Chapter 6

Development of low-voltage operating organic thin film transistor for ammonia and photo sensing applications

Abstract

A low operating voltage (≤2 V) organic thin-film transistor (OTFTT) is developed in top contact bottom gated configuration using a fibrous conducting polymer channel for its application as NH_3 gas sensor. For, this device fabrication, fibrous film of PBTTT-C14 is transferred onto the Li-alumina (Li-Al_2O_3) gate dielectric by the economical and facial Floating film transfer method (FTM).This fibrous PBTTT-C14 thin film has been prepared, as of our previous study, by utilizing the conception of solvent driven self-assembly of the polymer. To examine the ammonia sensing performance of the fabricated OTFT, a range of concentrations of the NH_3 have been exposed on the fibrous polymer based OTFT channel from 0 ppm to 20 ppm. From the electrical characteristics behavior of the OTFT we have investigated the sensitivity, and selectivity of the sensor. It was investigated that the OTFT device based sensor is very sensitive towards the analyte gas with response of ~ 69% at 20 ppm concentration, with the detection limit of 0.41 ppm, which validates its applicability for the lower concentration detection of ammonia. This OTFT sensor not only exhibits great selectivity to NH_3 gas but also maintain good linearity to concentration. Additionally, this TFT exhibits extremely high photosensitivity under white light illumination with increasing the device's "ON" and "OFF" currents and shifting the threshold voltage by around 1.5 V.

6.1. Introduction

Organic thin film transistors (OTFTs) are appealing building blocks for economical electronic devices like radio-frequency identification (RFID) tags, sensors, electronic paper, and backplane circuits for active-matrix displays [1, 196, 197].These OTFTs have multiple device parameters that determine its performance, including threshold voltage, sub-threshold swing, and mobility [161, 198]. These OTFs are commonly fabricated on top of Si/SiO_2 substrate where SiO_2 works as gate dielectric because of its advantages like low defect density, compatibility with CMOS technology, and good thermal conductivity. However, it requires a elevated operating voltage (>20 V) because of the low dielectric constant of SiO_2 (~3.9), restricting their application as portable electronics. [125, 161]. Besides, SiO_2 gate dielectric poses high tunneling current at low oxide thickness that causes a very significant static and dynamic power dissipation compared to high-k dielectric material-based OTFTs such as zirconium oxide (ZrO_2) [199], HfO_2 [200], and Ta_2O_5 [201]. The dissipation of power generates thermal energy, which raises the temperature. Such a situation can raise temperature quickly, especially in circuits with high-density OFETs. This may cause organic materials to gradually deteriorate and shorten the lifespan of the device [202].

Therefore, the development of gate dielectrics with a high areal capacitance is required for practical applications of OTFTs which can require few voltages to operate these devices [203, 204]. High-k oxide dielectrics are more susceptible to charge traps than SiO_2 due to defects states such as oxygen vacancies, poor surface roughness, and reduced band offset. These issues cause higher threshold voltage, decreased device mobility, and increased leakage current in the fabricated devices. Till date, several high-κ metal oxide dielectrics have been developed, which are appealing because of their compatibility with various organic semiconductors. The synthesis techniques of these high-κ dielectrics include metal anodization [47, 205], vacuum-based deposition [206, 207] and sol-gel technique [208].

This chapter explains the fabrication method of low operating voltage (≤2V) OTFT based NH_3 gas sensor by utilizing an ion-conducting gate dielectric and fibrous polymer thin film based semiconductor channel. During this fabrication an aligned nanowires/thin film of PBTTT-C14 polymer has transferred via economical and facial FTM method onto a Li-alumina (Li-Al_2O_3)

thin film which makes it work at lower voltage. This designed OTFT has been examined for the NH_3 gas detection application by exposing the channel to analyte gas. The change in the OTFT parameters was then recorded in order to investigate the sensitivity, selectivity, and other significant parameters. Additionally, I have also explored the photosensitivity of this device under white light, demonstrating its elevated photosensitivity to white light.

