CHAPTER 3

Ag/ZnO CQDs/Ag Based Spectrum Selective Ultraviolet Photodetectors on Glass Substrates*

Contents

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CHAPTER 3

Ag/ZnO CQDs/Ag Based Spectrum Selective Ultraviolet Photodetectors on Glass Substrates

3.1 Introduction

The narrowband optical systems require higher spectrum selective photodetectors for some practical applications. The metal-semiconductor-metal (MSM) photodetector structures have drawn considerable attention for achieving the desired responsivity and spectrum selectivity of the device due to their simplicity and easy fabrication (Bütün, 2011) and (Tsai *et al.*, 2013). The MSM device structure is easy to fabricate single layer grown on the low-cost glass substrates. In the previous chapter (Chapter 2), we have considered the Au/ZnO CQDs based Schottky UV photodiode fabricated on the Si substrate with incident illumination on the top of the device. When the illumination is provided from the gold side (i.e. from the top) of the Schottky photodiode, a significant amount of the incident light is lost by reflection from the surface of the gold electrode while the remaining part of light is entered into the active ZnO QDs layer (lying under the Schottky contact) to cause photocurrent in the device. It is shown that the Au Schottky metal works as a filter layer to provide the spectrum selective nature with FWHM ~90 nm at the cost of reduced responsivity of the Schottky photodiode considered in Chapter-2. The present Chapter reports the fabrication and characterization of the low-cost solution processed ZnO QDs based MSM spectrum selective UV photodetectors with enhanced responsivity on low-cost glass substrates without using any additional layer of optical filtering in the device. The colloidal ZnO QDs with radius less than the Bohr's radius have been synthesized and then deposited

on the glass substrates using the low-cost spin coating method. The effects of annealing at 450ºC and 600ºC in the ambient environment on the energy band gap of ZnO QDs have also been investigated. The responsivity and the time response characteristics have been studied and compared with the reported results. The outline of this chapter can be given as follows:

Section 3.2 presents the experimental details of the synthesis of ZnO QDs and the fabrication procedure of the photodetector on glass substrate. Section 3.3 includes the results and discussion regarding the film morphology and electro-optical characteristics such as current-voltage, time response and photo responsivity under dark and UV illumination of the PD.

3.2 Experimental Details

In this section, we have described the details of the experimental procedure used for fabrication of ZnO QDs based MSM Photodetector on glass substrates by solution processing. The fabrication process includes the substrate cleaning, ZnO QDs thin films deposition by on properly cleaned glass substrates, annealing of the films under ambient temperature, deposition of Ag metal interdigitated electrodes on ZnO thin films for Ohmic contact deposition under study. The above mentioned fabrication steps can be discussed in details in the following sub-sections.

3.2.1 Preparation of ZnO QDs

The synthesis of ZnO QDs is performed by dissolving zinc acetate dehydrate as a precursor in 2-methoxyethanol under the steady state flow of the nitrogen gas in the three-neck flask as described in chapter 2. The prepared solution is filtered using PVDF

membrane (0.22 μm) to filter out the unreacted particles from the solution for enhancing the surface uniformity.

