Chapter 1

Introduction and Scope of the Thesis

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1.1. Photodetector

Fast data transmission is crucial in the modern information age. Conventionally, data is transmitted as an electrical signal which is limited by the speed of the electron. At present, data transmission for long distances is dominated by the optical signal (light). Since electronic devices work on electrical signals so the optical signal (in optical communication) is converted to the electrical signal at the receiving end using a photodetector. Photodetectors are also used in many other electronic systems and perform a variety of functions such as image sensing, health monitoring, machine vision, drones, night surveillance, etc. [1]–[7]. Currently, the commercial photodetector is heavily dominated by inorganic semiconductors (i.e., silicon, indium gallium arsenide (InGaAs), etc.) because of their extraordinary charge carrier mobility, low exciton binding energy, and outstanding stability [8], [9]. Nonetheless, the use of inorganic-based photodetectors has been hampered by drawbacks such as limited mechanical flexibility, the requirement of sophisticated instruments in fabrication, high processing cost, and unsuitability for large areas.

Based on the region of detection (spectrum of wavelength), the photodetectors (PDs) can be further classified as ultra violet PD, visible PD, and infrared PDs. As the name suggests these photodetectors are sensitive in their respective region of incident wavelength. The visible PDs mainly finds their application in fiber optical communication channels, artificial vision and video imaging, while the infrared PDs are useful in biomedical diagnostic, meteorological predictions, defense setups, space telescopes[10], [11].

UV light has a wavelength range of 10 nanometers (nm) to 400 nanometers (nm). These wavelengths are shorter than visible light wavelengths but longer than X-ray wavelengths. UV- radiation in the range of 280 nm to 400 nm finds application in medical imaging system, 240 nm to 280 nm is used for DNA sequencing and analysis of protein, 250 nm to 300 nm is utilized for forensic sciences, and 193 nm deep UV (DUV) lithography. Considering these important applications, design of UV photodetectors is very important. Furthermore, the UV PDs find their application in chemical and biological sensors like ozone sensing, pollutant monitoring etc., gas sensing and flame detection[10]–[12].

For the past two decades, organic semiconductors (which include small molecules and polymers) based photodetectors have gained popularity because of their large area, low-temperature processing, low cost, and adaptability to the flexible substrate. However, the external quantum efficacy (EQE) of organic semiconductor-based photodetectors is generally low because of their lower efficiency of exciton dissociation, photon harvesting efficiency, and poor collection and transport of photogenerated carriers. It is observed that the use of heterostructures can help in the efficient separation of photogenerated carriers because of the built in field and thus reduce the recombination thereby improving photodetection performance[4]. Moreover, the use of low-dimension semiconductors in photodetectors has also shown improved performance because of their large surface-to-volume ratio, efficient carrier confinement effects, and optical wavelength tunability[13], [14]. In this thesis, we have explored some solution-processed ZnO colloidal quantum dots and organic semiconductor-based heterojunction photodetectors. In this first chapter, we introduce the basic structures of the photodetector, some semiconductor nanostructures, photodetector performance parameters, state-of-the-art review, motivation, problem statements, and objectives of the thesis.

1.2. Performance Parameters of Photodetectors

Some of the key performance parameters of a photodetector are responsivity (R), specific detectivity (D^*), external quantum efficiency, and response speed [15]–[19].

Responsivity (R): The responsivity (R) is defined as the ratio of the generated photocurrent to the incident optical power at a given wavelength of incident light.

The responsivity is expressed as:

$$\mathrm{R} = \frac{\text{Change in current / Effective area of device}}{\text{Incident power density on the device}} \tag{1.1}$$

Detectivity (D^*): The specific detectivity (D^*) is calculated by the following equation:

$$\mathrm{D}^* = \frac{\mathrm{R}}{\sqrt{2 \times \mathrm{e}^- \times \mathrm{J_d}}} \tag{1.2}$$

where R is responsivity, e^- is the charge of an electron, and J_d is the dark current density of the detector.

External quantum efficiency (EQE): The EQE is defined as the ratio of the number of electron-hole pairs collected at the external terminal to the number of photons of a particular wavelength incident on the device. The EQE is calculated as:

$$\mathrm{EQE}\ \% = \frac{1240 \times \mathrm{R}}{\lambda\ (\mathrm{nm})} \times 100 \tag{1.3}$$

where R is responsivity, and λ is the incident wavelength in nm. The EQE is a very significant parameter that represents the capability of optoelectronic conversion for an OPD.

Response speed: The response speed of any photodetector is expressed in terms of its rise time and fall time corresponding to an ON/OFF light pulse input signal. The rise time represents the time required for changing the detector current from 10% to 90% of its maximum value in response to a step change in its incident light intensity. On the other hand, the fall time represents the time required for changing the output current from 90% to 10% of its maximum value after the light source is switched off.

1.3. Materials for Photodetectors

Different materials for photodetectors are researched for a long time to improve the performance parameters. The most important component of a photodetector is semiconductor and most of the used semiconductors are inorganic. Silicon, germanium, gallium arsenide, etc. are few examples of inorganic semiconductors for photodetectors. However, the inorganic semiconductor has limitation for flexible and large-area device at low temperature processing. For the last two decades, organic semiconductors are widely used for the fabrication of photodetectors [1], [19]–[21].

1.3.1 Organic Semiconductors

Organic semiconductors can be classified as small molecules like pentacene and polymer-based semiconductors like F8BT, PQT12, etc. The polymer or small molecule semiconductors generally consist of π-conjugated structures. Owing to the significant overlap in wavefunction between the electronic ground state and the lowest excited state, organic semiconductors (OSCs) possess high exciton coefficients[21]. This unique characteristic helps the OSC to exhibit strong light absorption properties even in thin and flexible films, typically less than 200 nm in thickness [22]. In comparison to having the same light absorption, silicon requires a much thicker layer in order of several micrometers.

Furthermore, by simply modifying the organic materials, one can alter the absorption characteristics of OSC. Such a flexible way to modify the absorption coefficient offers novel functionalities in photodetection that are not achievable using traditional inorganic materials [23]. Processing of OSC can be done through either vacuum-based deposition or a solution route. While vacuum-based processing is the preferred choice in the case of small molecule OSC due to their poor solubility, whereas solution route is used for processing of polymer OSC. Basic solution processing techniques that are commonly used for polymer OSC are inkjet printing, spin coating, slot die, drop casting, floating film method, and blade coating. Solution processing route makes the OSC-based organic photodetectors (OPDs) low cost and suitable for large area processing [6], [15]–[17], [22], [24], [25].

