POLY(3-HEXYLTHIOPHENE) (P3HT) / GRAPHENE NANOCOMPOSITE BASED ORGANIC FIELD EFFECT TRANSISTORS

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4.1 Introduction

Nowadays organic field effect transistors (OEFTs) are used as fundamental component in micro- and nano-electronics devices. They have huge area of potential applications such as in digital switches, large-area display devices, gas sensors, RF identification tags, smart cards *etc*. [Brabec *et al.* (2001), Urien *et al.* (2007), Han *et al.* (2011)]. In recent years, a few OFETs are approaching the performance of traditional silicon FETs, therefore; such OFETs are preferred over silicon FETs in many applications.

Organic semiconductors are a new class of materials which promote the progress of plastic electronics due to their light weight and flexibility. They are used as conducting components in the production of a number of organic electronic devices such as diodes, batteries, solar cells, sensors and field effect transistors [Tusumura *et al.* (1986), Singh *et al.* (2008)]. Organic semiconductors show many fantastic properties such as inexpensive production, good processibility, high throughput, light weight, mechanical flexibility and huge opportunity in the area of fundamental research and applications [Yan *et al.* (2009), Singh *et al.* (2009)]. A popular conducting polymer, polythiophene and its derivatives such as poly-3-hexylthiophene (P3HT) are commonly used as active components in organic electronic devices such as photodiodes and field effect transistors in order to get high performance. P3HT shows high solubility, good processibility as well as stable

functionality which make it suitable for the fabrication of organic field effect transistors [Deen *et al.* (2004) Xue *et al.* (2005) Assadi *et al.* (1988)].

Compared to conventional semiconductor (silicon), organic semiconductors show poor carrier mobility and hence lot of research has been carried out for improving carrier mobility by developing modern materials and processing methods. Graphene, carbon nanotubes (CNTs) and many others carbon based materials exhibit excellent carrier mobility but suffer from poor ON/OFF ratio in the case of OFETs [Fuhrer *et al.* (2002), Snow *et al.* (2003)].

In 2004, first time graphene was discovered by Novoselov and Geim, and the synthesis techniques used was called mechanical exfoliation method [Geim *et al.* (2009)]. Graphene shows very good electronic properties and has hexagonal honeycomb arrangement in which carbon atoms are bonded with sp^2 hybridization. Graphene is a semimetal having excellent conduction capacity due to zero energy band gaps [Wang *et al.* (2011), Wang, *et al.* (2009), Wang *et al.* (2010), Liao *et al.* (2010)]. A number of investigations have been reported regarding the superb properties of graphene in conjunction with specific surface area of 2630 m^2g^{-1} [Stoller *et al.* (2008)], Young's modulus ≈1100 GPa [Lee *et al.* (2008)], charge carriers mobility nearly up to 200000 cm^2/Vs [Bolotin *et al.* (2008)], thermal conductivity ≈5000 $Wm^{-1}K^{-1}$ [Balandin *et al.* (2008)], and very much interesting transport mechanism (Quantum Hall Effect) [Zhang *et al.* (2005)]. By using chemical vapor deposition (CVD) method, about 1 to 12 layers of graphene films have been produced [Li *et al.* (2009), Berger *et al.* (2006)]. Apart from several advantages, graphene shows few drawbacks also. Preparation of graphene by using epitaxial method requires very high temperature (approximately 1000 ^{0}C) along with substantial vacuum atmosphere, which increases the graphene production cost and hence, reduce the wide area applications of graphene. Direct use of graphene in

electronic devices applications is limited due to many factors such as its extremely difficult processibility and unsuitability for huge production. Graphene are hydrophobic in nature. So, graphene sheets get quickly agglomerated in some organic solvent which is another drawback of graphene [Li *et al.* (2008)].

