Chapter-3

Highly Responsive Al/PTB7/Si/Al Vertical Structure Based White Light Photodetector using FTM Method

The Part of the work is adopted from-

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3.1 Introduction

To study the optoelectronic applications of PTB7-based devices, Al/PTB7/Al MSM configuration was investigated for visible light sensing in Chapter 2. In a previous study, the spin coating method was opted for thin film coating of polymer which resulted in decent improvement in optical performance. To further improve the responsivity of the device another solution processable, low-cost, low-temperature fabrication method [1] needs to be explored for good quality thin film. Typically, organic polymers have long carbon chains and good solubility in organic solvents are appropriate for solution methods at low temperatures for fabricating thin film devices on various substrates using low-cost spin coating [2], dip coating [3], bar coating [4], and Langmuir Blodgett (LB) technique [5]. Recently, the floating-film transfer method (FTM) or stamp film transfer method (SFTM) has been used to achieve polymer thin film with well-controlled crystalline orientations and self-assembled polymer chains on the substrates with minimal material waste [6][7]. The working of FTM is based on the Marangoni flow phenomenon which allows a solvent with lower surface energy to easily spread over the surface of a high surface energy solvent due to the surface pressure gradient between the air/liquid interface [8]. The polymeric solution, being hydrophobic, easily floats over the liquid base solution due to viscous force and driving force depending on the viscosity of the base solution [9]. The thickness of the FTM-derived polymer thin films can be effectively controlled by the concentration and temperature of the polymer solution [10].

In this chapter, we have explored the FTM-derived PTB7 thin film to demonstrate an Al/PTB7/Si/Al vertical structure-based white light photodetector. The vertical structure was considered to achieve a fast transient response of the photodetector. Section 3.2 of Chapter 3 presents the experimental procedure used for the fabrication and characterization of vertical photodetector. Further, results and discussion are included in section 3.3. At last, the summary of this chapter is included in section 3.4.

3.2 Experimental Details

3.2.1. Materials Preparation and Device Fabrication

The polymer PTB7, ethylene glycol, glycerol, chloroform, and other chemicals were procured from Merck/Millipore Sigma, (USA) with standard purity grade. The deionized (DI) water (~18 MΩ resistance) was obtained from the Milli-Q DI water plant. First, the p-type Si substrates were cleaned by the standard wet chemical method and dried in N_2 environment. The substrates were then processed for surface treatments using Hexamethyldisilazane (HMDS). To synthesize the polymer film, 6 mg/ml PTB7 polymer was first dissolved in 0.5 ml chloroform and the solution was then stirred for 10 hours at 40 °C. Glycerol and Ethylene glycol (in 1:1 ratio) were mixed properly in a petri dish to obtain the base solution/liquid substrate solution for the FTM method. Then 10 μL polymer solution was dropped onto the middle of the liquid substrate solution to form a thin film of the PTB7 polymer. A thin polymer film was found to be formed on the surface of the base solution due to the combined effect of the evaporative nature of the chloroform and the surface tension gradient at the interface of the two solutions [17]. The PTB7 polymer film was then transferred from the surface of the liquid substrate solution to the Si wafer by the stamp method [7].

Subsequently, the Si substrate was baked at 90 °C for 30 minutes to eliminate the residues of organic solvents. A thermal deposition unit (HIVAC SMART COAT 3.0) was used to deposit Al (~100 nm) metal film as back contact on Si substrate. Also, Al metal as dotted pattern (thickness ~70 nm) of 0.5 mm radius (indicated in **Figure 3.2(a)** was deposited on the PTB7 film by thermal coating using metal masks. The floating film transfer method and device schematic are illustrated in **Figure 3.1** and **Figure 3.2** respectively.