1.3.2 Semiconductor Nanostructures

The semiconductor structure (especially at the nanoscale) dominantly affects the performance of the photodetectors. The semiconductor nanostructures have garnered significant attention in the field of optoelectronics applications due to their unique characteristics, particularly their high surface-to-volume ratio compared to bulk counterparts. The electronic and optical properties of semiconductor nanostructure can be significantly altered by manipulating their size, shape, and arrangement. Notably, the size of these nanostructures plays a crucial role in modifying their electronic band structures, primarily due to a phenomenon known as the quantum confinement effect. This effect becomes prominent when the size of the particles falls within the range of 1- 10 nm or below Bohr's radius. Semiconductor materials can be divided into four sub-class based on dimension. Figure 1.1 illustrates the various dimension along with their respective effect on the density of states and degree of confinement[7], [13].

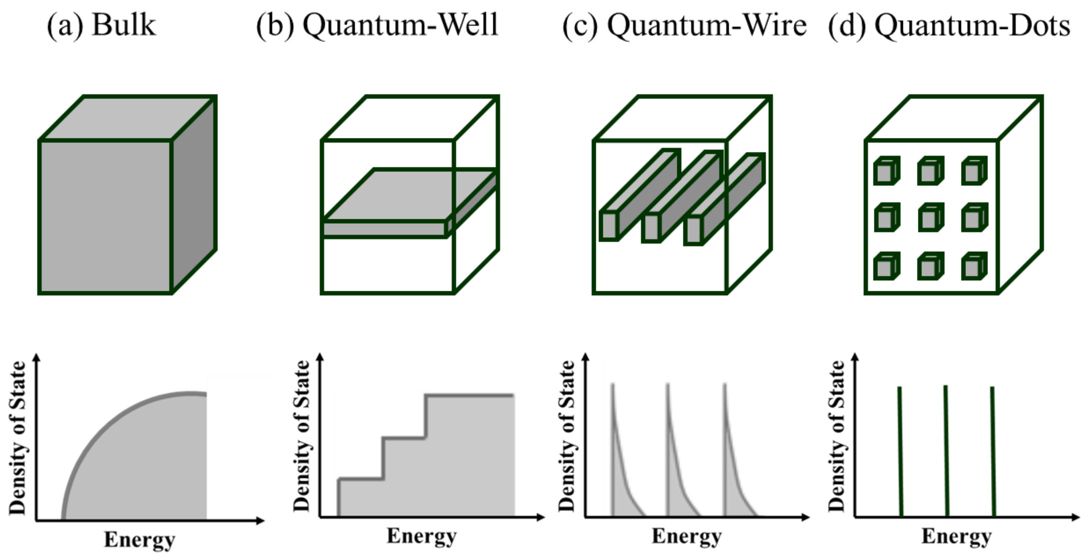

Figure 1.1: Diagrammatic representation of material structures and respective variation in density of state (DOS) and degree of confinement for (a) Bulk (3-D), (b) Quantum well (2-D), (c) Quantum wires (1-D), and (d) Quantum dots (0-D).

1.3.2.1 *Three Dimensional (3-D) Semiconductor*

A 3-D semiconductor has larger dimensions in all three directions. There is no confinement of particles in any direction. The charged particles are free to move in all directions. The 3-D semiconductor is a bulk semiconductor whose properties are not affected by the change in size and structure of the material[7], [13].

1.3.2.2 *Two Dimensional (2-D) Nanostructures*

2-D materials possess layered structures with respect to dimension, which helps in restricting particle movement in a single direction. In 2-D materials, the atoms within the plane are connected using normal covalent bonds while different layers are held together with weak Van der Waals forces. The distinctive nature of 2-D materials is attributed to their atomic level thinness which helps in carrier confinement in one direction. 2-D materials generally form quantum well where there is a significant potential barrier in one direction resulting in carrier confinement in that particular direction. The electron energy levels are determined by the dimensions of the quantum well [13].

1.3.2.3 *One Dimensional (1-D) Nanostructures*

Nanostructures that have two dimensions in the range of 1-10 nm, restricting the particle motion in two directions, thereby having effective confinement in two directions, are called 1-D nanostructures. The 1-D nanostructure has a larger dimension in one direction so the charge transportation generally took place in only one direction. General examples of 1D structures are Nanorods and Nanowires [13].

1.3.2.4 *Zero Dimensional (0-D) Nanostructures*

The nanostructures in which the quantum confinement phenomenon is possible in all three directions are called zero-dimension nanostructures or quantum dots (QDs). As particle motion is restricted in all three directions, the confinement effect is more prominent in QDs. The energy bands of QDs can be easily tuned by changing the size of QDs in comparison to 1-D and 2-D nanostructures. The effect of quantum size and respective bandgap tuning has been depicted in Figure 1.2. whereas Figure 1.3 illustrates the respective shift in the absorption spectrum with the modification in the size of QDs [7], [13].

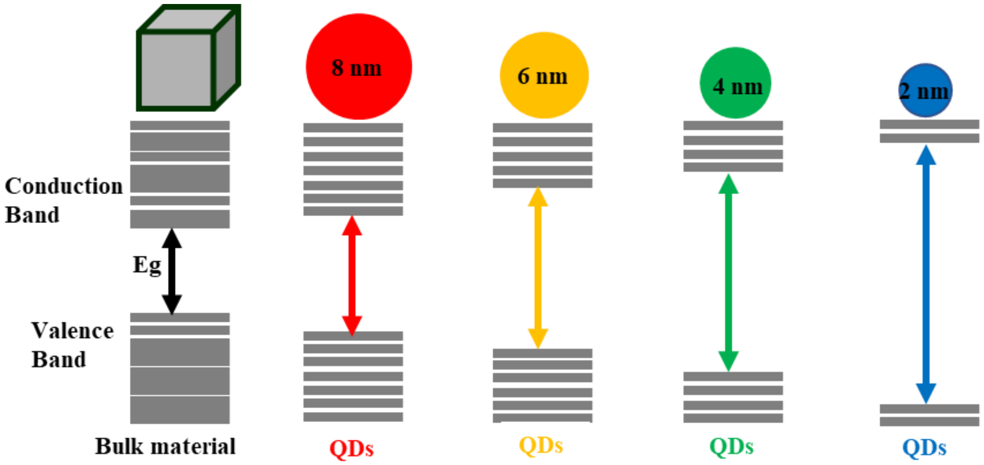

Figure 1.2: Size effect of QDs and bandgap tuning.