The performance of organic electronic devices can drastically be improved by incorporating a few graphene sheets into some polymeric or ceramic matrices. Homogeneously mixed graphene sheets into some conducting polymer or ceramic matrices transfer their many properties to the host matrices and therefore, remarkable improvement in the properties of particular host matrices is observed [Stankovich *et al.* (2006), Watcharotone *et al.* (2007)]. Such improved properties of organic semiconductors are applicable for the production of hybrid organic electronic devices. Therefore, graphene based organic composites fulfill the challenging goal of huge production and broad area applications in organic electronics. Lot of work has been reported concerned with the semiconducting polymer/carbon nanotube based high performance transistors [Bo *et al.* (2005), Bo *et al.* (2006)] which shows excellent charge carrier mobility owing to the regular incorporation of graphene or carbon nanotubes in the OFET channel film. These CNTs perform as conducting bridge amongst the numerous crystalline zones of the organic conducting thin-film [Singh *et al.* (2006)]. Addition of CNTs or graphene enhances the carrier mobility; on the other hand, at the same time the ON/OFF ratio decreases. The reduction in the ON/OFF current ratio is owing to the aggregation of the CNTs present in the organic semiconducting film. This aggregation may initiate even at low density of CNTs incorporated into OFET channel film. Therefore, addition of CNTs or graphene really increases the carrier mobility but makes the ON/OFF ratio to decrease owing to the percolation of graphene or CNTs.

As compared to CNTs, graphene sheets provide very high-quality of interconnections between various crystalline regions of the organic semiconductor film which drastically improve the OFET performance compared to CNTs based transistors [Huang *et al.* (2011)]. In this chapter we discuss the characteristics of OFETs fabricated based on (P3HT) / Graphene nanocomposite. Graphene composite based device performance is strongly dependent on the concentration of the graphene flakes in the composite.

4.2 Experiment Details

The structure of P3HT/Graphene based OFET was similar as discussed in earlier chapters. Top contact OFETs were fabricated on p^+-Si/SiO$_2$ substrates of dimension 1 cm ×1 cm. The p^+-Si substrates were used as a gate electrode for the OFETs. Before device fabrication, the substrates were treated in a mixture of hydrogen peroxide, distilled water and aqueous ammonia (having ratio 1:2: 1) for 1:30 h at 100 °C in order to get hydrophilic surface of the substrates and also to eliminate the impurities. After this treatment, these substrates were treated with octyltrichlorosilane (OTS) solution along with toluene in order to obtain hydrophobic substrate surface which enhances the formation of crystalline region in the organic semiconducting film. Further, in order to fabricate P3HT/Graphene nanocomposite based hybrid OFETs, P3HT was dissolved in graphene dispersions. The graphene suspensions of three individual concentrations were prepared via addition of 0.05, 0.1, and 0.2 mg graphene flakes into 1 ml chloroform (CHCl$_3$) (Merck, India).These suspensions were stirred for 30 min on magnetic stirrer, followed by 20 min ultrasonication for homogeneous solution preparation. The P3HT of 2 mg was further added into each graphene dispersed solution and again ultrasonicated for next ten minutes. Then after these solutions were spin coated (with 1000 rpm for 10 s followed by 3000 rpm for 50s) over a few substrates. The thin-film surface morphology and uniformity of the hybrid nanocomposite solution coated over FET channel was

studied by using scanning electron microscope (SEM; GEMINI Zeiss). The films thicknesses were measured and the estimated values found were in the range of 45-55 nm. These samples were annealed at 80 °C for 1 h in ambient condition. In order to fabricate OFET, further, the source and the drain electrodes of gold were thermally deposited on the top of the p^+-Si/SiO$_2$ substrates by using Ni-shadow mask at a pressure of 5×10^{-6} torr. The device dimensions (channel length and width) were 20 μm and 2 mm, respectively. A few P3HT based transistors were also fabricated at identical fabrication conditions in order to compare the performance of P3HT/graphene based hybrid OFET with respect to the only P3HT based OFET. The schematic structure of bottom gate top contact P3HT/graphene based hybrid OFET fabricated is shown in Fig. 4.1.
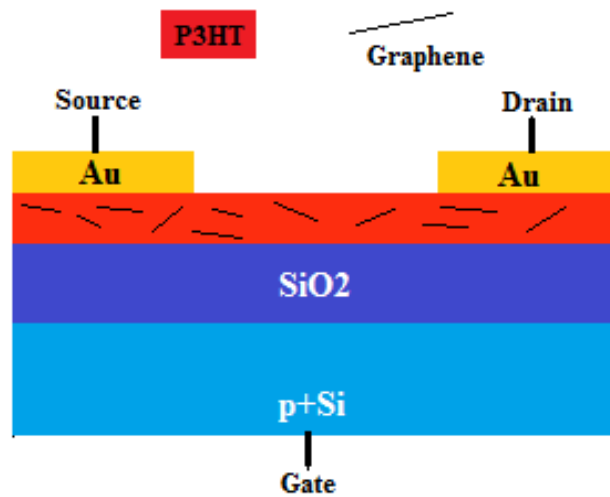