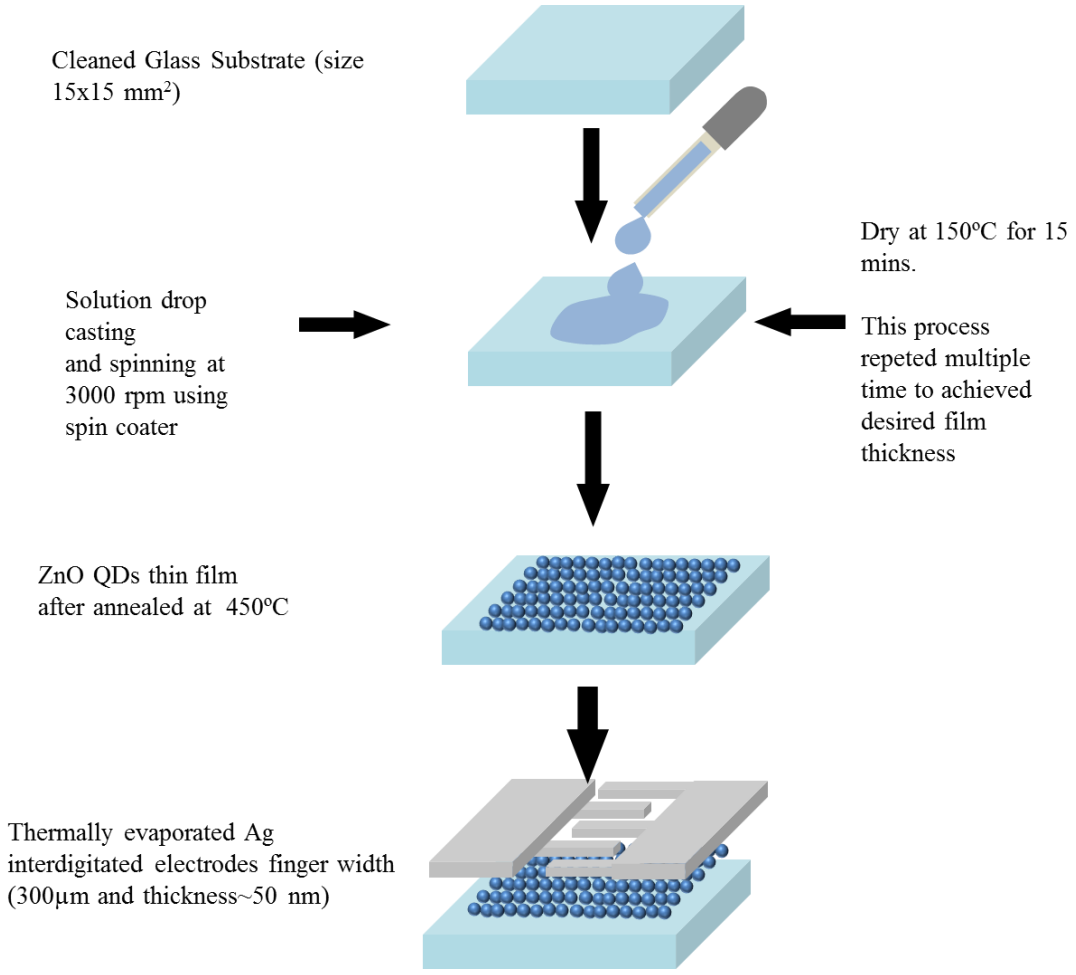


Figure 3. 1: Process flow of fabrication of Photodetector on glass substrate.

3.2.2 Fabrication of Photodetector

To fabricate the photodetector, on the glass substrate (15 x 15 mm^2) were cleaned thoroughly by using alcanox, deionized (DI) water, acetone and isopropanol subsequently and then dried at 90 ºC for 15 minutes. After that, the prepared solution of the colloidal ZnO QDs was deposited on the cleaned glass substrates by the spin coated with a speed 3000 rpm for 30 sec. The samples are immediately dried at 150 ºC on hot plate under the ambient environment for 15 min. This process was repeated multiple

times to achieve a desired thickness of ~ 80 nm finally measured by Reflectometer (F-20, Filmetrics). The complete fabrication flow of the process as shown in Figure 3. 1.

The spin-coated ZnO QDs on the two different glass substrate were annealed under ambient environment at 450 ºC and 600 ºC respectively. These two samples were processed for studying the absorption characteristics while the samples with 450ºC annealing was used for device fabrication. Interdigitated 50 nm thick ohmic contact Ag electrodes of 300 µm channel length 5 mm width were fabricated by thermal evaporation method (FL400, HHV). A distance of 18 cm was maintained between the source and target in the vacuum unit. The rate of evaporation and thickness of the metal film were monitored using the in-built digital thickness monitor (SQM-160, INFICON) of the evaporation unit. The complete device structure and fabricated device are shown in Figure 3. 2 (a) and (b) respectively.

