CHAPTER 7

Conclusion and Future Scope

Contents

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7.1 Introduction

The main objective of the present thesis is to provide some insights of ZnO and CdSe colloidal quantum dots (QDs) based self-powered and spectrum selective photodetectors (PDs). The CdSe QD layer has been used as active layer whereas the ZnO QD thin film has been mostly used as an electron transport layer (ETL) and filter layer to block short wavelength photons for achieving spectrum selective response. We have mainly studied three important structures for the self-powered and spectrum selective photodetectors: Au/CdSe QDs/ZnO QDs/n-Si, Au/CdSe QDs/PQT-12/ITO and metal (Pd, Au)/CdSe QDs/ZnO QDs/ITO structures. The Au/CdSe QDs/ZnO QDs/n-Si is an all organic self-powered front illuminated photodetector whereas second structure Au/CdSe QDs/PQT-12/ITO is a hybrid spectral selective self-powered photodetector where the PQT-12 is an organic semiconductor used for the hole transport layer (HTL) cum filter layer of the detector. In the third structure (metal(Pd, Au)/CdSe QDs/ZnO QDs/ITO structure), we have investigated the effect of the Schottky metal electrodes Pd and Au on the performance of the detector illuminated from the back side. Since ZnO QDs have been used as the ETL in the photodetectors, we have first investigated the effect of annealing temperature in the ambient environment of the ZnO QD ETL on the performance of ITO/ZnO QDs/CdSe QDs/MoO_x/Ag photodetector where MoO_x layer is used as the HTL. We have then investigated the effect of MoO_x HTL annealed at 270^{o}C as HTL in the Ag/MoO_x/ZnO QDs/ITO photodetector structure. It is observed that MoO_x deposited on conducting substrate (like ITO coated glass) or

conducting QDs (i.e., CdSe and ZnO QDs) is not a good HTL for QDs based photodetection applications. Further, as per the reported results, Ag/MoO_x is as good as Au electrode based HTL for solution processed QDs. Thus we have used Au as the HTL in place of MoO_x in the self-powered and spectrum selective photodetector stuctures discussed earlier. The present chapter is devoted to summarize and conclude the works carried out in various chapters of this thesis as discussed in the following:

7.2 Summary and Conclusion

Chapter-1 discusses a brief introduction to semiconductor physics, semiconductor material and quantum dots (QDs). The various synthesis and characterization techniques, as well as size-dependent physical, electronic and optoelectronic properties of the QDs, are also briefly discussed in this chapter. A detailed literature survey on the colloidal QDs based photodetectors in general and, self-powered and spectrum selective photodetectors, in particular, have been carried out. The literature survey shows that there is ample opportunities for research in the area of fabrication and characterization of colloidal CdSe and ZnO QDs based self-powered and/or spectrum selective photodetectors using low-cost large-area solution processed techniques. Based on the observations of the literature survey, the scopes of the present thesis have been outlined at the end of this chapter.

Chapter-2 investigates the effect of heat treatment of the colloidal ZnO QDs based ETL on the overall performance of ITO/ZnO QDs/CdSe QDs/MoO_x/Ag based PDs. In this structure, colloidal CdSe QDs are used as the active layer, and MoO_x is used as the HTL in the PDs. The ZnO QDs thin films are characterized after annealing in ambient atmosphere at three temperatures namely 250°C, 350°C and 450°C. The major observations from the chapter are summarized below:

(i). We have synthesized CdSe QDs and ZnO QDs with diameters ~1.83–2.43 nm and ~4.84–5.85 nm respectively.

(ii). It is observed that the particle size and absorption of the ZnO QDs are increased with the annealing temperature.

(iii). The dark current of the PDs using annealed ZnO QDs ETL is also increased with the annealing temperature.

(iv). The achieved particle size of ZnO QDs and CdSe QDs are less than the Bohr's radius of the respective material.

(v). The average response time, dark current, and contrast ratio (i.e., the ratio of photocurrent to dark current) of the PDs are measured as 25.5 ms, –0.02 µA, and 1216 for 250°C; 31.7 ms, –0.06 µA, and 170.8 for 350°C; and 56.31 ms, –0.37 µA, and 7 for 450°C, respectively.

(vi). The responsivity, detectivity, and external quantum efficiency at wavelength of 386 nm for an applied bias of –0.1 V are measured as 32.4 mA/W, 1.22×10^{12} Jones, and 10.88% for 250°C, 11.2 mA/W, 5.64×10^{11} Jones, and 3.62% for 350°C, and 2.2 mA/W, 4.69×10^{9} Jones, and 0.706% for 450°C, respectively.