Fig. 4.1 Systematic structure of P3HT/graphene nanocomposite based OFET

4.3 Results and Discussion

Electrical characteristics of all fabricated hybrid OFETs were measured at room temperature by using Semiconductor Parameter Analyzer under proper vacuum condition, and are shown in Fig. 4.2. The OFET performance parameters such as I_{ON}/I_{OFF} ratio, carrier field-effect mobility, threshold voltage, transconductance, and sub-

threshold slope were calculated by using these (output and transfer) electrical characteristics and few typical mathematical equations derived (discussed in the earlier chapters) for traditional FET models under saturation region. The cyclic output and transfer characteristics of each hybrid OFETs fabricated using P3HT/graphene as conducting channel material for distinct graphene concentrations (0, 0.05, 0.1, and 0.2 mg/ml) in P3HT are given in Fig. 4.2 (a-c). The characteristics showed that all OFETs were operating mainly in accumulation mode due to the accumulation of holes at the semiconductor/insulator interface. The I-V characteristics were similar to the electrical characteristics of traditional p-channel field effect transistors. When positive V_{GS} was applied, transistors were operating in depletion mode and for negative applied V_{GS} they were operating in accumulation mode. Therefore, all fabricated organic transistors were "normally on" type p-channel OFETs. The threshold voltage of OFETs were calculated by putting a tangent on the $I_D^{1/2}$ versus V_{GS} curve drawn at a fixed $V_{DS} = -60$ V. The extended tangent intercepts the x-axis at a V_{GS} value which is the threshold voltage.

The carrier mobility for all graphene concentrations (0.05, 0.1, and 0.2 mg/ml) in P3HT based FETs were determined at fixed $V_{GS} = -60$ V and $V_{DS} = -60$ V and the values were found to be $\mu = 1.08 \times 10^{-3}$ cm^2/Vs, 6.58×10^{-3} cm^2/Vs, and 4.48×10^{-2} cm^2/Vs, respectively. These values were 6 times, 33 times, and 224 times higher than the carrier mobility of only P3HT based FET. The various important key parameters of OFETs were calculated and the variation in the value of parameters due to the effect of graphene concentrations in the P3HT channel of P3HT/Graphene based OFETs are listed in the Table 1. The high mobility in P3HT/graphene based transistors was due to the presence of graphene sheets in the organic transistor channel.
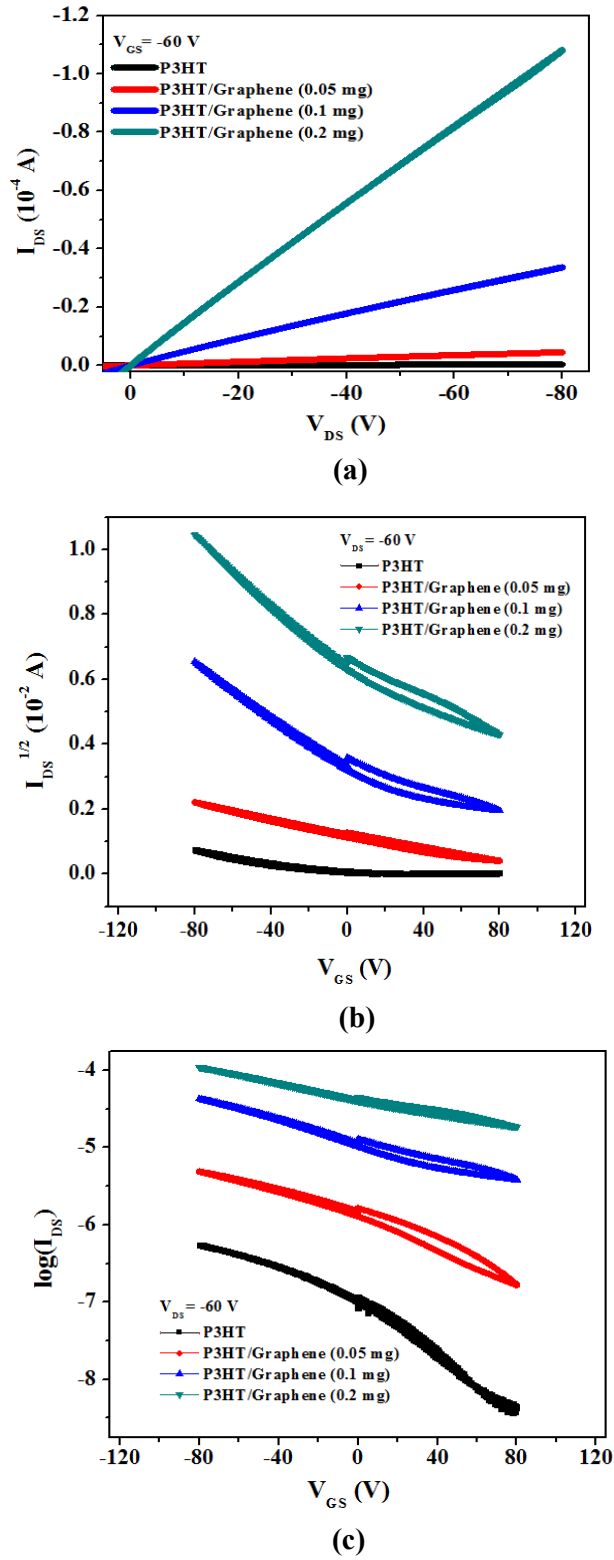
(a)