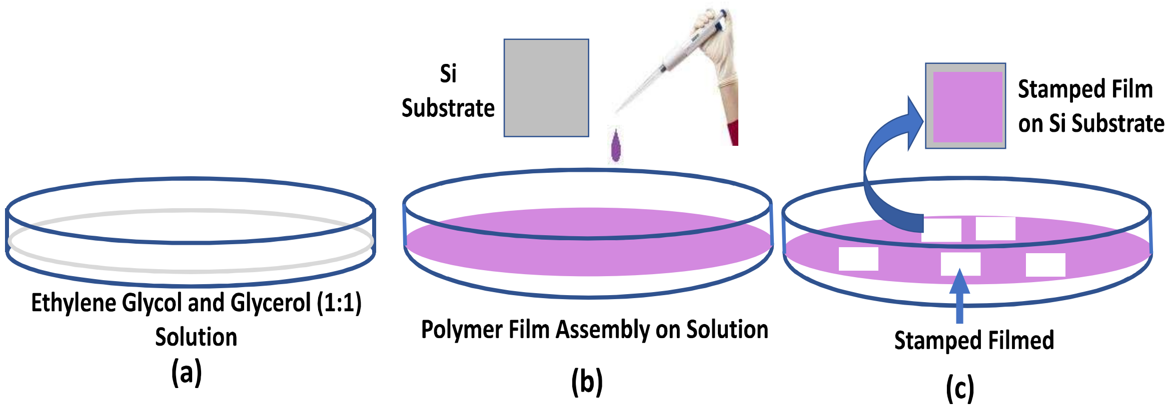

Figure 3.1 Steps of floating film transfer method.

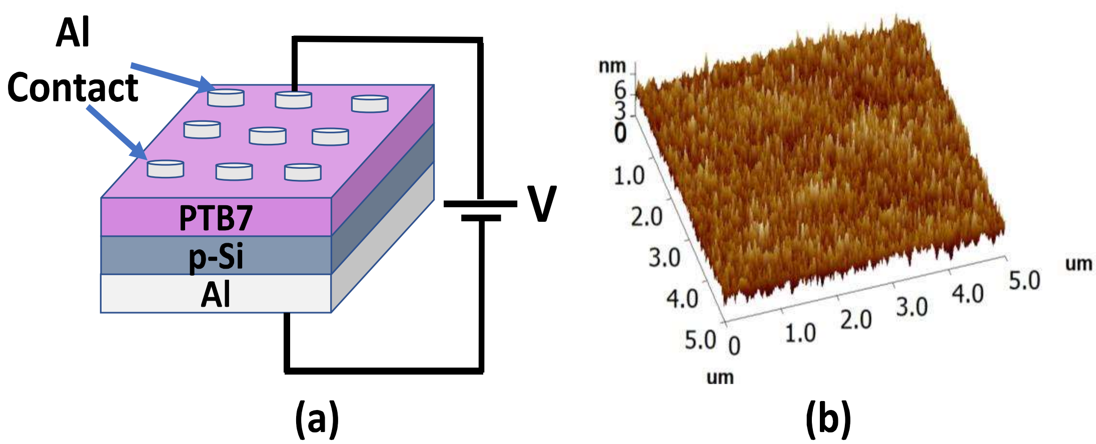

Figure 3.2 (a) Schematic of device structure, (b) 3D AFM image of the polymer film.

3.3 Results and Discussion

3.3.1. Thin Film Characterization

The thickness of the PTB7 film was estimated as ~90 nm by reflectometer measurements (Filmstrips F-20). The surface topography of the polymer thin film on Si substrate was characterized by AFM is shown in **Figure 3.2(b)** which shows an average roughness of ~0.703 nm.

3.3.2. Optoelectronics Characterization of the Device

The energy band diagram of our proposed photodetector is illustrated in **Figure 3.3(a)**. When white light is illuminated on the sensing surface of the fabricated device, photons are absorbed to create electron-hole pairs in the device [18]. These photogenerated E-H (electron-hole) pairs generated in the PTB7 film are drifted out in opposite directions by the built-in potential at the Al/PTB7 Schottky junction interface which results in a photocurrent of the device [13]. The absorbance characteristic of the FTM-derived PTB7 sensing film shows a broad absorbance spectrum in **Figure 3.3(b)** with peak absorbance over ~640–680 nm (using Jasco V-730 spectrophotometer). The absorbance characteristic of the Al-contact (of ~ 70 nm thickness) is shown in **Figure 3.3(c)**. Clearly, it shows absorbance mainly in the visible region. However, its absorbance is much smaller than that of the PTB7 active layer shown in **Figure 3.3(b)**. Further, it may be noted that we have used Al-metal dots instead of an Al-metal film for contact electrodes. Hence the maximum amount of light directly enters into the active PTB7 layer with only a fractional absorption in the Al-metal dots. The fabricated device was processed for electrical characterizations under dark and illuminated conditions using Keysight B1500A. White light was illuminated from a monochromator (Model SP2150i, Princeton Instruments) with varying intensity from 0.228 mW/cm^2 to 12.98 mW/cm^2 for optical characterization of the proposed photodetector device.