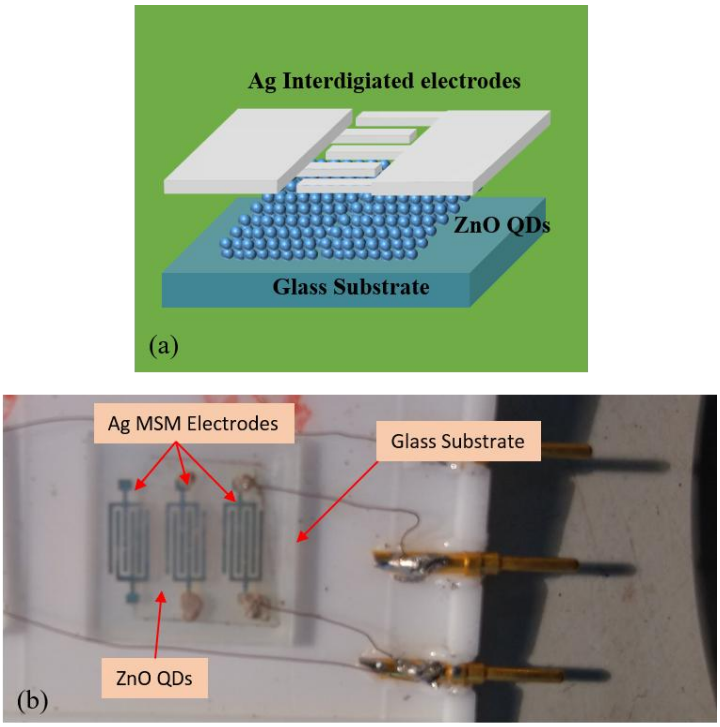


Figure 3. 2: (a) Device structure and (b) frond view of fabricated device on glass substrate

3.3 Results and Discussion

3.3.1 Optical Characterization

The particle size of ZnO QD achieved after annealing at 450 ºC is ~13.80 nm which is larger than the Bohr's radius of ZnO (~2.87 nm) but remains under the quantum confinement regime (Mosquera *et al.*, 2013). This quantum confinement will tend to decrease with increase of particle size thereby reducing the band gap of the QDs as demonstrated in Figure 3. 3 (a). The conduction and valence bands of QDs consist of discrete atomic-like states with energies determined by the radius of the QDs ($E_g \propto 1/R^2$). As the size of QDs is increased with annealing temperature, the discrete energy states start merging to form continuum states in valance and conduction bands due to reduction in quantum confinement and the QD based materials moves towards the bulk (Klimov, 2010). As a consequence, the discrete impulse-like absorption peaks in QDs with higher quantum confinement at lower particle size of the QDs starts broadening with the increase in the particle size and may finally lead towards a broad continuous absorption spectrum of the bulk as shown in Figure 3. 3 (b).