(b)

(c)

Fig. 4.2 Combined I-V characteristics of OFETs having different concentrations of graphene flaks in their P3HT active channel (a) I_{DS} Versus V_{DS} at V_{GS}= -60 V, (b) $I_{DS}^{1/2}$ Versus V_{GS} at V_{DS}= -60 V, (c) log(I_{DS}) Versus V_{GS} at V_{DS}= -60 V

The regular distribution of graphene flakes in P3HT coated on OFET channel is shown in Fig. 4.3 (a). Thick coating of P3HT/graphene nanocomposite material clearly demonstrated the morphology of the nanocomposite film in which graphene flakes of similar and comparable size were uniformly distributed as shown in Fig. 4.3 (b). The graphene sheets incorporated in the organic semiconducting nanocomposite thin-films provide "fast tracks" or the conduction bridge for the charge carriers, so, thin-film conductivity enhances drastically. Consequently carrier mobility of P3HT/graphene based FETs also gets improved highly compared to FETs based on only P3HT [Huang *et al.* (2011)].
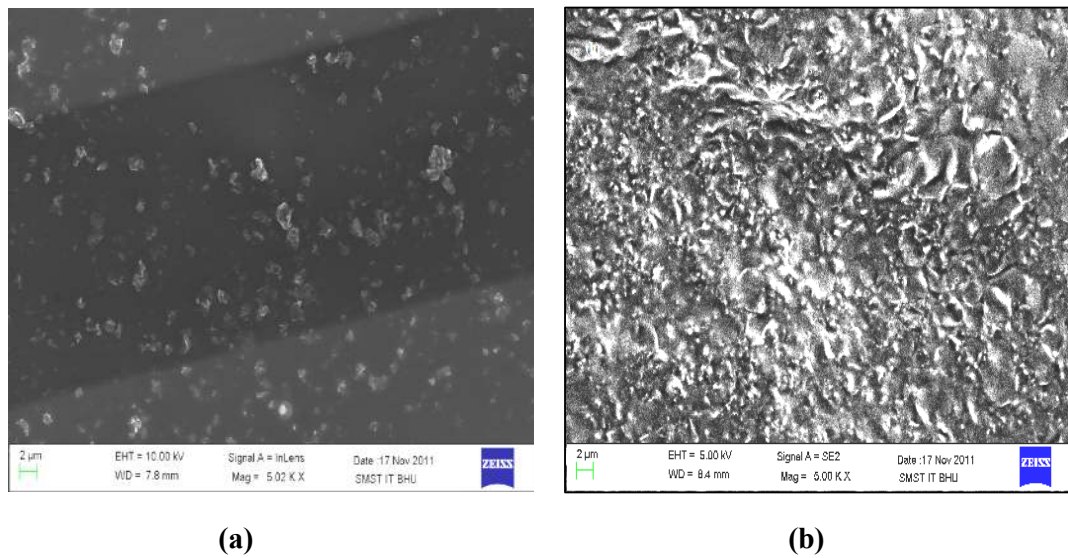

| (a) | (b) |

Fig. 4.3 SEM image of **(a)** P3HT/graphene thin-film coated FET channel, **(b)** P3HT/graphene hybrid nanocomposite material.