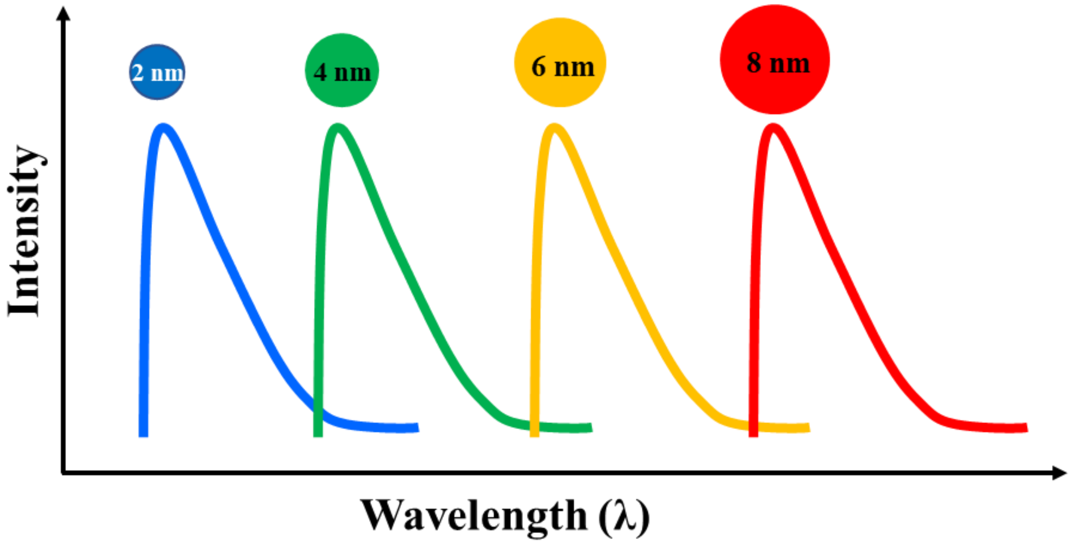

Figure 1.3: Size effect of QDs and shift in peak intensity from blue to red on increasing Size.

1.4. Photodetector Structures

The performance and application of the photodetectors commonly depend on their structure. The uses of photodetectors are outlined in Figure 1.4. Photodetectors are broadly classified into three different structures, namely photoconductor (PC), photodiode (PD), and phototransistor (PT). PC is a two-terminal device, as shown in Figure 1.5 (a), which works by introducing photocurrent gain or photomultiplication effect resulting in EQE greater than 100%. Nonetheless, the application of such photodetectors is limited by their poor signal-to-noise ratio (SNR) and response time. PT (as shown in Figure 1.5 (b)) is a three terminals device, namely a source, drain, and gate. In PT, EQE can attain a value greater than 100% owing to the basic transistor action enabled by gate modulation. However, three terminals and complex biasing circuits restrict the use of PT in many applications. The third structure commonly used is PD (as shown in Figure 1.5 (c)). PD structure is formed by two semiconductors. If both the semiconductors are similar then it is called as homojunction photodetector whereas if two semiconductors are de-similar then it is called as heterojunction photodetector. PD has the advantage of a built-in electric field, which helps in the efficient charge extraction and transport of photogenerated carriers. Moreover, different heterostructures can be used to further enhance charge separation and efficient transportation, thereby minimizing recombination[4].

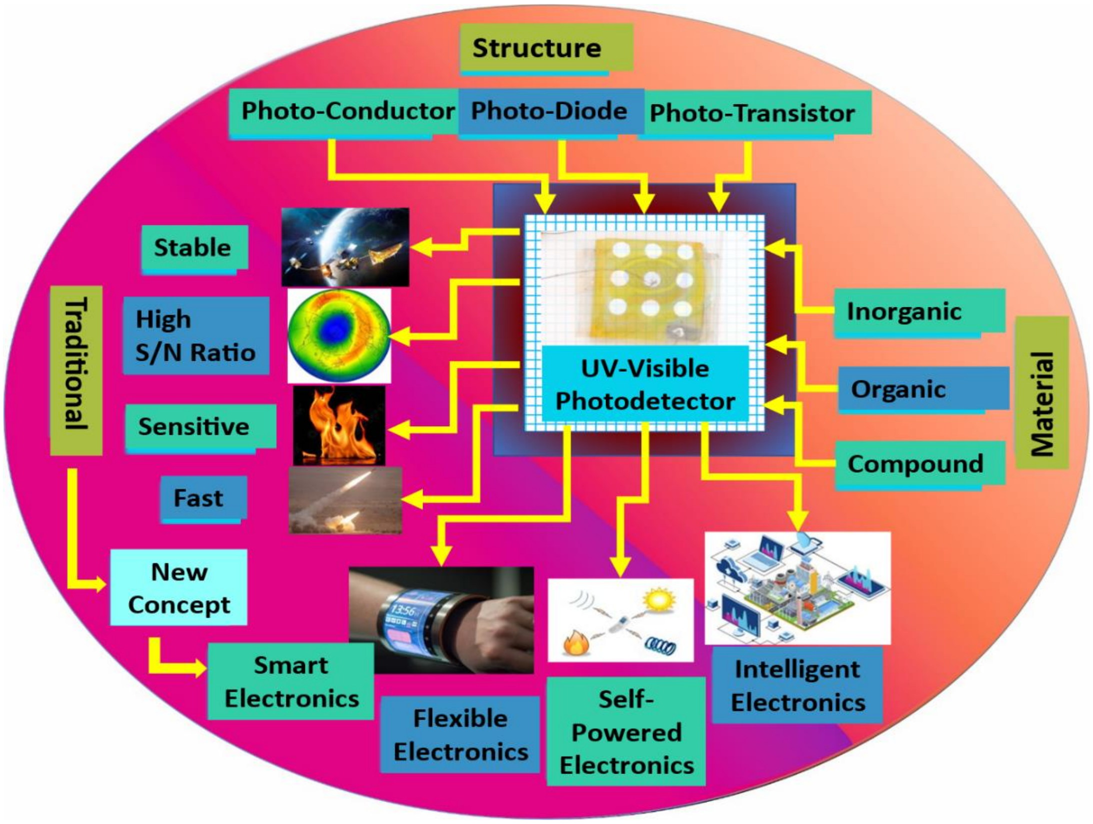

Figure 1.4: Photodetector structures and some applications redrawn [26]