6.2. Experimental section

To synthesize dielectric lithium beta alumina (Li-β-Al_2O_3), 500 mM precursor solution is made by combining 98% pure aluminum nitrate nonahydrate [$Al(NO_3)_3$, $9H_2O$] (SDFCL) and >98% pure lithium acetate (CH_3COOLi) (TCI) in an 11:1 molecular ratio. After dissolving the combination in 2-methoxyethanol, it was stirred for around 6 hours. To encourage gelation, the prepared solution was aged for a full day. A 0.45 μm PVDF syringe filter was used to filter it before spin coating deposition on the desired substrate.

6.2.1 Device fabrication

Figure 6.2 (a) illustrates the fabricated bottom gate top contact geometry based OTFT device. Silicon substrates (p+-Si) were first cleaned with soap solution and then ultrasonically sonicated with DI water, acetone, and isopropanol before being dried in order to fabricate the device. Clean substrates were treated with oxygen plasma for 10-15 minutes prior to spin coating of the dielectric material in order to remove organic residue and make them hydrophilic. The fabrication of the gate dielectric thin film in TFTs requires a homogeneous, pinhole-free thin film, which hydrophilic substrates aid in coating. Then, the substrates were spin-coated with a 500 mM Li-Al_2O_3 precursor sol at 5000 rpm for 50 s, followed by 30 minutes of annealing at 350 °C. To obtain the appropriate thickness, the procedure was executed three times. Lastly, the dielectric material coated substrates were annealed for 30 minutes in a preheated furnace at 500°C, resulting in a thick film of Li-Al_2O_3. To create a hydrophobic self-assembled monolayer, the dielectric film was then subjected to a vapor phase hexamethyldisilazane (HMDS) treatment. Afterward, the floating film of the active layer was stamped via FTM procedure as the previous study over the hybrid dielectric film that had been treated with HMDS and then annealed at 80°C [209]. A thermal evaporator was used for gold electrode deposition that works as source/drain contact of OTFT.

6.2.2 Characterization tools

TEM micrographs and SAED patterns of polymer films over Cu grid were acquired via TECHNAI $G^2$20 TWIN (New Zealand). The electrical characterizations and sensing measurements of the fabricated OTFTs were carried out by a semiconductor parameter analyzer (Keysight B1500A). In addition, the investigation of the Photosensitivity of the OTFT has been studied by electronic characterization of the OTFT in the presence of white light of different intensities by using a xenon lamp.

6.3. Results and discussion

6.3.1 Structural investigation of the Fibrillar PBTTT-C14

By transferring the film using the FTM process onto a carbon-coated TEM grid, TEM analysis was performed for the structural investigation of the FTM coated fibrillar polymeric film. Figures 6.1(a) and 6.1(b) shows the polymer film's TEM micrograph and SAED pattern, respectively. This figure clearly indicates a uniformly distributed aligned nanowire formation of polymer film that has an average width of ~300 nm. Additionally, formation of the SAED pattern shows the nano-wires are crystalline in form.

