT) resistance due to the lowering of the image force [Zhang *et al.* (2010)]. The space between transport level and Fermi level is also reduced with increasing doping concentration. So, owing to these reasons, the charge injection rate from electrodes to the channel has enhanced. Therefore, increased carrier injection rate enhances the doped film conductivity as well as mobility [Chao *et al.* (2010), Tunc *et al.* (2012), Zhang *et al.* (2010), Koch *et al.* (2005), Coehoorn *et al.* (2005)].

From the Table 6.1, it can also be observed that the ON/OFF current ratio of TCNQ doped P3HT FET initially increases for smaller range (0 to 5 %) of TCNQ doping concentrations in channel film, and then decreases for high doping concentrations. It was analyzed from the output and transfer characteristics that with increasing doping concentrations, both currents ("ON" and "OFF") had increased. Enhancement in "ON" current was observed more compared to increase in "OFF" current for the smaller doping concentrations range (0 to 5 %) and thus, the ON/OFF current ratio improved for this range (0 to 5 %) of TCNQ doped P3HT FETs; however, for the higher doping concentrations (10 and 20 %), the increase in "OFF" current was more compared to the increase in "ON" current, so, the OFETs ON/OFF current ratio decreased. So, for the high doping concentrations of TCNQ in P3HT film coated at FET channel, the performance of the OFET degraded in term of ON/OFF current ratio.

Therefore, in order to overcome this drawback associated with highly TCNQ doped P3HT FETs, a smart technique was developed which drastically improved the device ON/OFF current ratio along with other performance parameters of the device. In this

technique, a metal (Al) ultra-thin-film (non conductive) of 10 nm was thermally deposited on top of the highly TCNQ doped P3HT FET channel which showed specific surface morphology as shown in the Fig. 6.1 (f). The interface of Al particles and doped P3HT film formed schottky contact which resulted in the formation of a depletion layer width in the channel. This depletion layer was responsible for decrement in the "OFF current" of OFET as well as the threshold voltage of the device. A large amount of decrement in the "OFF" current was observed due to Al coating at channel film; however, the effect of Al coating on the "ON" current was not significant. It was because the high level molecular doping of TCNQ in the P3HT channel film generated large amount of hole charge density in the conducting channel film whereas Al thin-film coated at the channel is an electron donator and reduced the number of conducting holes in the conduction channel film, but, only small reduction in "ON" current was observed due few electron-hole recombination in the channel compared to the generation of large amount of dopant-induced holes due to high TCNQ doping in P3HT channel film.

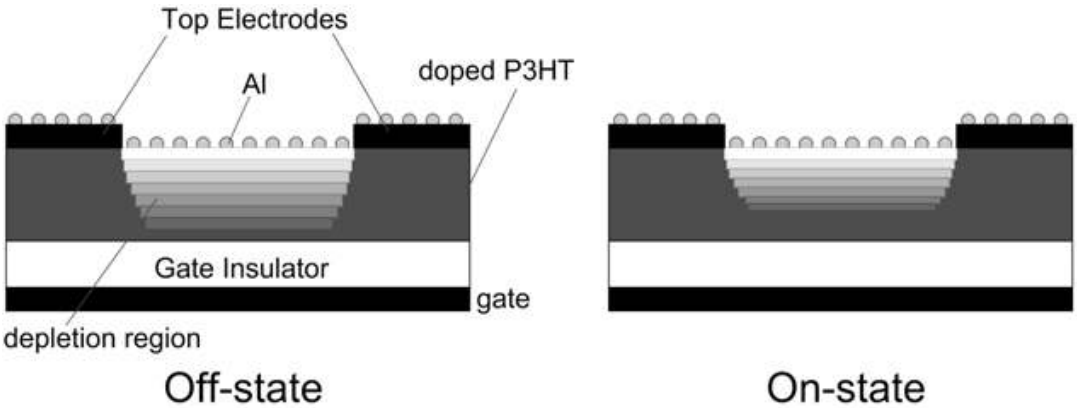


**Fig. 6.3** Structure of the OFF- and ON-states of doped-P3HT OFET with thin-Al-coating and the depletion layer formed in the channel. The relative conductance is represented by more darkness

Thus, due to the ultra-thin layer of Al coating at the conducting channel film, a small reduction in the "ON" current was observed, whereas a large decrement in "OFF" current was measured. So, the ON/OFF current ratio was greatly improved.