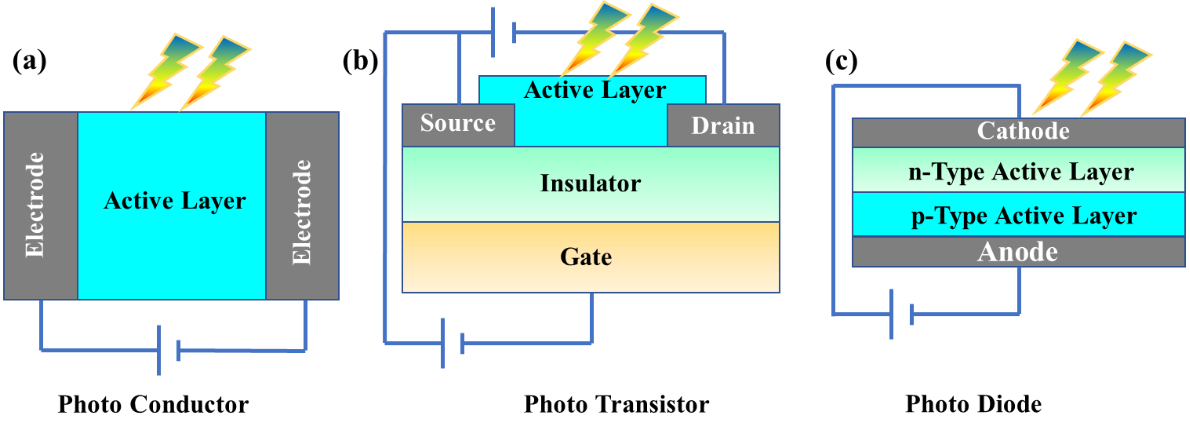

Figure 1.5: Some key structures for Photodetectors (a) Photoconductor (b) Phototransistor, (c) Photodiode. redrawn [4]

The exciting performance improvement in the optoelectronic characteristic can be achieved when the photodetectors are fabricated as heterojunction. The organic semiconductors form heterojunction with either inorganic or organic semiconductors. The organic semiconductor based heterojunctions have exhibit enhanced optoelectronic properties [20]. One important strategy to use heterojunction-based photodiodes is its inbuilt field which help in the efficient separation and transportation of photogenerated carriers [4], [27]–[30]. Heterojunction is commonly defined as a metallurgical junctions made out of two dissimilar semiconducting materials having dissimilar energy bandgaps. Preston in 1950, reported the first heterostructure [31]. As per the Anderson Model, some interfacial discontinuities or offsets are created at valence or conduction bands owing to dissimilarity in work function, electron affinity, permittivity, and band gap energy of different semiconductors [32], [33]. Energy band alignment and the nature of majority carriers on either side of the junction are two significant criteria for the classification of heterostructures. As per band alignment criteria, major categories of heterostructures include (1) type I, (2) Type II, and (3) Type III. As represented in Figure 1.6 (a), the band gap of the material with the smaller band gap is enclosed within the band gap of the material with the bigger band gap in a straddling or Type I heterojunction. In order to have carrier transition, such alignment requires a particular amount of energy for the electrons and holes from the two materials. Whereas in staggered or Type II heterostructures (as represented in Figure 1.6 (b)), there is the accumulation of electrons in one material and holes in another owing to special band alignment, i.e., both conduction (CB) and valence bands (VB) is positioned lower than that of the CB and VB of the other material. In simple words, due to their confinement within discrete energy levels in the individual semiconductors of the heterojunction, electrons, and holes in Type II heterojunctions flow asymmetrically between the two materials. The Type

III heterostructure, which is shown in Figure 1.6 (c), is a subset of the Type II heterostructure with a band alignment such that the VB of one Semiconductor lies below the CB of the other. Out of all the discussed Heterostructures, Type II structures are the most useful for designing organic photodetectors owing to their efficient extraction, separation, and transportation of photogenerated carriers[32], [33].

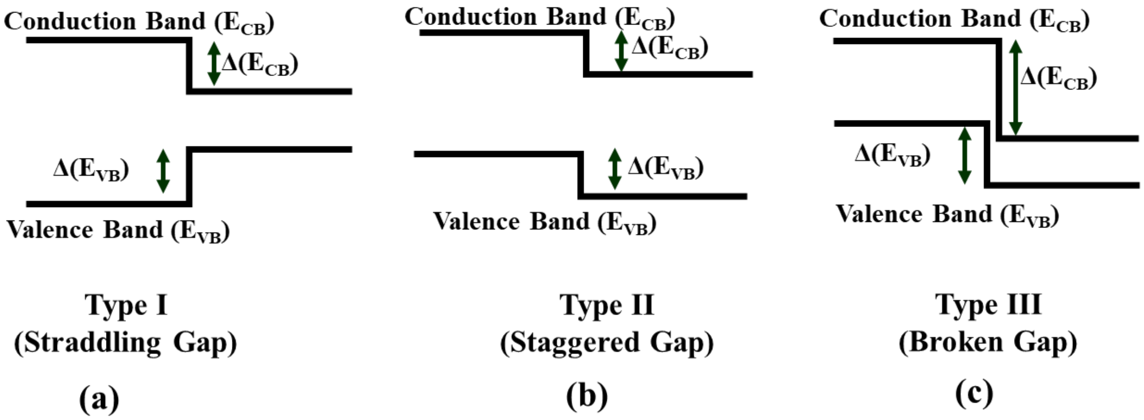

Figure 1.6: Type of Heterostructures based on Band Alignment.

The performance of heterojunction photodetectors is further improved through internal photo multiplication and photovoltaic property. Therefore, the heterojunction photodetectors can further be classified as photomultiplier-based photodetector and self-powered photodetector.

1.4.1 Photomultiplier based Photodetectors

A High responsivity is a basic requirement, especially if the light signal is very weak. However, some photodetectors have poor responsivity. One important strategy to improve responsivity is the photomultiplication (PM) effect. In these sections, we will discuss the basics of PM effect, review of common PM strategies and their effects. An important but simplistic approach for achieving photocurrent multiplication is utilizing charge tunneling injection from an external circuit. The basic steps involved in photomultiplication in a heterojunction photodetector can be summarized as follows[17]:

i) Firstly, upon illumination, the exciton formation and separation occur, which resembles the mechanisms reported in heterojunction photodetectors.

ii) The transportation and collection of majority carriers at an electrode is facilitated by the active layer. However, the minority carriers (when they move in opposite directions) get trapped by the charge traps or suitable charge blocking layer. This results in the accumulation of minority carriers at the injection electrode.

iii) Accumulation of trapped minority carriers at the injection electrode results in the formation of a coulombic field which helps in lowering the injection barrier of Majority carriers (opposite charges).

iv) Subsequently, the lowering of the injection barrier followed by interfacial band bending facilitates the tunnelling injection of the majority charge into active layer from the external circuit at the injection electrode.