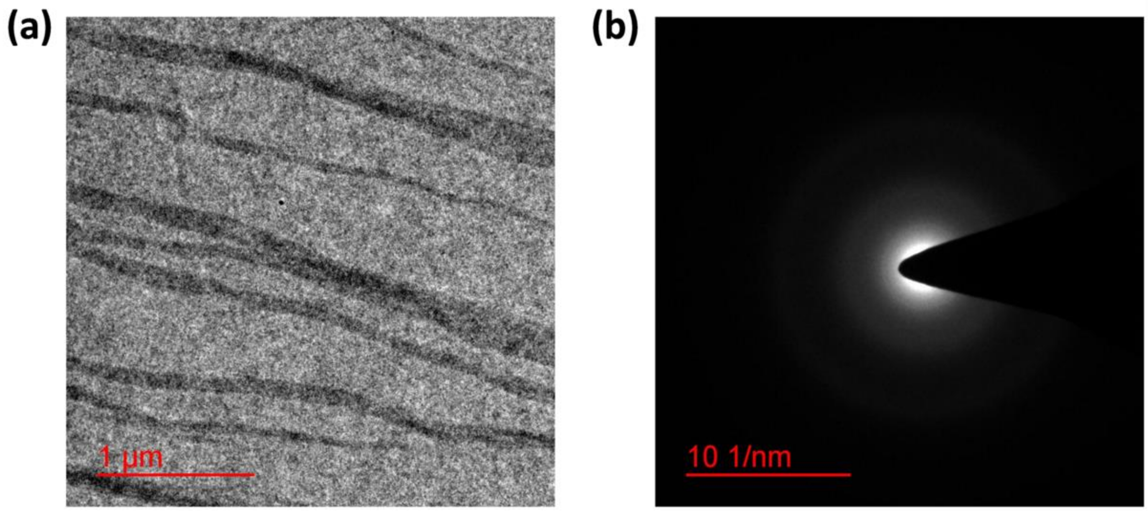

Fig. 6.1. (a) TEM image and, (b) SAED pattern of FTM coated fibrous PBTTT-C14 thin film.

6.3.2. Electrical Characterization

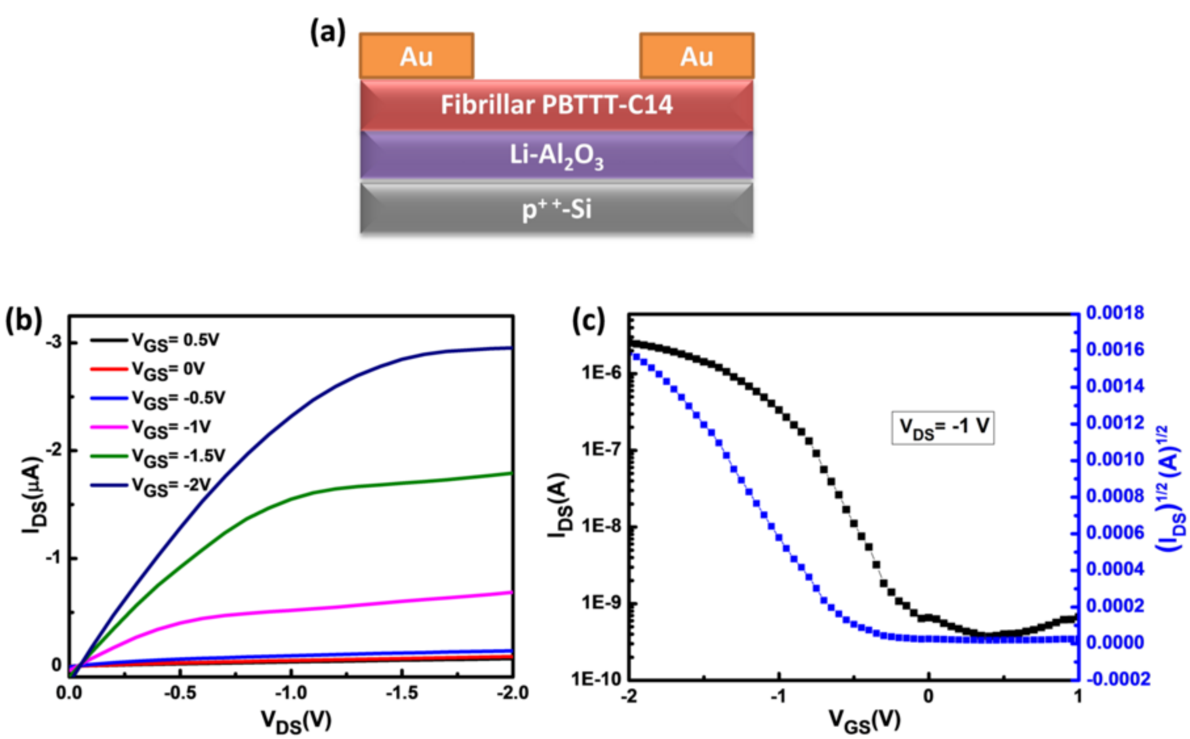

Fig.6.2.(a) Device schematic; (b) Output, and; (c) Transfer characteristics of fibrous homo-juntion based OTFT.