(vii). The ZnO QDs with a lower particle size (~4.42 nm at 250°C temperature) is found to be the best suitable ETL for photodetector applications regarding the reduced dark current and improved photoresponse characteristics.

(viii). The electron transfer rate in ZnO QDs increases with increasing size. Thus, the ZnO QDs thin film annealed higher temperatures (e.g., 450°C (~ with

particle size 13.84 nm)) may not be suitable for photodetection applications but for other electronic devices such as the thin film transistors (TFTs).

(ix). A TiO_2 floating gate based TFT is fabricated to demonstrate the application of the ZnO QDs annealed at 450°C (~ with particle size 13.84 nm). The device shows a low-voltage kink effect due to increased electron transfer rate in the ZnO QDs ETL layer.

(x). The size-dependent properties of the ZnO QDs ETL can be explored for designing PDs with tunable characteristics.

Chapter-3 reports the post-device fabrication annealing effect of solution processed and thermally grown MoO_x based Ag/MoO_x/ZnO QDs/ITO heterojunction photodetectors. The ZnO QDs layer is annealed at 250°C for achieving optimum performance as discussed in Chapter-2. The solution-processed MoO_x is annealed at 270°C while no annealing is used for thermally grown MoO_x layer before processing for the fabrication of the electrode contacts of the device. The fabricated photodetectors with two types of MoO_x films are annealed at 280°C. The device under study is back illuminated by using a UV LED source with an optical power density of 800 μW/cm^2 at 365 nm. The major observations of this chapter can be summarized as follows:

(i). The PL spectrum of ZnO QDs shows the narrow-band emission spectrum with a full-width at half-maximum (FWHM) of 72 nm. The spectrum selectivity of ZnO QDs implies the synthesis of high-quality and monodispersity of the ZnO QDs.

(ii). The PL spectrum of MoO_x shows the FWHM of 125 nm with no trailing edge. This confirms that the MoO_x are free from any surface defects.

(iii). The solution-processed MoO_x based diode shows stable results after post-fabrication heat treatment. However, the performance of the thermally grown MoO_x based diode is deteriorated after post-fabrication annealing.

(iv). The rectifying nature of the thermally grown MoO_x based heterojunction deteriorates severely after post-fabrication annealing. The noise current is increased by nearly 100 times after the heat treatment.

(v). The thermally grown MoO_x/ZnO QDs shows a very low value of the built-in potential V_{bi} (0.046 V) and high value of ideality factor (~ 6.14). It implies that the heterojunction between the thermally grown MoO_x and ZnO QDs is of very poor quality.

(vi). The responsivity of the solution processed MoO_x based diode is 3.93 mA/W at 365 nm, which is ~7198 times higher than the solution processed MoO_x without post-fabrication heat treatment.

(vii). The device with solution-processed MoO_x layer annealed at 270°C shows better response over the device with un-annealed solution processed MoO_x film. Thus the solution processed MoO_x film grown on colloidal QDs (e.g., CdSe QDs) based active layer synthesized at a lower temperature (below at 270°C) is not suitable for acting as HTL in the PDs.

Chapter-4 presents the fabrication and characterization of low-temperature processed Au/CdSe QDs/ZnO QDs/n-Si Schottky photodiode based self-powered photodetectors where ZnO QDs film annealed at 250^{o}C we used as the ETL and the colloidal CdSe QDs layer has been used as the active layer in the device. Further, the major observations from the chapter are summarized below:

(i). The sharp luminescence peak of CdSe QDs is observed at a 612 nm wavelength with a very narrow FWHM of 37.30 nm for the excitation wavelength of 335 nm. The selective and single peak of CdSe QDs exhibits the high quality of synthesized QDs.

(ii). The measured *J-V* and *C-V* characteristics are used to extract the carrier density, ideality factor, built-in potential, barrier height and width of the depletion region at zero applied bias as ~2.30×10^{17} cm^{-3}, 2.27, 0.34 V, 0.67 eV and ~26.9 nm respectively.

(iii). The PD gives a responsivity of 10.23 mA/W, and detectivity of 8.81×10^{9} Jones under 0 V applied bias. The rise time and fall time of the device are 17.9 ms and 18.0 ms, respectively.

(iv). The self-powered PD under study is fabricated using low-cost and low-temperature solution processed techniques as compared to other inorganic self-powered photodetectors.

(v). The present work is believed to be stepping stone towards the development of colloidal QDs based self-powered photodetectors with inorganic materials.