The I_{ON}/I_{OFF} current ratio of a transistor is the ratio of maximum "ON" drain current to the minimum "OFF" drain current at a particular V_{DS} value. As the mobility enhances, the I_{ON}/I_{OFF} ratio seems to be reduced simultaneously because of few reasons that are already discussed in literature [Huang *et al.* (2011) Fuhrer *et al.* (2002) Snow *et al.* (2003) Xia *et al.* (2010)]. The first reason is that usually graphene or graphene composite

based transistors cannot switch-off successfully. It is because graphene does not show forbidden energy band gap. Another cause for reduction in the I_{ON}/I_{OFF} current ratio is due to the percolation of graphene flakes incorporated into organic semiconducting film. This percolation may start even at very low graphene density. So, as the mobility raises fervently, it is observed that graphene flakes density reaches close to the percolation threshold and starts to percolate. This may be another reason for decrease in I_{ON}/I_{OFF} current ratio of organic semiconductor/graphene base hybrid transistors. These kinds of organic transistors are generally useful in RF circuits and the places where switched-off form of FETs is not essential; each and every FET is always operated in switched-on mode only. Thus, considerable work has already been done in the order to investigate and improve the RF performance of such transistors. The I_{ON}/I_{OFF} current ratio for all P3HT/Graphene based transistors having distinct graphene concentration at their active channel was calculated by using Fig. 4.2 (c), and the estimated values are listed in Table 1.

Table 4.1: Effect of graphene concentrations on the key performance parameters of P3HT/Graphene based OFETs

Active channel material	I_{ON} (A)	I_{OFF} (A)	V_{TH} (V)	μ_{sat} (cm^2/Vs)	SS (V/dec)	g_m (nS)
P3HT	7.35×10^{-7}	4.25×10^{-9}	5	2.01×10^{-4}	12	18
P3HT/Graphene (0.05 mg)	5.82×10^{-6}	8.32×10^{-7}	40	1.08×10^{-3}	21	108
P3HT/Graphene (0.1 mg)	5×10^{-5}	3.51×10^{-6}	80	6.58×10^{-3}	28	921
P3HT/Graphene (0.2 mg)	1.15×10^{-4}	1.85×10^{-5}	120	4.48×10^{-2}	35	8080

The threshold voltage for all P3HT/graphene based transistors was also calculated by drawing a tangent on the $I_{DS}{}^{1/2}$ versus V_{GS} curve at $V_{DS} = -60$ V, as shown in the Fig. 4.2 (b) and calculated values are listed in the Table 1. By observing the Table 1, it can be found that with increase in graphene concentration in the OFET channel threshold voltage shifts along more positive values. Shifting in threshold voltage (V_{TH}) towards more positive gate-source voltage (V_{GS}) may perhaps be owing to the change in the work function of P3HT and graphene. The value of work function for P3HT and graphene is about 5.1 eV and 4.6 eV, respectively as reported earlier [Yip *et al.* (2008), Liu *et al.* (2012)]. This difference allows electrons to move from graphene to P3HT film and therefore, the graphene film becomes p doped. It is also well known that Dirac point shifts towards the positive gate voltage for p-type doping in graphene. This may be the cause for the shift in V_{TH} across more positive V_{GS} in P3HT/Graphene based OFETs with increasing graphene concentration in their channel. Sub-threshold slope and transconductance for all the fabricated transistors were also calculated and the values are listed in Table 1. Thus, by observing Table 1 it can be found that the performance of a graphene or graphene composite based OFET is strongly dependent on the graphene concentration on its active channel.

4.4 Conclusions

In this chapter, P3HT/graphene nanocomposite based hybrid thin film field effect transistors were fabricated and their electrical performance and structural morphology were studied. Key performance parameters of nanocomposite based transistors were also compared to the parameters of only P3HT based FETs. It was found that the drain saturation current and the mobility of hybrid transistors were enhanced radically due to graphene flaks merged in the P3HT film providing "swift lanes" for the charge carriers which results in enhancement in the conduction property of the P3HT nanocomposite

thin-film. However, I_{ON}/I_{OFF} current ratio of hybrid transistors was reduced due to percolation of graphene flakes and also due to the absence of forbidden energy gap in grapheme, which could not turn-off the OFETs effectively. The mobility of hybrid nanocomposite transistors (in which P3HT active channel was incorporated with 0.2 mg/ml graphene flakes) was approximately 223 times higher than the mobility of only P3HT based transistors. So, it was found that the performance of a transistor greatly depends on graphene concentrations in a polymer matrix used at its active channel. Therefore, it is anticipated that the incorporation of graphene with an organic semiconductor is an easy, low-cost, and novel route in order to get high performance organic transistors.