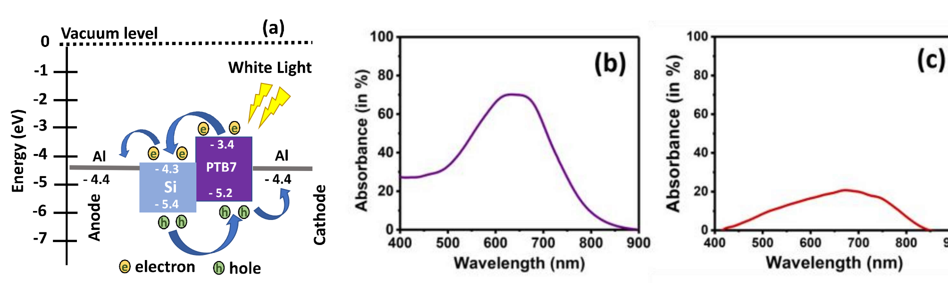

Figure 3.3 (a) Energy band diagram of the fabricated device representing the HOMO and LUMO energy levels of polymer before biasing, (b) UV absorbance spectra of the polymer thin film, (c) UV absorbance spectra of the Al contact.

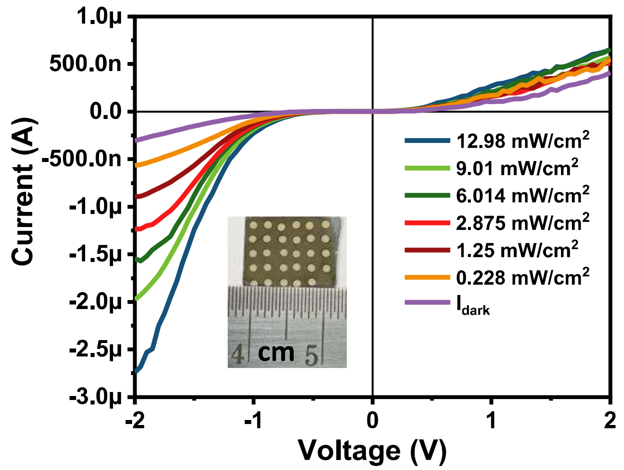

Figure 3.4 Current - Voltage plot of the as-fabricated device with varying incident white light irradiation and device image in inset.

Figure 3.4 depicts the current vs. voltage (I-V) plot of the device under different white light intensities under same ambient conditions. The proposed white light photodetector shows a very low dark current (I_{dark}) as compared to current under illumination (I_{light}).

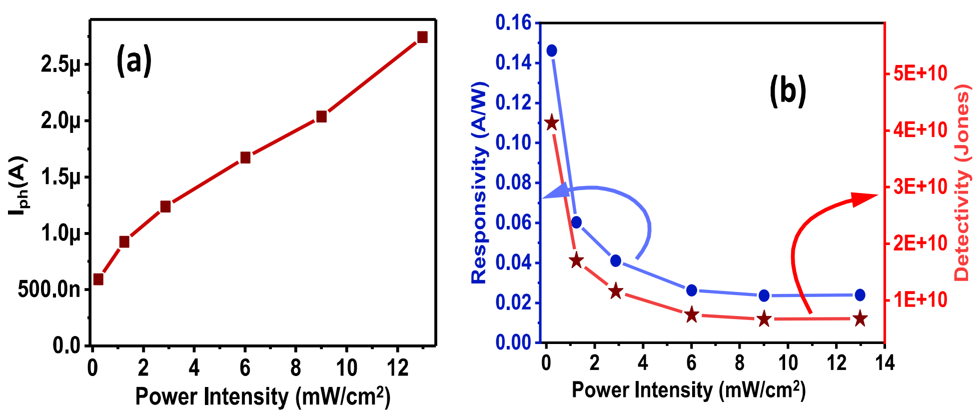

Figure 3.5 (a) Device current as a function of incident optical power, (b) responsivity and Specific detectivity plot of the fabricated device with respect to the power intensity of incident white light.

Figure 3.5(a) gives a nearly linear co-relation between the photocurrent ($I_{ph} = I_{light} - I_{dark}$) and incident optical irradiation (I_{opt}) on the device. The increase in power density increases the photogenerated electron-hole pairs, which in turn, enhances the photocurrent. The responsivity (R) is formulated as the ratio of the photocurrent (I_{ph}) to the incident power and specific detectivity (D^*) is expressed (in the unit Jones) as given below [19][20][21][22]:

$$R = \frac{I_{ph}}{I_{opt}} \qquad \& \qquad D^* = R \times \sqrt{\frac{A}{2 \times e \times I_{dark}}} \tag{3.1}$$

where, A is the effective sensing area of the device and e is the charge of an electron. The maximum responsivity of ~146.13 mA/W was obtained for the white light intensity of 0.228 mW/cm^2 under the bias of -2 V.