A significant decrement in the mobility was observed compared to the mobility of (20%) TCNQ doped P3HT FET without Al coating. It might be due to the deep penetration of depletion layer in the thin conducting channel film which reduces the effective channel width that supports the flow of maximum mobile carriers through the channel. So, due to insufficient effective channel depth, sufficient conducting carriers cannot transfer from source to drain in the channel which may be responsible for reduction in the drain current and mobility. Therefore, the thickness of the conducting channel film was increased to get sufficient effective channel depth (which supports high current through the channel) even after the formation of the depletion layer in the channel. The thickness of the doped conducting film was increased by reducing the speed of the spin coating unit to half (1500 rpm for 1 min) compared to previous coating speed. Now, the film thickness was measured and found to be approximately 170 nm. Further, an Al thin-film (10 nm) was deposited on top of this highly doped P3HT FETs. This large thickness ensured that despite the fact the schottky contact produced at Al/P3HT interface might have induced a depletion layer in the conducting channel, sufficient effective channel depth must be remaining for the transfer of maximum mobile carries through the channel. Therefore, a high "ON" current was flowing through the device channel and at the same time, a suppressed (minimum) "OFF" current was flowing due to Al coating. For this reason, the ON/OFF current ratio of the device got enhanced. Ultra-thin-Al-non conductive-coating at the highly doped channel provides clear off-sate and reduced threshold voltage which can be clearly observed in their transfer characteristics. So, the on-set performances of the transistor get improved by

reducing the subthreshold slope and threshold voltage. These findings specify that the electron-donating effect of a thin (nonconductive)-Al-coating to P3HT channel builds a thin depletion region surface in the P3HT layer. Therefore, the doping and the depletion contribute for better performance of the OFETs, the doping promotes the ON-state characteristics and depleting improves the OFF-state characteristics of the transistor. The "ON-state" and "OFF-state" of TCNQ doped P3HT OFETs with thin-Al-coating on the channel and the depletion layer formed in the channel is shown in the Fig. 6.3. The key parameters such as, ON/OFF current ratio, $\mu_{sat}$, $V_{TH}$, $g_m$ and *SS* of this device (Al coated 20 % TCNQ doped P3HT FET with active channel thickness of about 170 nm) were measured and the values were found to be $10^{5.5}$, $1.85\times10^{-2}$ $cm^2/Vs$, 10 V, 1165 nS and 12 V/dec, respectively. Hence, after comparing with the performance of all other doped OFETs fabricated, it was concluded that the best performance was obtained for Al coated 20 % TCNQ doped P3HT FET with slightly thick (~ 170 nm) conducting channel film.

**Conclusions**

In this chapter, doping method was used to improve the performance of an OFET. Here, a strong electron acceptor (TCNQ) doped P3HT OFETs were fabricated and the effect of doping concentrations on the OFET electrical performances, and thin-film structural morphology were studied. A range of TCNQ concentrations (0 to 20%) were used to dope the P3HT (0.2 wt%) film deposited at FETs channel. It was observed that the device mobility increased with doping concentrations, but the ON/OFF current ratio improved first for the lower molecular doping concentrations (0 to 5 %) and then decreased for higher doping concentrations (10% to 20%). To overcome this drawback, a metal (Al) ultra-thin-film was deposited on top of this device. The interface of the Al particles and doped P3HT films formed schottky contact, inducing a depletion layer in the channel which reduces the "OFF" current. However, there was also reduction in the

"ON" current due to Al thin-film coating, but this reduction was not significant due to the effect of high doping of TCNQ in P3HT film coated at the channel. Thus, there was an overall increase in the ON/OFF current ratio. However, the depletion layer induced in the channel due to Al thin-film coating decreased the effective channel depth which resulted in a slight decrease in the carrier mobility, and this was rectified by coating a slightly thicker film of highly doped TCNQ (20%) P3HT at the FET channel, so that enough effective channel depth was available for sufficient carrier transfer for conduction. With the slightly thicker highly doped TCNQ P3HT channel film coated with thin Al film on top, much improved performances were observed compared to others doped and undoped OFETs fabricated in this study. The carrier mobility for this device was approximately 93 times higher than the undoped P3HT FET. The ON/OFF current ratio had improved from $10^{2.5}$ (undoped P3HT FET) to $10^{5.5}$ (highly doped optimized device).

Thus, it can be concluded that the highly doped TCNQ P3HT FETs fabricated with thin Al film coating on top of the channel with slightly thick conducting channel film, gives overall improved performances as compared to the undoped as well as the doped channel OFETs without Al thin-film coating on top.