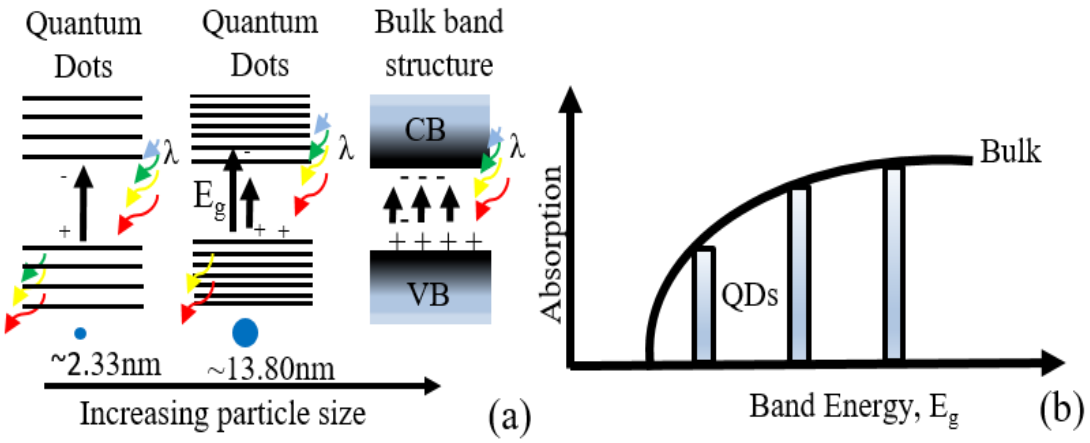


Figure 3. 3: Energy band diagram of QDs with the change of particle size, increase in the particle size leads the discrete bands of QDs to continuum state.

The absorbance of the annealed ZnO QDs thin film measured by UV-Visible measurements (F-20, Filmetrics) as shown Figure 3. 4 (a) and the Figure 3. 4 (b) shows a shift in the band gap of the ZnO QDs from 3.23 eV to 3.13 eV with the change in the annealing temperature from 450 ºC to 600 ºC.

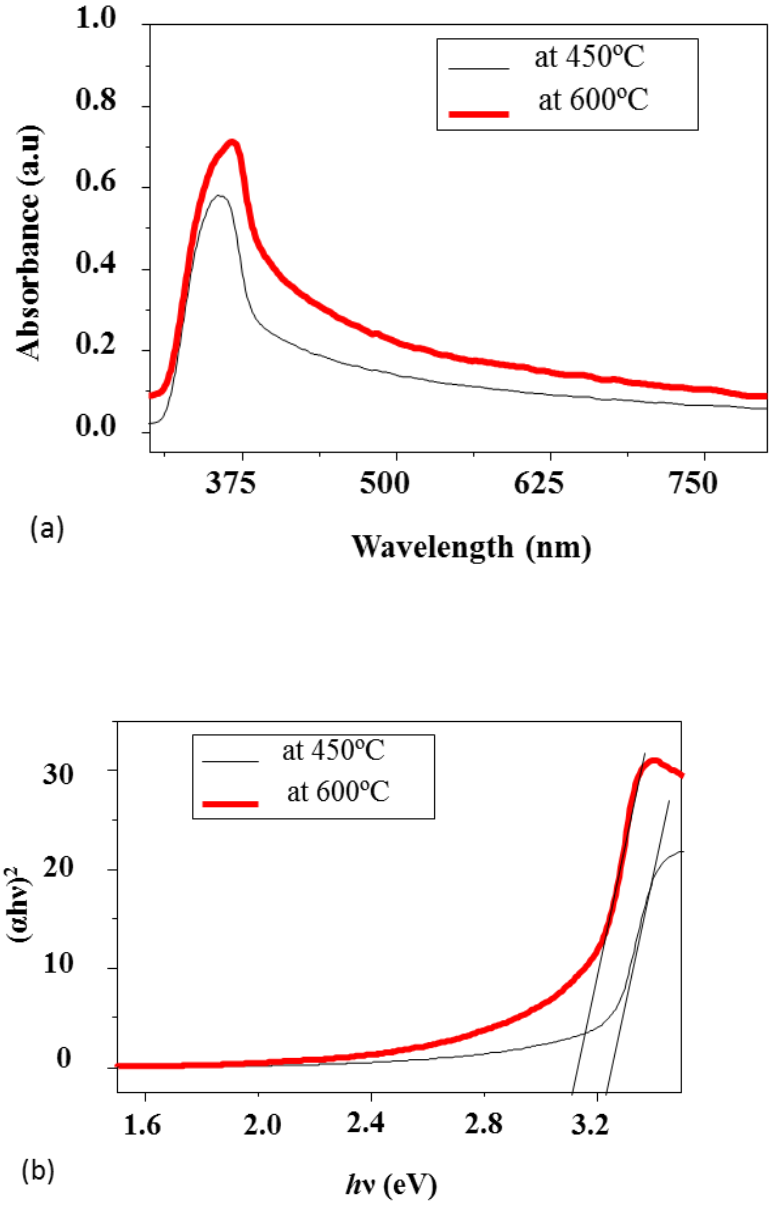


Figure 3. 4: Absorption Spectra of ZnO QDs Thin film at 450ºC and 600ºC, and (b) the energy band gap of ZnO QDs at both temperature.