To investigate the electronic performance of the fabricated device, output and transfer characteristics have been studied. For the output characteristics drain voltage is swept from 0 V to -2 V with constant gate bias voltage ranging from 0.5 V to -2 V with a step of 0.5 V. The graphic of the device clearly displays the linear and saturated region of the output characteristics as displayed in Fig. 6.2(b), indicating the device can be operated with 2 V power supply. The transfer characteristic of OTFT is shown in Fig. 6.2(c), implying its ON/OFF ratio of **X**. During this study, the gate to source voltages is swept from - 0.2 V to 1 V keeping drain voltage constant at -1 V for both devices. Important transistor electrical parameters, like mobility (μ_h) and threshold voltage (V_{TH}), can be derived from transfer characteristics of the device by using the following equation (3.1).

6.3.3. Ammonia sensing

For NH_3 sensing measurement, the OTFT device is subjected to varying concentrations, from 0 ppm to 20 ppm of the NH_3 gas, at 27°C under the regulated flow of dry air inside a sealed container with 50% relative humidity, as seen in Fig. 6.3(a). Then, the gate bias (V_{GS}) is swept from 0 to -2 V throughout the sensing measurement while the constant drain voltage (V_{DS}) is set to -1 V. The transfer characteristic shows that the drain current (I_{DS}) of the OTFT steadily drops as soon as the NH_3 concentration rises and almost quenches after being exposed to 20 ppm NH_3 gas concentration.

With the decrement in current (I_{DS}) the corresponding OTFT parameters also tend to decrease with the ammonia concentration and that is caused by the NH_3 molecule’s charge-trapping and charge-quenching effects on the positive charge carriers (holes) in the p-type OTFTs. The charge density in the conduction channel decreased as the injected NH_3 gas concentration increased. As a result, the threshold voltage (V_{TH}) gradually shifted in the negative direction. The variation in threshold voltage (V_{TH}) and effective charge mobility (μ_h) of the devices as a function of NH_3 concentration is depicted in Fig. 6.3(b). The results demonstrate that there is a change of V_{th} of more than 0.5 V during the variation of NH_3 concentration, with high linearity up to 20 ppm. Additionally, the designed sensor's effective carrier mobility also decreases from 0.053 to 0.026 $cm^2\ V^{-1}sec^{-1}$, which is about 50% of its initial value (Fig.6.3(c)).

