ABSTRACT

Photodetector is a device that converts an optical signal into an electrical signal. The converted electrical signal can be processed for optical communication and computing, environmental monitoring, surveillance, image sensing and many more. In general, most of the commercial photodetectors are based on inorganic semiconductors materials such as silicon (Si) and III-V materials. Higher carrier mobility, smaller exciton binding energy, higher temperature processing and higher stability may be the major reasons for preferring the inorganic materials over the organic semiconductors for electronic device applications. However, the fabrication process of inorganic materials-based photodetectors requires many expensive sophisticated analytical equipment which, in turn, increases the fabrication and manufacturing costs of these devices. Further, inorganic semiconductors are not suitable for flexible electronic device fabrications due to mechanical rigidity. That is why, a number of researchers have been trying to explore the organic semiconducting compounds for fabricating the optoelectronic devices due to their lower fabrication cost by solution methods, lower temperature processing, lighter weights, and better mechanical flexibility of the organic materials over the inorganic semiconductors during last two decades.

In general, most of the reported organic photodetectors use two terminal device structures similar to the photovoltaic devices. Such devices mainly consist of an active layer sandwiched between the anode and cathode. In this type of photodetector structure, either the cathode or anode electrode is made to be transparent to the incident light so that light can be entered into the active layer of the device through it. In particular, the active layer in an

organic photodetector may either be an organic semiconducting material or an inorganic - organic hybrid nanocomposite material.

From the structural point of view, organic photodetectors are mainly classified into three types phototransistors-based OPDs (PT-OPDs), photoconductors-based OPDs (PC-OPDs), and photodiodes-based OPDs (PD-OPDs). Every device structure has its individual merits and demerits for various applications. The PT-OPDs have normally three-terminals namely source, drain and gate like the field effect transistors (FETs) The PT-OPDs provide photocurrent gain due to transistor action. In addition, a photoconductive gain can also be obtained by modulating the conductivity of the channel through the bias voltage applied to the Gate electrode. The PC-OPDs are two-terminal devices like inorganic photoconductors. PC-OPDs can provide photocurrent gain by photocarrier multiplication or photocurrent multiplication or simply photomultiplication (PM) effect, which, in turn, results in the high responsivity, more than 100% external quantum efficiency (EQE) and high detectivity of the PC-OPDs. Recently, nanocomposites of conducting polymers and inorganic semiconductors have been used for fabricating high performance wideband photodetectors.

The present thesis deals with the fabrication and characterization of some PM effect based organic-inorganic hybrid broadband photodetectors. The present thesis aims to the performance optimization of such inorganic-organic photoactive material based broadband photodetectors through device structural engineering and active material engineering. A relatively less explored PTB7 polymer for the broadband photodetector applications. PbS QDs and CdSe tetrapod shaped nanocrystals (NCs) are also used as sensitizers in organic photoactive material to modify its absorption spectra. This thesis includes five chapters. The layout of the present thesis is briefly described in the following:

Chapter 1 includes a brief introduction about the basics of organic photodetectors and the used strategies for the developing high-performance photodetectors. Some important performance parameters of the photodetectors are also discussed. A detailed literature survey on various inorganic-organic photodetectors is then presented. Various strategies used for the performance optimization of the organic-inorganic broadband photodetectors are also reviewed. Emphasis has been given primarily on the binary and ternary blend of organic-organic and organic-inorganic based photodetectors. Based on the observations from the literature survey, the scopes of the present thesis are finally defined.

Chapter 2 presents a novel technique for enhancing the responsivity and EQE of a FTO-coated glass/ZnO nanorods arrays (NRAs)/PCDTBT:PCBM:PbS QDs/Ag structure based broadband photodetector. The ZnO NRAs layer acts as the electron transport layer (ETL), the hybrid organic-inorganic nanocomposite layer of the PCDTBT: PCBM: PbS QDs acts as the active layer and the MoOx layer acts as the hole transport layer (HTL) in the photodetector. The ZnO NRAs ETL is first grown on the cleaned FTO-coated glass substrates by hydrothermal method. The PCDTBT:PCBM:PbS QDs active layer is then grown on the ZnO NRAs ETL by spin-coating method in such as way that the ZnO NRs are penetrated vertically inside the active layer to improve the charge extraction and transportation from the active layer. The PbS QDs in the active layer act as an effective photosensitizer for enhancing the absorption in the visible region of the PCDTBT: PCBM polymer. The combined effects of the ETL engineering, ternary nanocomposite based active material engineering and vertical structure engineering enabled the proposed device to achieve high responsivities of ~ 213.77 A/W at 380 nm (UV), ~28.57 A/W at 550 nm

(Visible), and ~7.22 A/W at 860 nm (NIR). The proposed photodetector showed a high external quantum efficiency (EQE) of greater than 1000 % at a low reverse bias of -1.5V.

Chapter 3 explores the ternary inorganic-organic nanocomposite of PCDTBT: PCBM: CdSe tetrapod shaped nanocrystals (NCs) for broadband photodetector applications. A device structure of FTO/ZnO NRs/PCDTBT:PCBM:CdSe NCs/MoOx/Ag is fabricated on the FTO-coated glass substrate. The CdSe tetrapod shaped NCs is used to act as a sensitizer while the PCDTBT: PCBM composite polymer provides functional interfaces for extracting charge carriers from the inorganic sensitizer to improve the transportation photogenerated charge carriers. The used polymers not only facilitate efficient charge extraction from the inorganic NCs but also allow ambipolar transport in the ternary blend nanocomposites-based proposed device. The CdSe tetrapod shaped NCs are shown to improve the performance over the commonly used spherical shaped inorganic NCs. Under a reverse bias voltage of -2 V, the proposed photodetector showed excellent photoresponse characteristics with a responsivity of 1.830 A/W (0.344 A/W), detectivity of 1.75×10^{12} (3.3×10^{11}) Jones, a rise time of 5.73 s (0.02 s) and fall time of 6.41s (0.14 s) at UV-375 nm (Visible-540 nm) under a low intensity of indent light of 13.1 μWcm^{-2} (41.2 μWcm^{-2}).

Chapter 4 presents a simple low-cost approach to fabricate a p-PTB7/n-ZnO NRs heterojunction based high performance wideband photodetector. The main objective of this chapter is to explore the relatively less-explored PTB7 organic semiconductor material for broadband photodetection applications. The performance of an FTO/ZnO NRs/PTB7/MoOx/Ag structure is investigated in this structure. The basic objective of this study was to replace the ternary organic-inorganic nanocomposites (considered in previous chapters) by the single high-quality PTB7 ploymer to reduce both the fabrication complexity and cost of the broadband photodetectors. The PTB7 polymer serves as visible light absorber cum hole transport layer (HTL) while the ZnO NRs layer serves as the UV light absorber cum electron transport layer (ETL) in the proposed device structure. Under a relatively low reverse bias voltage of -1 V, the proposed device showed a high responsivities of ~ 307.18 A/W and ~ 33.64 A/W at 380 nm (UV) and 640 nm (Visible) wavelengths, respectively. The proposed device also showed the detectivities of $\sim 1.56 \times 10^{13}$ Jones and $\sim 1.7 \times 10^{12}$ Jones with the EQEs values of $\sim$ 100230 % and ~ 6510 % at 380 nm and 640 nm wavelengths under a low −1 V bias, respectively. The rise time of ~13.8s and fall time of ~ 15s were measured under an incident optical pulse of 380 nm with $\sim$ 20.07 μWcm^{-2} intensity.

Finally, **Chapter 5** is devoted to summarize the major findings of the present thesis. Some future scopes of works related to this thesis are also outlined in this chapter.