3.3.2 Electro-Optical Characterization

The section has described the photoconduction mechanism and electrical characteristics of the MSM photodetector from the applied bias 0 to 10 V under the dark and UV illumination. The electrical characteristic determined the photoconductive behavior between the Ag and ZnO QDs. The electro-optical characteristics, responsivity vs wavelengths and time response are measured under the dark and UV illumination.

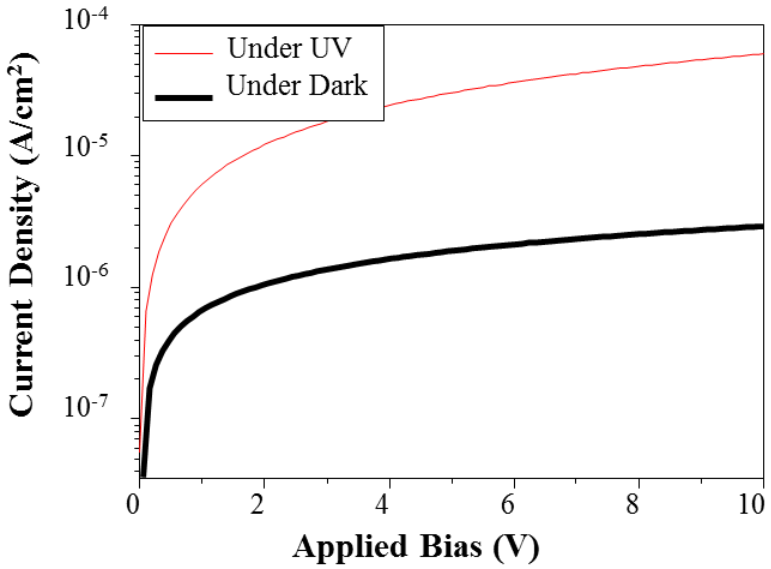


Figure 3. 5: Current density versus applied voltage and device structure fabricated on Glass Substrate.

3.3.2.1 Current Voltage Characterization

The current-voltage characteristics as shown in Figure 3. 5 measured under dark and UV illuminations from bias voltage of 0 to 10 V using the semiconductor parameter analyzer (KeySight, B1500A) of the device structure under study is shown in Figure 3. 2 (a). The monochromatic light of power density ~70 μW/cm^2 (measured by PM100D, Thorlabs) at ~360 nm wavelength was used for the UV light source. A significant change in the current under UV illumination clearly shows the potentiality of the device for UV detection applications.

3.3.2.2 Responsivity Characterization

The improvement in the photocurrent clearly indicates a certain amount of other active factors, which is participating in the photoresponse including with oxygen chemisorption phenomenon already discussed in chapter 2. Figure 3. 6 shows the energy band diagram and photodetection mechanism.