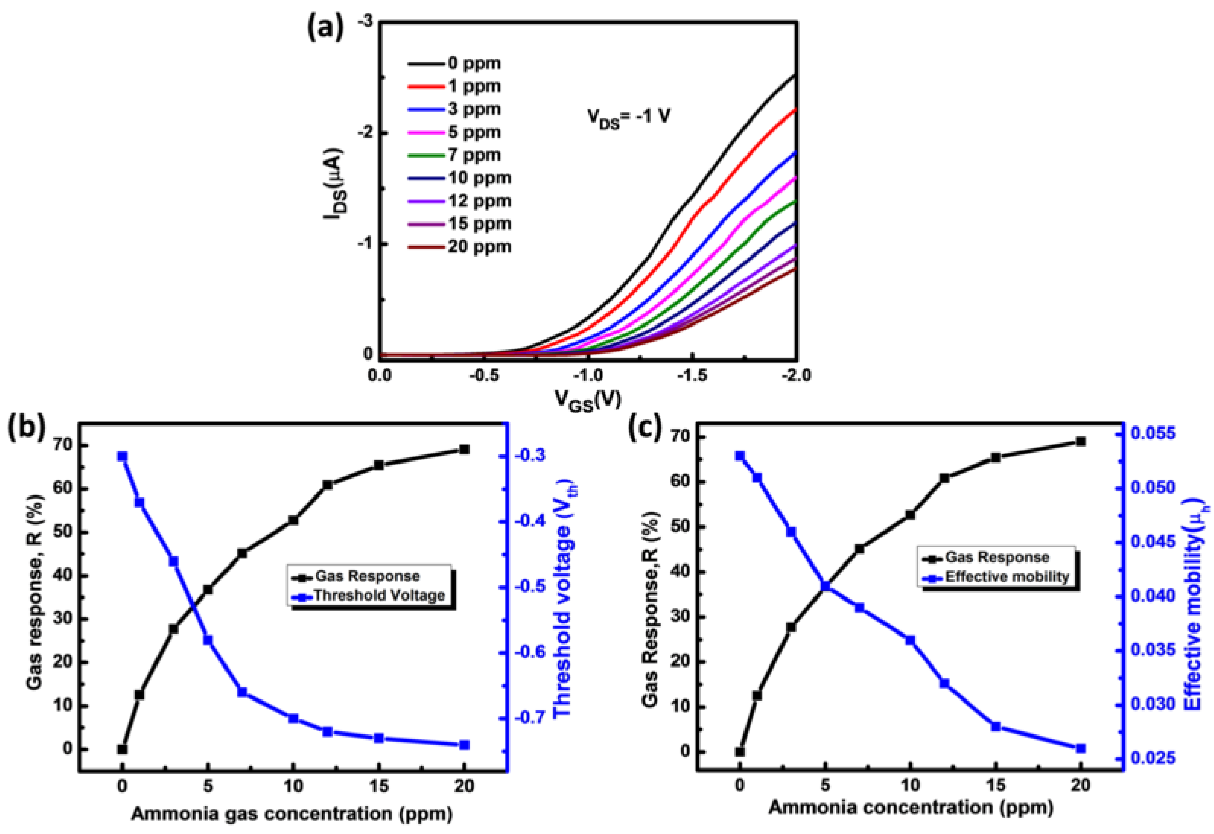

Fig. 6.3. (a) Transfer characteristics of fibrous polymer film based OTFT sensor at V_{DS} = -1V, and (b), & (c) Corresponding Shift in threshold voltage (V_{th}) and mobility (μ_h) with different concentrations of ammonia (0 ppm-20 ppm).

As a function of NH_3 concentrations Fig. 6.3(b) shows the fast sensing response of the OTFT sensor. When the artificial OTFT channels are exposed to ammonia gas, equation (3.2) can be used to determine the sensor's response (R).

Table-6.1: Variation in OTFT parameters and the sensitivity of polymeric fibrous film with different NH_3 concentrations

NH_3 (ppm)	**On current I_{on} (μA)**	**Effective Mobility μ_h ($cm^2V^{-1}sec^{-1}$)**	**Threshold voltage V_{TH} (V)**	**Gas Response R (%)**
0	-2.53	0.053	-0.48	0
1	-2.21	0.051	-0.56	12.50
3	-1.83	0.046	-0.64	27.70
5	-1.60	0.041	-0.69	36.72
7	-1.39	0.039	-0.76	45.11
10	-1.19	0.037	-0.80	52.71
12	-0.99	0.032	-0.82	60.84
15	-0.87	0.028	-0.84	65.44
20	-0.78	0.026	-0.85	69.04

The response (sensitivity) of the pure polymeric fibrous OTFT sensor at 5 ppm concentration of NH_3 is 69.04 %, which is calculated by the constant value of V_{DS}= -1 V corresponding to the Fig 6.3(a). The limit of detection of the sensor was also estimated with help of the following equation (3.3). And the calculated the LOD of the fabricated is 0.41 ppm. Which shows additionally that, even at lower ammonia concentrations, the fibrous polymer based sensor exhibits a rather acceptable response. If I compared this study to the previous one which is discussed in chapter 5, it can be concluded that this ionic dielectric based OTFT works significantly wider range of concentration of NH_3 gas w.r.t the SiO_2 gate dielectric device whereas sensitivity of earlier device is more in lower concentration range.