It is also observed that the introduction of trap states in the active layer is the most common strategy to achieve photomultiplication in OPDs. Broadly this approach can be categorized into two groups, namely a) Introducing Nanoparticles or dyes into the active layer and b) utilization of a restricted number of acceptors as traps in the active layer. PM OPDs can be classified into three categories, namely a) PM by introducing taps in the active layer, b) PM by introducing taps in the interfacial layer, and c) PM by introducing the interfacial blocking layer. A diagrammatic illustration of the photomultiplication effect in OPDs with the location of traps in different layers is shown in Figure 1.7.

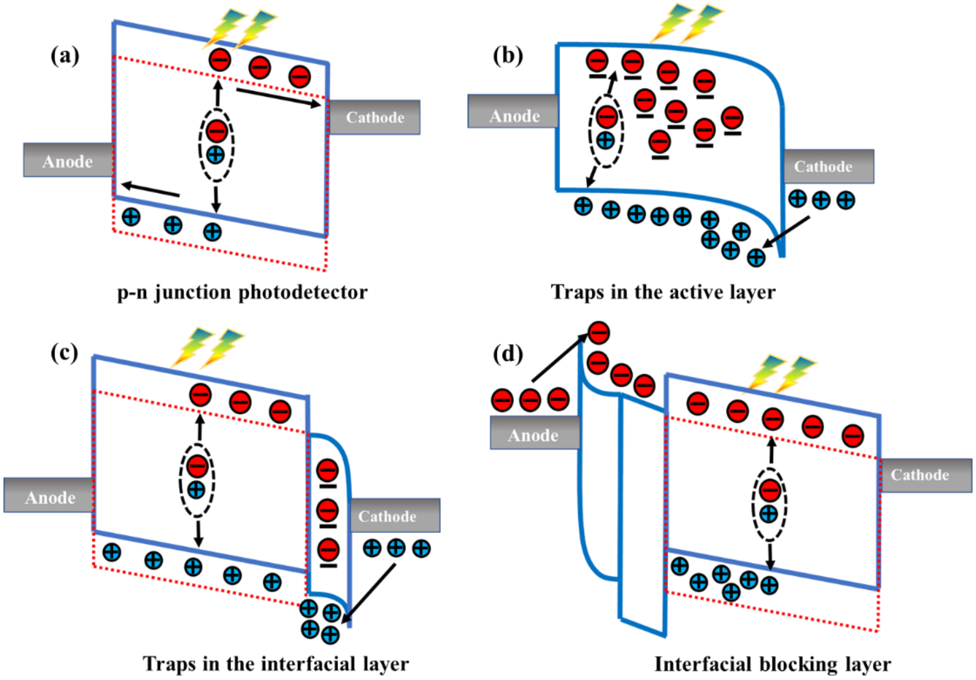

Figure 1.7: (a) Basic working of OPD (b) Photomultiplication based OPDs with electron traps in active layer (c) Photomultiplication based OPDs with traps in interfacial layers (d) Photomultiplication based OPDs using interfacial blocking layer.

1.4.2 Self Powered Photodetectors

Self powered photodetector works on the principle of generation of photocurrent under photovoltaic phenomenon. No external biasing is required in self powered photodetector. The basic mechanism of photodetection consists of the generation of e-h pairs followed by the separation and transportation of these photogenerated carriers. The separation and transportation of photogenerated carriers happens under the influence of the field. This electric field can be either intrinsic (like in the case of the Schottky junction or p-n junction) or external. Notably, the first method (intrinsic field) results in a self-powered operation. A self-powered photodetector does not require an external voltage source for its operation and generally finds application in portable low power consumption devices. The photovoltaic effect can be utilized to design the self-powered photodetector. Self-powered photodetectors that employ the photovoltaic effect are classified into three categories based on the properties of charge separation at the interface: Schottky junction and p-n junction. A traditional photodetector consists of a semiconductor with two ohmic metal contacts. However, such devices require an external power source for the separation of photogenerated carriers. Nonsymmetrical Schottky contact devices can be created by replacing one of the two Ohmic contacts ends with a Schottky barrier contact. When the Schottky junction is illuminated, the built-in electric field at the interface helps in the efficient separation and transport of photogenerated carriers leading to the flow of current. This makes Schottky contacts suitable for light detection even without external bias. Similarly, the built-in field and asymmetry at the p-n junction facilitate the enhanced separation and transportation of photogenerated electrons and holes constituting the electric current, thereby rendering them suitable for light detection even at Zero bias[20], [34]–[36].

1.5. Literature Review

The literature review in this section is mainly focused on the heterojunction organic photodetectors, photomultiplier based photodetectors, and self powered photodetectors. The detailed literature on above three types of photodetectors is discussed separately in subsequent sub-sections:

1.5.1 Review on Some Heterojunction based Organic Photodetectors

As discussed in previous section, the heterojunction is formed between two dissimilar semiconductors. The heterojunction based photodetectors are most researched devices for the optoelectronic applications. In this subsection, a brief review on the heterojunction based organic photodetection is summarised as below:

Bilgaiyan et al. [27] fabricated ZnO nanorods /P3HT based heterostructures for UV visible photodetector. They introduced an interfacial layer of dc sputtered gold nanoparticles (~ 5 nm) which helped in the improvement of responsivity from 10.7 A/W to 17.7 A/W. They observed the thin gold nano interfacial layer enhanced the absorption of ZnO in UV and visible region and also improved light extraction efficiency. However, the device is not completely solution processed as DC sputtering for the interfacial gold layer was used, thereby increasing the fabrication cost Wei Li et al. [37] fabricated bulk heterojunction-based OPD using the thick junction strategy to reduce the dark current. They utilized a blend PTB7-Th:CO1-4Cl to cover the visible and NIR region. The device structure was ITO/ZnO/PTB7-Th:CO1-4Cl/MoOx/Ag. Interestingly they used interfacial engineering by introducing MoOx as an electron blocking layer. However, the responsivity is just 0.5 A/W in NIR region. Zhi Liu et al. [38] has used the strategy of the ternary blend (donor (D: PTB7-Th) and two acceptors (A_1: CO_i8DFIC and A_2: $PC_{71}BM$)) to extend the range of photodetection and BHJ for improving the transportation and extraction efficiency of photogenerated carriers. They also utilized the thick junction concept to suppress dark current and MoOx as electron blocking layer. The device showed a responsivity of 0.35 A/W. J. Liu et al. [39] used a semi-tandem structure using ITO/ZnO/PTB7- Th:ITIC/PTB7-Th:FOIC/MoO3/Ag structure for UV-Vis photodetector. The device showed maximum responsivity of 0.48 A/W. Z. X. Liu et al. [38] used compositional tuning of the ternary blend of PTB7-Th: IFIC-i-4F:PC71BM with device structure of ITO/ZnO/PTB7-Th: IFIC-i-4F:PC71BM/MoO3/Ag to fabricate photodetector having detectivity of 1×10^{14} Jones. They showed that simply adjusting the composition of the ternary blend can shift the working mechanism of the photodetector. The findings demonstrate that by adjusting the fullerene/non-fullerene ratio in a ternary blend, one shifts the operational mechanism of the device. This transition facilitates the smooth transfer and transport of photogenerated carriers and effectively reduces the dark current through trap limitations. D.C Perng et al. [29] reported a UV photodetector by using interfacial engineering in which they introduced an electron blocking layer of poly-(N-vinyl carbazole) (PVK) in between layers of a Cu_2O and ZnO nanorods (NRs) . Moreover, PVK also acts as a hole transport layer. The device showed a responsivity of ~ 13.28 A/W. K S Ranjith et al. [30] demonstrated ZnO nanorods and PEDOT: PSS based organic, inorganic hybrid heterojunction photodetector. Heterojunction helped in efficient charge separation with a responsivity of 5.046 A/W. Table 1.1 compiles all the reviewed OPDs with their performance parameters.