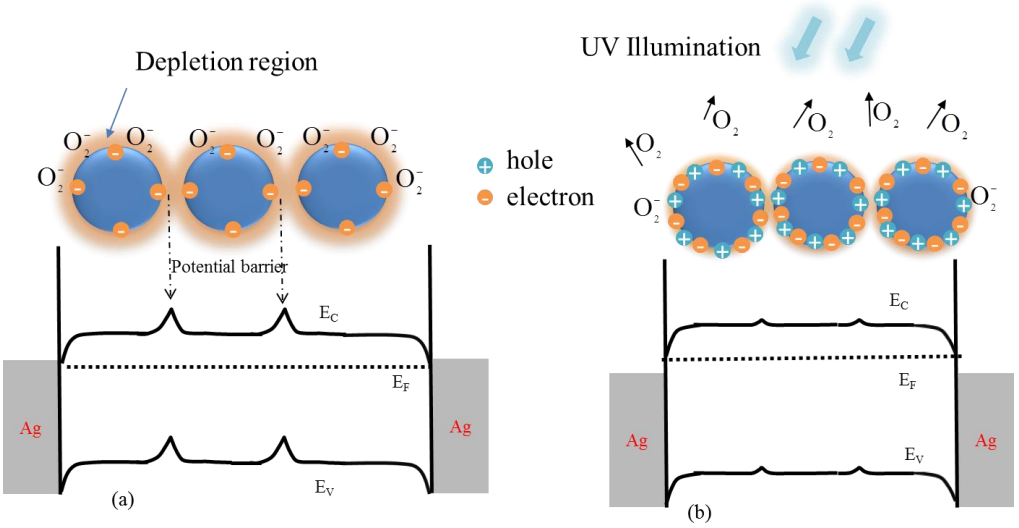
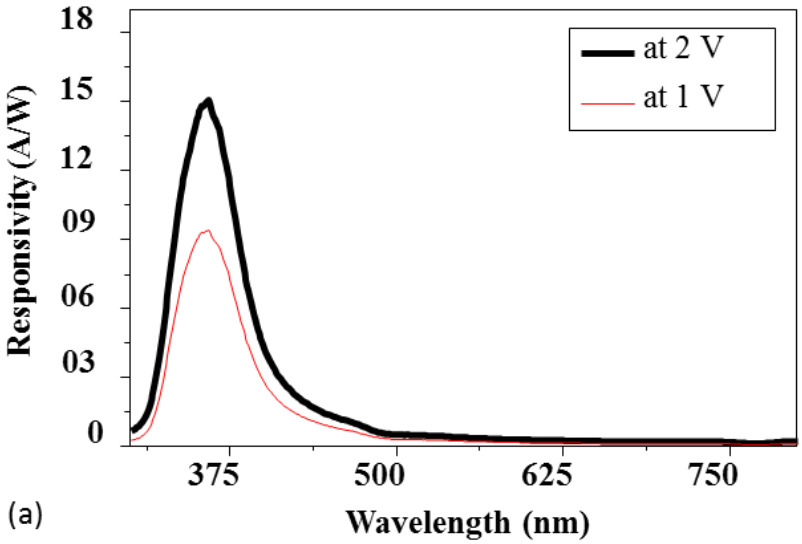


Figure 3. 6: Charge distrbution and energy band diagram of three conjoint quantum dots (a) dark and (b) with UV illumination.



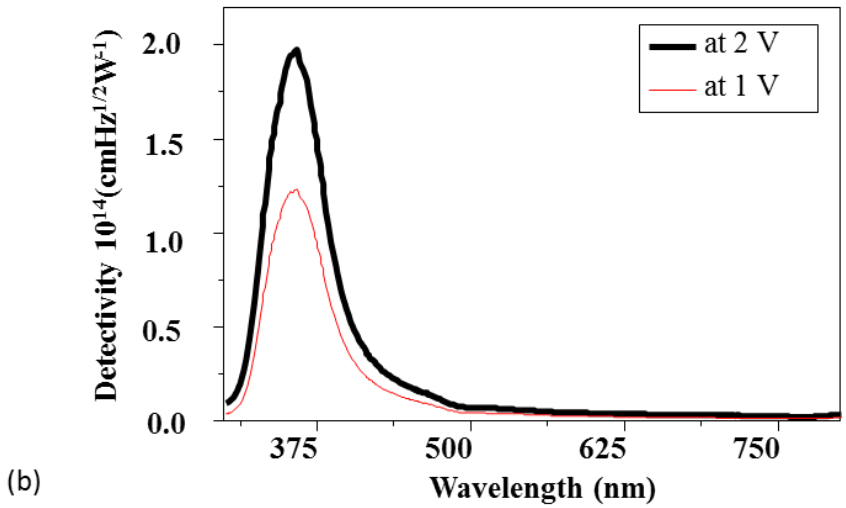


Figure 3. 7: Photoresponse characteristics (a) and (b) detectivity of the device annealed at an applied bias 1 and 2 V.