Chapter-5 reports a novel Au/CdSe QDs/PQT-12/ITO structure based dual-junction self-powered spectrum selective hybrid photodetector using colloidal CdSe QDs as an active layer (~50-nm thickness) and PQT-12 polymer as the HTL cum filter layer. The major observations of the present chapter are listed below:

(i). The colloidal CdSe QDs are deposited on the PQT-12 film at 80°C, which is much smaller than the growth temperature (of usually >300°C) of the other inorganic active layer reported by others for the hybrid self-powered photodetectors.

(ii). The Au metal dots are deposited on the CdSe QD layer for anode electrodes while the ITO acts as the cathode electrode of the device. Two asymmetric depletion widths formed at PQT-12/CdSe and Au/CdSe junctions at two sides of the active layer controls the operation of the self-powered photodetector.

(iii). The photodetector shows a perfect band-pass response with a sharp cut-off at ~610 nm. The maximum responsivity and detectivity of this self-powered photodetector are ~3.3 mA/W and $5.4x10^9$ Jones, respectively at ~420 nm under the incident optical power density of 130 $\mu W/cm^2$.

(iv). The transient response of the photodetector shows the rise time and fall time as ~12.01 ms and ~15.32 ms, respectively under the pulsating white LED light with a period of 1 sec.

(v). The high detectivity of the proposed hybrid detector is believed to be used for detection of very weak optical signals in the visible region.

(vi). The obtained responsivity and detectivity of the hybrid self-powered photodetector is low compared to inorganic self-powered photodiode as discussed in chapter 4 due to high carrier mobility and high absorption coefficient of inorganic ZnO QDs.

(vii). The hybrid self-powered photodetector shows faster transient response than inorganic self-powered photodiode considered in Chapter 4.

In **Chapter-6**, we have investigated the effect of metal electrodes over the CdSe QDs active layer on the performance of back-illuminated metal (Pd, Au)/CdSe QDs/ZnO QDs/ITO based self-powered spectrum selective PDs for two different Schottky metals Pd and Au. Thin film (~260 nm) of ZnO QDs layer annealed at 250°C is used as the ETL, and CdSe QD (~80 nm) film is used as the active layer in the device. The Pd or Au is used for the Schottky contact on the CdSe QDs layer. The major observations of the chapter are listed below:

(i). The optical illumination is coupled into the device through the substrate side. Since the ZnO has larger band gap than CdSe, the entered light through the ZnO ETL into the CdSe QDs layer are reflected back and forth from the metal/CdSe QDs interface and CdSe QDs/ZnO QDs interface. Thus the CdSe QDs layer act as an optical cavity to enhance the optical absorption in the active layer by multiple reflections from both of the metal (Pd, Au)/ CdSe QDs and CdSe QDs/ZnO QDs interfaces.

(ii). The Pd electrode based photodiode shows nearly three times larger photoresponse with a responsivity of 7.48 mA/W), detectivity of 1.3×10^{10} $cmHz^{1/2}W^{-2}$, and EQE of 2.21% than those of the Au electrode based photodiodes over a spectral range of ~380 nm to ~610 nm.

(iii). The larger photoresponse in the Pd electrode based photodiode is attributed to larger absorption in the active layer due to larger reflection of light from

Pd/CdSe QDs layer interface than that from the Au/CdSe QDs layer interface.

(iv). The Pd based device shows an FWHM of ~ 61 nm which is much smaller than the FWHM of ~190 nm of the Au based device. Thus Pd based PDs have higher responsivity with better spectrum selectivity than the Au based device.

(v). The response times of the Pd and Au based photodetectors are 17.15 ms and 28.9 ms respectively. Clearly Pd based detectors have a faster response than the Au based devices.

(vi). The improvement in both the responsivity and selectivity by simply changing the metal electrodes from Au to Pd is demonstrated possibly for the first time in this thesis.

7.3 Future Scope of Work

(i). Introduction of other novel materials such as perovskite can improve the efficiency of self-powered photodetectors by improving the open circuit voltage.

(ii). Colloidal QDs of other materials (e.g., PbS) with wide absorption characteristics can be used to achieve wide spectrum photodetectors with a panchromatic response.

(iii). To achieve colloidal QDs based spectrum selective photodetectors with higher selectivity, a separate filter layer can also be introduced in addition to the ETL or HTL layer in the photodetectors.

(iv). Multiple sized colloidal QDs of multiple materials can be intermixed for achieving new self-powered and/or spectrum selective photodetectors.

(v). Different sizes of colloidal QDs of the same materials can be used for filtering short and high wavelength photons to achieve spectrum selectivity in photodetectors.

(vi). Doped colloidal QDs of multiple materials can also be explored for spectrum selective and self-powered photodetectors.

(vii). The core-shell and alloyed QDs can also be explored for photodetection applications.