The responsivity and specific detectivity are dependent on incident optical power as shown in **Figure 3.5(b)**. The maximum specific detectivity of ~4.13751 × 10^{10} Jones was obtained at the incident optical power intensity of ~0.228 mW/cm^2.

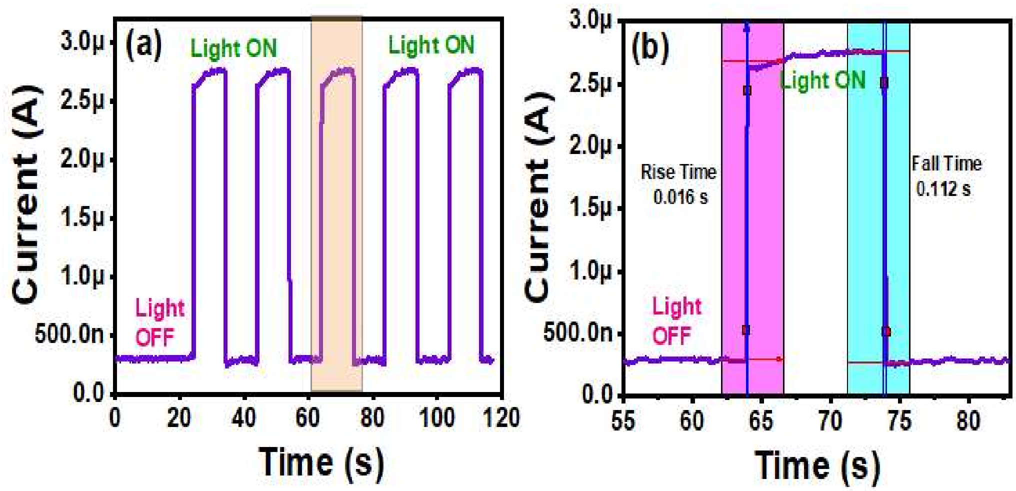

Figure 3.6 (a) Transient response characteristics of the fabricated photodetector at -2 V under the illumination of 12.98 mW/cm^2 white light power, (b) rise time and fall time calculation of the fabricated device.

The speed of operation of a photodetector is characterized by the response/recovery time of the output current plot corresponding to a pulsed (ON/OFF) light incident on the device. This transient characteristic of the proposed photodetector is studied by using a white light pulse of 12.98 mW/cm^2 power intensity with unity on/off ratio displayed in **Figure 3.6(a)**. The response time (recovery time) is defined as the time required to change the output current from 10% to 90% (from 90% to 10%) of the peak value at the rising (falling) edge of the switch current pulse. **Figure 3.6(b)** demonstrates the measurement of the rise/fall time as ~0.016/~0.112 s respectively. The slow time response may be attributed to the poor conductivity of the organic polymer PTB7 thin film used as the active material in the device.

Table 3.1 Comparison of the optical parameters of white light photodetectors

Device/structure	Bias (in Volts)	Incident Power Intensity (mW/cm^2)	Responsivity (mA/W)	Detectivity (Jones)	Rise Time/Fall Time (in sec)	References
ITO/ZnO/$BiFeO_3$/PEDOT:PSS/Ag	-2 to 2	0.040	34	--	7.2 s and 6.2 s	[132]
PET/ITO/ZnO/BFO/PEDOT:PSS/Au	-1 to 2	--	40	--	9 s and 6 s	[133]
FTO/BI-TU/Carbon	-1 to 1	100	0.0028	4.06×10^7	--	[134]
$Cs_4CuSb_2Cl_{12}$ microcrystals/Al	-2 to 2	197.5	0.170	4×10^8	0.12 s and 0.18 s	[135]
$MAPbI_3$ powder crystals	-1.5 to 1.5	19	1.3	8.2×10^{11}	0.2 s and 0.5 s	[136]
Al/PTB7/Si/Al	-2 to 2	0.228	146.13	4.137×10^{10}	0.016 s and 0.112 s	**Proposed Work**

3.4 Conclusion

This chapter reports an Al/PTB7/Si/Al vertical structure-based white light photodetector where the organic thin film (PTB7) is deposited by using the floating-film transfer method. To the best of our knowledge, this is the first attempt to investigate FTM-derived PTB7 thin film for use in white light detection. The proposed photodetector showed the maximum values of the detectivity and responsivity of ~4.137×10^{10} Jones and ~146.13 mA/W respectively at the incident optical power intensity of 0.228 mW/cm^2. The rise/fall time of the fabricated device was obtained from the transient characteristics as ~0.016/~0.112 s, respectively. The proposed photodetector is believed to be used for image-sensing applications.