1.5.2 Review on Some Photomultiplication based Organic Photodetectors

In this subsection, the photomultiplication based organic photodetectors are reviewed. Hiramoto et al. [40] reported perylene pigment film sandwiched between gold electrodes with remarkable amplification (~10000) of photocurrent. This effect was observed at the interface of gold and perylene pigment film. They discovered this is due to the depletion layer formed between pigment and gold electrodes under a high electric field. This was the first report on OPD based on the PM phenomenon. They attributed this effect to the structural traps generated by defects at organic-metal contact. In 2008, H Chen et al. [41] reported PM OPD through the introduction of CdTe nanoparticles in the P3HT polymer matrix as traps. The CdTe traps helped achieve EQE of 8000 % at - 4.5 V. Chen et al. [42] demonstrated that mixing of an organic dye called 4,5-benzoindotricarbocyanine (Ir-125) into a polymer blend of P3HT:PCBM (1:1, wt/wt) resulted in EQE of 7000% and notable responsivity of 32.4 A/W. This was achieved with the help of hole tunneling injection by electron trapping at the calcium electrode in an active layer interface [3]. Dong et al. [43] in 2014 reported the introduction of ZnO nanoparticles in the polymer blend to achieve an EQE value of 1624 % by photoconductive gain at - 4 V. ZnO nanoparticles acted as electron traps, thereby assisting hole tunneling injection while PbS Nanoparticles broaden the range into NIR region.

TABLE 1.1: REVIEW OF SOME HETEROSTRUCTURE BASED ORGANIC PHOTODETECTORS

Device Structure (Year)	**Detectivity (Jones), Bias (V)**	**Responsivity (A/W), Spectral Range (nm)**	**EQE (%) , Bias (V)**	**Ref.**
ITO/ZnO/PBDB-T: PNDI-FT10/P3HT/MoO3/Ag (2018	5.8×10^{12}, −3	0.34, 300-850	65, -3	[44]
ITO/ZnO/PTB7-Th:CO1-4Cl/MoOx/Ag (2019) (Interfacial Engg. Blend)	$3.3x10^{13}$, -0.1	0.45, 400-1100	65, -0.1	[45]
ITO/ZnO/PEIE/PTB7-Th: COi8DFIC:PC71BM/MoOx/Ag (2019) (Interfacial Engg Ternary Blend)	7×10^{11}, 0	0.35, 400-1000	--, --	[37]
ITO/ZnO/PTB7-Th: IFIC-i-4F:PC71BM/MoO3/Ag (2019)	1×10^{14}, 0	--, 300-1000	--, --	[38]
ITO/ZnO/PTB7-Th: ITIC/PTB7-Th: FOIC/MoO3/Ag (2020)	2.6×10^{11}, −0.1	0.48, 300-1000	75, -0.1	[39]
ITO / ZnO NR /P3HT / Au NPs / PEDOT:PSS /Ag (-2V)	--	17.7 (370 nm)	--	[27]
ITO / Cu2O / PVK / ZnO NR / Ag (-1 V)	1.03×10^{13}	13.28 (360 nm)	----	[29]
ITO / ZnO NR / P3HT / PEDOT: PSS / Ag -2 V	----	10.7 (370 nm)	-----	[27]
ITO / TiO2 / P3HT:PCBM /Al -1 V	1.9×10^{12}	0.5 (550 nm) 0.2 (370 nm)	113	[30]

Li et al. [5] in 2015 demonstrated all polymer base PM OPD by incorporating a PC71BM in the P3HT polymer layer to achieve EQE of 16700%. Enhanced injection of holes through hole tunneling due to trapped electrons in PC71BMs at the vicinity of the aluminum electrode was the main reason for this PM phenomenon. They further verified this effect by varying the PC71BM doping ratios and calculating the EQE. Li et al. [46] again demonstrated PM-OPDs by introducing 1% PC71BM in the P3HT blend. This device also used the concept of active layer electron traps introduced by PC71BM. The polymer photodetectors (PPDs) demonstrated a continuously exceptional external quantum efficiency (EQE) value after undergoing a burn-in treatment of 2000 seconds, reaching almost 12,600% under a bias of -19 V. This remarkable performance can be attributed to photogenerated electrons that are trapped close to the Al electrode helping to improve hole tunneling injection. The initial distribution of photogenerated electrons within the active layer and the subsequent redistribution of these electrons in response to changing biases can both be taken into account to effectively explain the EQE spectral characteristics and the response speed of the PPDs. Jang et al. [47] reported a planar heterojunction (PHJ) device with the structure of ITO/PEDOT: PSS/P3HT/PCBM/Al. The reported device used a heterojunction between P3HT and PCBM. However, the active layer in all prior photomultiplication organic photodetectors (OPDs) has been a bulk heterojunction (BHJ), which has limitations in terms of stability and thickness. Due to the necessity to avoid the creation of electron percolation routes, which is a crucial component for accomplishing photomultiplication, it is challenging to reduce the thickness of the active layer (about 250 nm), which is a fundamental constraint of photomultiplication BHJ-OPDs. So, this was the first report utilizing PHJ for photomultiplication, thereby reducing the thickness. Neethipathi et al. [3] demonstrated an OPD with structure ITO/PEDOT: PSS/P3HT/PCBM/Al with an optimized active layer thickness of ~ 70 nm by introducing an optical sensitizer called IDIC. This study suggested a unique technique for the photomultiplication of organic photodetectors (PM-OPDs) that uses a thinner active layer to increase external quantum efficiency (EQE). As an alternative to the traditional PC71BM, the IDIC non-fullerene acceptor is used as an optical sensitizer.