The responsivity (R_e) and the detectivity (D^*) are calculated using Eq. (1.10) in chapter 1 and Eq. (2.1), (2.2) in chapter 2 respectively. The responsivity and detectivity characteristics shown in Figure 3. 7 were measured at fixed bias voltages and different wavelengths of incident light. The responsivity was measured using a monochromator (SP2150i, Princeton Instruments) set up along with a digital multi-meter (Agilent, 34410A) and power meter (PM100D, Thorlabs). The peak responsivity of the photodetector is measured ~15.04 A/W while the peak detectivity ~1.97x10^{14} cmHz$^{1/2}$·W^{-1} at 2 V for ~360 nm wavelength. Note that both the responsivity and detectivity values are larger than those of spectrum selective detectors reported by Wang et al., Zhu et al., Zhang et al., and Ni et al. (Zhu *et al.*, 2008; Wang *et al.*, 2010; Zhang *et al.*, 2011; Ni *et al.*, 2012) as well as non-spectrum selective ZnO nanostructured photodetectors reported by (Yu *et al.*, 2012; Chen *et al.*, 2013; Lee *et al.*, 2013). The detector under study represents a good spectrum selective UV detector with a FWHM of ~49 nm. Although, the FWHM is larger than the spectrum selective

detectors reported in (Zhu *et al.*, 2008; Wang *et al.*, 2010; Zhang *et al.*, 2011; Ni *et al.*, 2012) but its higher responsivity, simpler structure (due to the absence of any supplementary layer for absorption tuning) and lowest fabrication cost could be of great interests to many researchers. This spectrum selective characteristics of ZnO QD based photodetector is attributed to the particle size dependent quantum confinement phenomenon already discussed earlier in Figure 3. 3.

The ZnO QDs with discrete energy states absorb only a part of the photons (with energy exactly equal to the difference between an energy state at the conduction band and an energy state at the valence band for excitation of an electron from the valence band to the conduction band after photon absorption) while leaving the majority of the photons are not absorbed. However, once the discrete energy states start merging toward continuum states with increased particle size (due to increased annealing temperature), they lose the quantum confinement and more number of photons with energy spreading over a large range are absorbed and thereby making the spectrum wider (Klimov, 2010) as discussed earlier related to Figure 3. 3. Finally, the absorption characteristics of the ZnO QDs annealed at 450ºC and 600ºC at the ambient environment measured by (F-20, Filmetrics) have been compared in Figure 3. 4. It is clearly observed that while absorption is reduced with increased annealing temperature, a reverse trend is observed in FWHM possibly due to the increased grain size with the annealing temperature. Since the particle size beyond 20 nm results in negligible quantum confinement (Mosquera *et al.*, 2013). Note that the QDs size at 450^{o}C annealing temperature used in our device is ~13.80 nm ± 5% which results in a strong carrier confinement, thereby leading to the spectrum selective narrow peak in the responsivity characteristics. Finally, various performance parameters of the present and other spectrum selective UV detectors

reported in (Zhu *et al.*, 2008; Zhang *et al.*, 2011; Ni *et al.*, 2012) have been compared in Table 3.1.