6.3.4. Selectivity Analysis

As illustrated in Fig. 6.4, the OTFT sensors were used for other interfering gases as methane (CH_4), propane (C_3H_8), carbon dioxide (CO_2), carbon monoxide (CO) to identify the general applicability of the sensor to examine the response of other reductive and oxidative gases. Even at lower NH_3 concentrations than any other gases, the device responded to NH_3 gas considerably more strongly than any other gas. This finding implies that the fibrous OTFT sensor exhibits notable improvements in selectivity, and indicates its considerable potential for use in low-cost, portable chemical sensors.

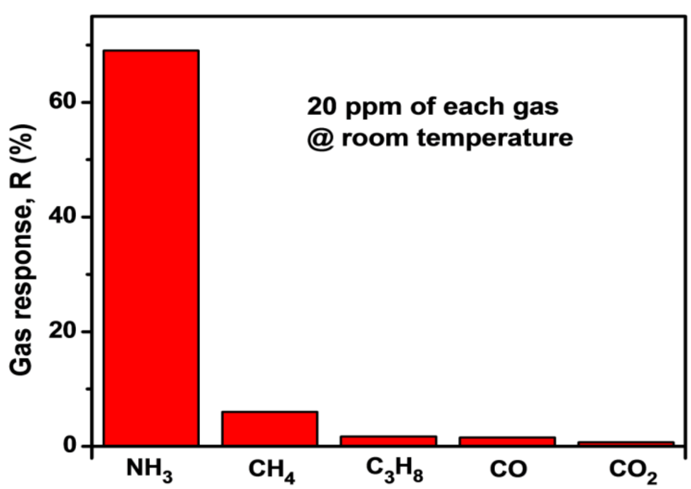

Fig. 6.4. Selectivity analysis of homo-junction based OTFT sensor.

Table-6.2: Comparative performance of the NH_3 sensor w.r.t the earlier reports.

Device design	**Sensing material**	**Film deposition technique**	**Operating voltage/ Temp.**	**Response (Gas concentration)**	**Resp. /Rec. time**	**Remark**
OTFT	P3HT-MoS_2	FTM	-60V/25°C	63% (100PPM)	-	High operating voltage [210]
MSM	PQT-12	Spin coating	-5 V/RT	8% (100 PPM)	8s/103s	Poor sensing response [24]
OTFT	PQT-12/CdSe	FTM	-40 V/RT	51% (100PPM)	50s/200s	High response time/ high operating voltage [211]
OTFT	PBTTT Nanowire	FTM	-30V/25°C	74.8% (5 PPM)	2s/12s	High operating voltage [212]
OTFT (This work)	PBTTT Nanowire	FTM	-2 V/25°C	69.04% (20 PPM)	5s/10s	Low operating voltage/ quick response-recovery time