Temperature-dependent J-V measurements and analysis using the diode equation have shown that this replacement causes the creation of a more effective Schottky-Ohmic tunable junction at the P3HT/Al interface. Zhao et al. [18] fabricated an OPD having structure ITO/ZnO/PC71BM: P3HT/Au, which uses the incorporation of active layer traps by using ZnO and PCBM. Yang et al. [48] in 2020 reported a PM-OPD with structure ITO/PEDOT: PSS/PZ1/PBDB-T: Y6/Al. The device used a wideband gap polymer PBDB-T and a narrow band gap small molecule Y6 for broadband operation. For performance enhancement, an interfacial layer of n-type polymer PZ1 was introduced in between PEDOT: PSS and the active layer, which acted as a hole blocking layer. The blocking of photogenerated holes resulted in interfacial band bending, which in turn facilitated efficient electron injection from the ITO electrode to the active later during reverse bias.

Additionally, PM by interfacial engineering can be done either by 1) modifying the work function of the electrodes by introducing a suitable interfacial layer [49]–[52] or 2) by introducing an effective charge blocking layer (either electron blocking layer (EBL) or hole blocking layer (HBL))[53]–[55]. Both these interfacial modification strategies aim at impeding the charge injection, thereby reducing the dark current density and hence improving the detectivity (D^*). Nie et al. [56] reported a device structure ITO/lysine/PBDTT-DPP: PC71BM/MoO3/Al for photodetector using active layer and interfacial modification. The device showed a responsivity of 936.05 A/W at 10 V, while no gain was recorded at reverse bias. This configuration uses a cathode made of transparent indium tin oxide (ITO) that has been treated with lysine (Lys) and has a low work function. The anode, on the other hand, is made of MoO_3/Al. The photomultiplication-induced gain due to accumulation of minority carriers results in resemblance of gain characteristics similar to phototransistor.

Han et al. [57] in 2018 fabricated a photodetector with a device structure of ITO/AZO: PDIN/DPP-BBT-DTP: PC71BM/MoO_3/Al. In this, they used three polymer blends of PDIN, DPP-BBT-DTP, and PC71BM, along with an electron blocking layer of MoO_3. They demonstrated the OPD with or without gain. For trap centers, they used Aluminum doped ZnO (AZO) nanoparticles along with PC71BM polymer. The summary of review on the photomultiplication based photodetectors is listed in Table 1.2.

TABLE 1.2: REVIEW OF SOME ORGANIC PHOTODETECTORS BASED ON THE PHOTOMULTIPLICATION PHENOMENON

Device Structure (Year)	**D (Jones), Bias (V)**	**R (A/W), Spectral Range (nm)**	**EQE (%), Bias (V)**	**Ref.**
Au/Me-PTC/Au (1994)	--, --	--, 350-700	10000, 16	[40]
ITO/PEDOT: PSS/P3HT: PCBM: CdTe /Ca/Al (2008) (Active layer traps) [2]	--, --	--, 350-750	8000, -4.5	[41]
ITO/PEDOT: PSS/P3HT: Ir-125:PCBM/Ca/Al (2010) (Active layer traps) [3]	--, --	32.4, 300-900	7000, -1.5	[42]
ITO/PEDOT: PSS/P3HT: PCBM: PbS: ZnO/Al (2014) (Active layer traps) [4]	1.01×10^{12}, -3	5.6, 320-1000	1624, -4	[43]
ITO/PEDOT: PSS/P3HT:PC71BM/LiF/Al (2015) (Active layer traps and Interfacial both)	--, --	51.7, 300-700	16700, -19	[5]
ITO/PEDOT: PSS/P3HT:PTB7-Th: PC71BM/Al (2015) (Active layer traps)	1.91×10^{13}, -25	229.5, 320-800	38000, -25	[46]

Device Structure (Year)	**D (Jones), Bias (V)**	**R (A/W), Spectral Range (nm)**	**EQE (%) , Bias (V)**	**Ref.**
ITO/lysine/PBDTT-DPP: PC71BM/MoO3/Al (2017) (interfacial and active layer both)	$1.03x10^{14}$, 1	29.69, 300-900	5008, 1	[56]
ITO/AZO: PDIN/DPP-BBT-DTP: PC71BM/MoO3/Al (2018) (interfacial and active layer both)	$3x10^{11}$, -2	9.28, 300-1300	1392, -2	[57]
ITO/PEDOT: PSS/P3HT/PCBM/Al (2018) (active layer)	$1.3x10^{12}$, -5	--, 300-700	120700, -19	[47]
ITO/PEDOT: PSS/P3HT/IDIC/Al (2019)	$4x10^{12}$, -10	--, 300-700	60700, -19	[3]
ITO/ZnO/PC71BM:P3HT/Au (2020) (active layer)	$3.2x10^{12}$, -5	23, 300-800	4900, -5	[18]
ITO/PEDOT: PSS/PZ1/PBDB-T: Y6/Al (2020)	$2.13x10^{12}$, 2	--, 350-950	8600, 2	[48]

1.5.3 Review on Some Self-Powered Photodetectors

A brief review on the self powered photodetectors is presented in this subsection. T. Park et al. [1] reported inorganic, organic heterojunction based self powered UV photodetectors with responsivity of 20 mA/W using ZnO nanoparticles and F8BT polymer. The device showed a rise time of 36.6 ms. Alwadi et al. [58] reported a p-n junction-based self-powered UV photodetector. They used spray-coated ZnO quantum dots for n-type material while pulsed laser deposited CuO micro-pyramids acting as the p-type layer. However, the use of pulsed laser deposition made this process costly. Using laser beam epitaxy, Wu et al. [59] reported self powered deep UV photodetector (responsivity of 0.76 mW/A), which used B-Ga2O3/Ga:ZnO based hetrojunction. The lattice-compatible Ga: ZnO was used to form highquality heterojunction. However, the process of fabrication is costly and not suitable for large area fabrication. Bo Tan [60] demonstrated self-powered and externally powered UV photodetectors using heterojunctions based on hydrothermally developed ZnO nanorods (ZnO NRs) and copper iodide. The simple solution-processed method of hydrothermally growing ZnO and dropcasting for CuI film was used, thereby covering the whole ZnO rods.