Table 3.1: Comparison of Responsivity, Detectivity and FWHM of the ZnO QDs based photodetector with other similar work

Parameters	**This Work**		(Zhu *et al.*, 2008)	(Zhang *et al.*, 2011)	(Ni *et al.*, 2012)		(Wang *et al.*, 2010)	(Yu and Tian, 2016)
Bias (V)	1	2	0	4	-5	0	-5	3
Responsivity (A/W)	9.38	15.04	1 µ	1.8	4.91	30 µ	0.11	0.052
Detectivity ($cmHz^{1/2}\cdot W^{-1}$)	1.228 E^{14}	1.97 E^{14}	1.41 E^{8}	-	-	-	-	-
FWHM (nm)	49	49	17	7	9	-	26	10
Filter Used	Not Used	Not Used	p-GaN	MgZnO	n-ZnO		PVK and ITO	ZnO nanoparticles
Deposition Techniques	Solution processed		MBE	PLD	MBE		Electro-deposition	Magnetron sputtering

3.3.2.3 Time Response Characterization

The Time response characteristics as shown in Figure 3. 8 of the detector has been performed by using the UV LED (4x4 array) (central frequency at 390 nm with optical power density of 3.50 mW/cm^2, measured by PM100D). The UV LED switching provides the UV pulses and it is controlled by the Arduino controller. The rise time and recovery time are estimated to be 7.2 sec and 18.5 sec, respectively, under a 2 V bias condition. The UV pulses of 30 sec duration and power density of 3.50 mW/cm^2 were generated by an in-house designed microcontroller driven UV LED system. The rise time is 2.5 times faster than the corresponding recovery time, and the delay time is calculated to be 3.6 sec. The recovery time of (~18.5 sec) is the best among the

photoconductor devices fabricated by colloidal ZnO nanoparticles (Jin *et al.*, 2008) or solution-processed techniques (Basak *et al.*, 2003).

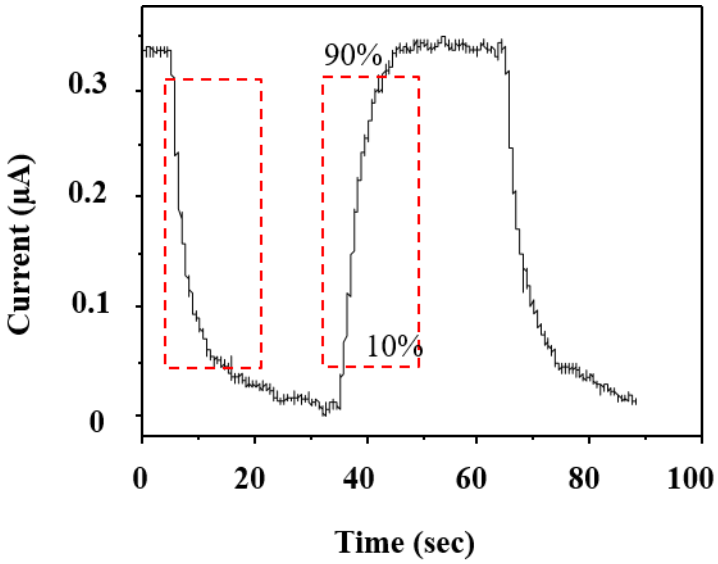


Figure 3. 8: Time Response characteristics of MSM photoconductor under UV pules illumination.

3.4 Conclusion

In this chapter, a low-cost solution processed ZnO QDs based spectrum selective photodetector is fabricated on glass substrate with Ag interdigitated electrodes without using any additional layer for optical filtering. ZnO QDs thin film that has been annealed in the ambient environment at 450ºC has been successfully utilized for the fabrication of narrow absorption band UV detector in MSM structure. Such kind of photodetector showed a FWHM of ~49 nm with peak responsivity and detectivity of ~15.04 A/W and ~1.97x10^{14} cm$Hz^{1/2}W^{-1}$ at 2 V for ~360 nm respectively. The time response characteristics of this detector shows that the rise time and recovery time of 7.2 sec and 18.5 sec respectively. The obtained recovery time is believed to be the best among the reported results. The band gap of the ZnO QDs is observed to be decreased from 3.23 eV to 3.13 eV with the change in the annealing temperature from 450 ºC to

600 ºC due to the effect of quantum confinement. Thus the spectrum selectivity of the ZnO QDs can be easily tuned in the UV region by changing annealing temperature of the ZnO QDs.