6.3.5. Broadband photo sensing properties

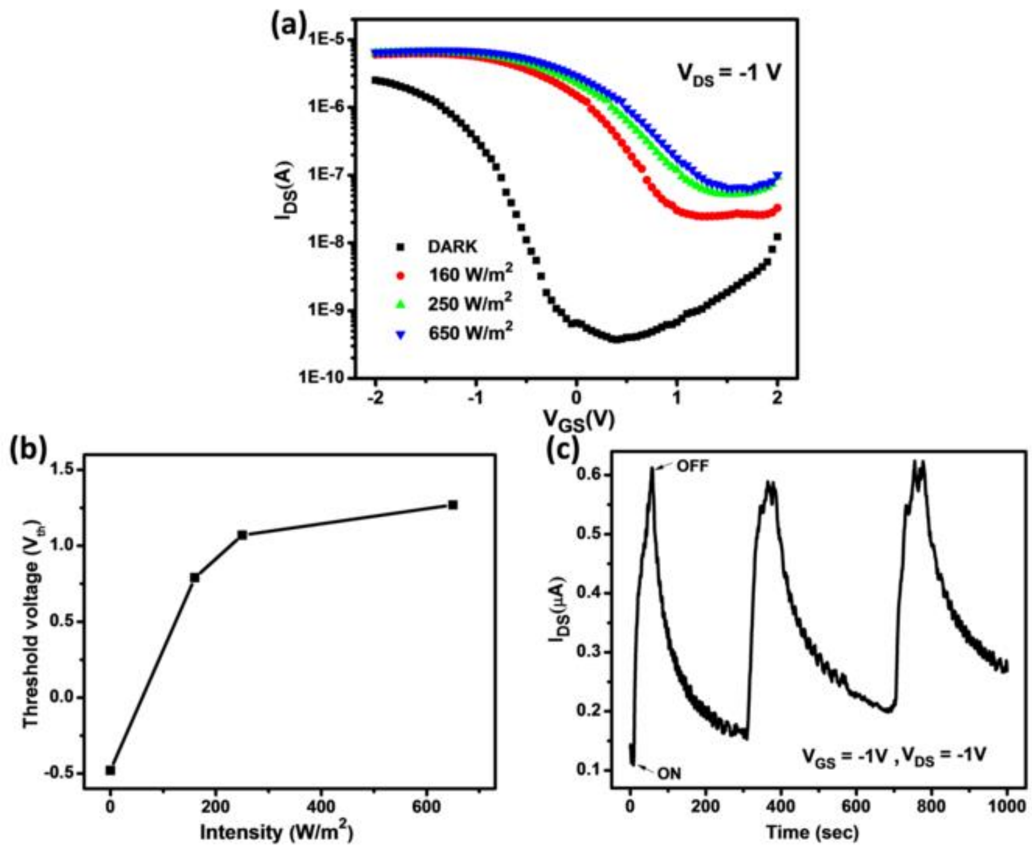

Fig. 6.5. (a) Transfer characteristics of homo-junction photosensitive OTFT (V_{DS} = - 1 V) in dark and under various intensities of white light, (b) Threshold voltage shift of the photo-detector under a range of white light intensities, (c) Transient analysis of the designed photo-detector at V_{DS} = - 1 V and V_{GS} = - 1 V.

Apart from NH_3 sensitivity, we also examined the photo-detection capabilities of the designed OTFT in ambient circumstances. The electrical properties of fabricated phototransistors under a range of white light intensities, from dark to 650 W/m^2, are demonstrated in Fig. 6.5(a). This electrical statistics, which is the result of photocurrent production in the OTFT hybrid channel, suggests a significant improvement in both ON and OFF currents.

Based on the findings, it appears that the variation of OFF current this device is significantly higher than it's ON current variation, which can be recognized to the large number of photo-generated carriers (both electron and hole) that reduces the sheet resistance largely. The photo-generated charge carrier in this depleted region greatly enhances the channel conductivity and increases the OFF current of the device.

In addition, the shifts of threshold voltage the photo-transistor varied largely under intensities of white light as illustrated in Fig. 6.5(b). With 650 W/m^2 light intensity, the threshold voltage shift can reach up to ~2 V. Fig. 6.5(c) shows the phototransistor's transient photo-response, indicating a rapid response but a longer decay time for the device. This larger decay time of the photocurrent is because of the large channel length of OTFT and lower carrier mobility of PBTTT-C14 polymer film.

6.4. Conclusion

A highly sensitive, low operating voltage OTFT based NH_3 sensor and broadband photo-transistor has been fabricated by a simplistic, cost-effective and high yield method. Fibrous polymer thin film of PBTTT-C14 has been used as the NH_3 and photo-sensitive film of the OTFT device. A significant variation in the accumulation mode drain current of the OTFT has been observed due to the minute variation in NH_3 gas concentration, which leads to the considerable variation in OTFT parameters and acquired a response of ~ 69% at 20 ppm concentration of NH_3. In addition, this homo-junction based sensor demonstrates exceptional sensitivity, selectivity with a low concentration detection limit of NH_3 up to 0.41 ppm. Besides, this fabricated device also shows large OFF current variation under various white light intensities demonstrating its high photo-sensitivity under white light. Briefly, this polymer homo-junction based OTFT meets the majority of the basic necessities for its realistic application as an NH_3 sensor and broadband photo-detector. It attains exceptional sensitivity with rapid response/recovery times with an extensive range of detecting abilities.