TABLE 1.3: REVIEW OF SOME SELF-POWERED UV PHOTODETECTORS

Device Structure	**R (mAW^{-1})**	**τ_{on} (ms)**	**τ_{off} (ms)**	**Ref.**
ITO/PEDOT: PSS/F8BT/ZnO/Ag	20	36.6	37	[1]
Au/CuO /ZnO/ITO	29	80	80	[58]
B-Ga2O3/Ga:ZnO	0.76	179	275	[59]
ZnO Nrs/ Cul	86.84	110	110	[60]
ZnO/ Cul ZnO/ Cul/Au	17.7 61.5	410 410	240 80	[61]
In/PANI/Mg:ZnO/In	0.16	300	300	[62]
FTO/ZnO QD/ P3HT/MoO$_x$/Ag	3.04	28	200	[2]

The introduction of CuI resulted in the efficient suppression of emissions contributed by defects in ZnO. In order to preserve the iodine layer, a post-treatment using novel space-limited domain annealing was used for drop casted CuI layer. The photodetector showed a responsivity of 86.84 mA/W at 0 V bias. F Cao et al. [61] demonstrated ZnO/CuI/Au heterojunction-based self-powered UV photodetector with a responsivity of 61.5 mA/W. The introduction of gold nanoparticles helps in getting high-performance self-powered UV photodetector. H. Chen et al. [62] reported a self-powered organic-inorganic hybrid heterojunction-based UV photodetector. They selected polyaniline (PANI) as organic material, while for inorganic n-type, they chose MgZnO. However, the obtained value of responsivity was just 0.16 mW/A. Y. Tan et al. [2] demonstrated a self-powered UV photodetector using ZnO quantum dots with different thicknesses utilizing a hybrid heterostructure with P3HT. the device showed a responsivity of 3.04 mW/A. They also used MoOx interfacial layer as electron blocking structure. Table 1.3 include the summary of review on the self powered photodetectors.

1.6. Motivation

Photodetectors are widely used in different applications including optical communication/data transmission. In recent years, organic photodetectors have attracted more owing to their unique advantage of low cost and low temperature solution processing, suitability for large area flexible and wearable electronics. The organic semiconductor-based photodetectors are finding applications in, environmental monitoring, biomedical surveillance, and optical communication field [22], [63]. We carried out a detailed literature survey on recently reported OPDs enlisting various performance enhancement methodologies like the use of heterostructures and the photomultiplication effect [17], [20]–[22], [33]. While significant progress has happened in the field of development of OPDs, we observed that existing OPDs have low responsivity while the OPDs using the photomultiplication effect are operating at very high voltage or are not completely solution processed. The large area suitable solution process technology is of more interest to developing countries like India. Additionally, the as photodetectors are key components in image sensors so we need high responsivity in order to process weak signal while operating at low voltage without the need of any bulky and costly preamplification signal processing circuitry, which will hinder the portability of the device and require additional biasing circuits.

Furthermore, with advancement in the field of low-dimensional nanomaterials, which shows interesting optoelectronic nature owing to their high surface-to-volume ratio and ability of bandgap tuning with size effect, we were motivated to explore heterostructures based on zero-dimensional material (i.e., quantum dots) with solution-processed organic semiconductor which provides exciting opportunities with respect to improving carrier transport phenomenon and light absorption owing to their interesting carrier confinement nature.

1.7. Problem Statement

Based on the extensive literature review as presented in the previous section, we have enlisted the following research gaps:

1. The reported OPDs based on photodiode architecture have very low responsivity. However, a highly sensitive optical detection works for weak optical signal, especially in the field of biomedical, optical communication, and environmental monitoring. Thus, highly sensitive detection requires high responsivity for optimum performance. Moreover, photodetectors are basic building blocks of image sensors. They require high responsivity for faithful operation. If responsivity is low then a pre-amplifier-based signal processing units will be required, which in turn are bulky and require additional biasing circuits, thereby increasing power consumption thus defeating the low-cost fabrication advantage.
2. There are many reported OPDs utilizing the photomultiplication phenomenon to increase responsivity. However, the majority of them require high operating voltage, thereby rendering them unsuitable for portable applications.
3. Most of the reported self-powered OPDs have poor light-to-dark current ratio and large response times.
4. Largely used polymers like P3HT, PQT12, PEDOT: PSS, and PCBM have poor air stability, so the devices would not be suitable for long term use or require another

encapsulation layer, thereby increasing the cost of fabrication.

1.8. The objective of the Thesis

The research works in this thesis have been carried out with the following objective:

1. To explore the low-cost synthesized zero-dimensional material and their incorporation with small organic molecules or a blend of small OSC and polymer for heterojunction-based photodetector for efficient extraction and transport of photogenerated carriers.
2. To maximize responsivity by using the photomultiplication phenomenon by introducing suitable traps/ defect states for electrons in the active layer.
3. To further improve the performance by the introduction of an interfacial blocking layer for electrons, thereby preventing recombination.
4. To explore and fabricate a self-powered UV photodetector for ultra-low power application.

1.9. Scope of the Thesis

The importance and working of the photodetectors have been discussed here. We have classified the photodetectors based on materials and the structures. A brief summary of relevant research on the heterojunction photodetectors, photomultiplication based photodetectors, and self powered photodetectors have been presented in this chapter. Based on the literature survey and the observation from the literature, the thesis is divided in SIX chapter including present one. This first chapter includes the overview of the photodetectors, research gaps, and other details required for subsequent chapters. The outline for the remaining chapters is as follows:

Chapter-2 demonstrates solution-processed ZnO Colloidal Quantum dots CQDs and TIPS-Pentacene based heterostructure for UV-Vis photodetector. ZnO CQD layer worked as the Electron transport layer while TIPS pentacene was used as the Hole transport layer. The chapter includes detailed optoelectronic characterization of various layers along with detailed electrical and time response analysis. The devices show very high responsivity, EQE and detectivity.

Chapter-3 explores the performance enhancement of ZnO CQDs/TIPS pentacene-based heterostructure by the introduction of MoOx interfacial layer, which worked as a hole transport layer as well as an Electron blocking layer. This chapter also covers detailed optoelectronic and Electrical Characteristics of the fabricated device along with time response. Improved values of Responsivity and detectivity were reported.

Chapter-4 demonstrates p-type polymer F8BT (poly(9,9-dioctylfluorene-alcohol-benzothiadiazol)) and ZnO CQDs based heterojunction for UV vis photodetector instead of small molecule TIPS Pentacene. Moreover, the effect of the introduction of an interfacial layer of MoOx was also examined, which acted as a performance enhancer by favoring hole transport and blocking electrons. Like all chapters, it covers detailed optoelectronic and electrical characterizations of both devices, i.e., with or without the use of the MoOx interfacial layer. Furthermore, the device with MoOx shows a good self-power phenomenon.

Chapter-5 presents UV Vis photodetector-based heterostructure utilizing ZnO CQDs and a blend of TIPS-Pentacene and F8BT. Furthermore, the Role of the MoOx layer was also studied with this structure.

Chapter-6 presents a summary of our contribution, the insightful contribution of this thesis, and future scope.