Chapter 5

Ultraviolet Detection Characterstics of Pd/ZnO Nanoparticles (NPs) Based Schottky Diodes Grown on Sn Seed Layer Coated n-Si Substrates

5.1 Introduction

It is already discussed in Chapter 1 and 2 that ZnO nanostructures based Schottky ultraviolet (UV) photodetectors [Liang *et al*. (2001), Lin *et al.* (2008), Zhu *et al*. (2008)] have drawn considerable attention due to their large surface-to-volume ratio with the carrier and photon confinements in two dimensions, superior stability owing to high crystallinity and possible surface fictionalizations with target-specific receptor species [Lin *et al*. (2008), Das *et al*. (2010b), Su *et al*. (2010), Wu *et al*. (2011)]. Further, from the discussions of Chapter-4, we have observed that only the ZnO films deposited on the Sn seed layer coated n-Si substrates possesses the preferential growth plane of (002) while the same for the vacuum deposited ZnO films on the bare n-Si as well as on the ZnO and Zn seed layer coated n-Si substrates is the (101) plane. It may be mentioned that the ZnO thin films with a preferential growth plane of (002) plane is commonly believed to be very sensitive to the UV light. In view of the above, the present chapter has been developed for reporting the UV detection properties of the Pd/ZnO nanoparticles (NPs) based Schottky diodes grown on Sn coated n-Si substrates by thermal evaporation method already discussed in Chapter-4. The layout of this chapter is given as follows:

In the present chapter, we have determine UV detection characteristics of Pd/ZnO nanoparticles (NPs) based Schottky diodes grown on Sn coated n-Si substrates by thermal evaporation method. In this view, Section 5.2 presents experimental details for fabrication of Pd/ZnO NPs Schottky diodes on n-Si substrates. The results and discussions are presented in Section 5.3. Finally, Section 5.4 presents summary of the chapter.

5.2 Experimental Details

The synthesis of ZnO NPs on the Sn seed layer coated n-Si substrates has already been discussed in Chapter.4. As discussed, the Sn seed layer of ~50 nm was first deposited on the properly cleaned n-Si substrates using thermal evaporation method. Using the same growth conditions, a thin layer (~300 nm) of ZnO was then grown on the Sn seed layer by the thermal evaporation technique. The Pd Schottky contacts were then fabricated on the ZnO NPs deposited on the Sn coated n-Si substrates as discussed in Chapter 4. The as grown Pd/ZnO NPs/Sn/n-Si Schottky diodes were then exposed to the UV light to determine photodetection characteristics of the diodes under consideration. The UV lamp (BENCHMARK, India) used for our experiment was operated at 365 nm wavelength with an optical power of 650 μW measured by a power meter (Model No. FOMP-101 of BENCHMARK, India). The schematic of the proposed vertical Pd/ZnO NPs Schottky device structure under the UV illuminations is shown in Fig. 5.1 where the voltage source is used to vary the biasing condition of the diode and any arbitrary Pd metal dot is considered as the Schottky electrode of the Pd/ZnO photodiodes under consideration. Since Pd dots are normally opaque to the incident UV radiation, the light enters into the device through the open area excluding the area under Pd metal dots to contribute the photo current in the device.

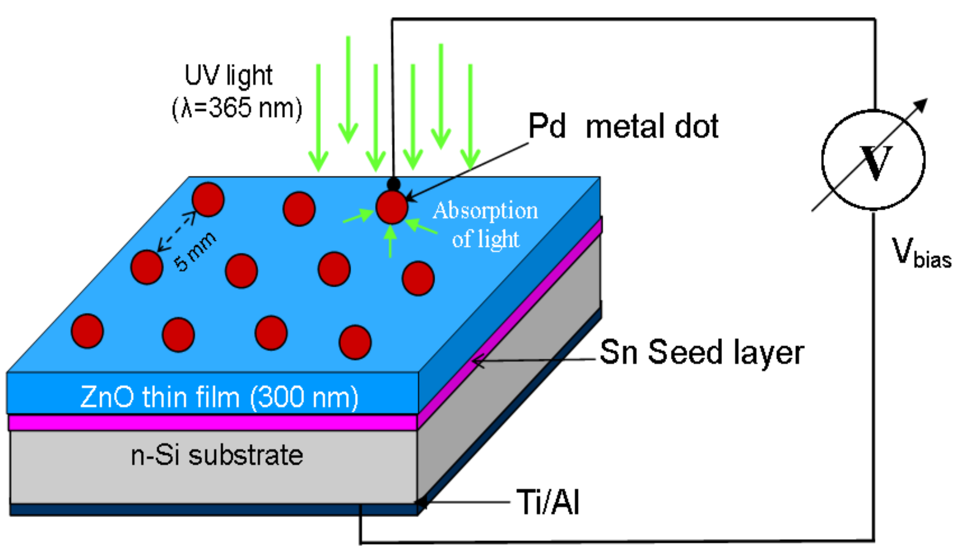

Figure 5.1: Schematic diagram of Pd/ZnO NPs Schottky diode grown on n-Si substrates under UV illuminated condition

5.3 Results and Discussions

The structural properties of the ZnO films grown on the Sn coated n-Si substrates and the electrical properties of the Pd/ZnO NPs/Sn/n-Si diodes have already been discussed in Chapter-4. However, we have elaborated some of the discussions already presented in Chapter-4 just for the sake of a better understanding of the structural and optical characteristics of the ZnO films grown the Sn seed layer coated n-Si substrates as well as on the bare n-Si substrates. The structural properties of the ZnO films have been studied by analyzing the FESEM images and XRD pattern (as discussed in Chapter-4), while the optical properties have been investigated by the PL spectroscopy measurements. Finally, the UV detection characteristics of Pd/ZnO NPs based Schottky diodes under study have been investigated in the present section.

5.3.1 FESEM Images of ZnO Nanoparticles (NPs)

The surface morphology of the ZnO thin films studied characterized by the FESEM (ZEISS SUPRA-40 model) images has been shown in Fig 5.2 (a) and 5.2 (b) for the ZnO thin films grown on the bare n-Si substrates and Sn seed layer coated n-Si substrate respectively. As observed in Chapter-4, the vacuum deposited ZnO thin films grown directly on the bare Si substrates possesses a nanocrystalline surface morphology (see Fig. 5.2 (a)) whereas the surface morphology of the ZnO films grown on the Sn seed layer coated n-Si substrates shows a homogeneous distribution of ZnO nanoparticles (NPs) (see Fig. 5.2 (b)) over the whole surface area of the Si substrates.

For a better clarity, a high resolution (~200 nm) FESEM image is also shown in Fig. 5.2 (c). The estimated diameter values of the as-grown ZnO NPs vary between ~30 nm to ~70 nm. The surface area-to volume ratio of the ZnO NPs are larger than the traditional nanocrystalline ZnO thin films [Ali and Chakrabarti (2012)], which in turn, can improve the UV light sensing capability of the ZnO films grown on the Sn seed layer.

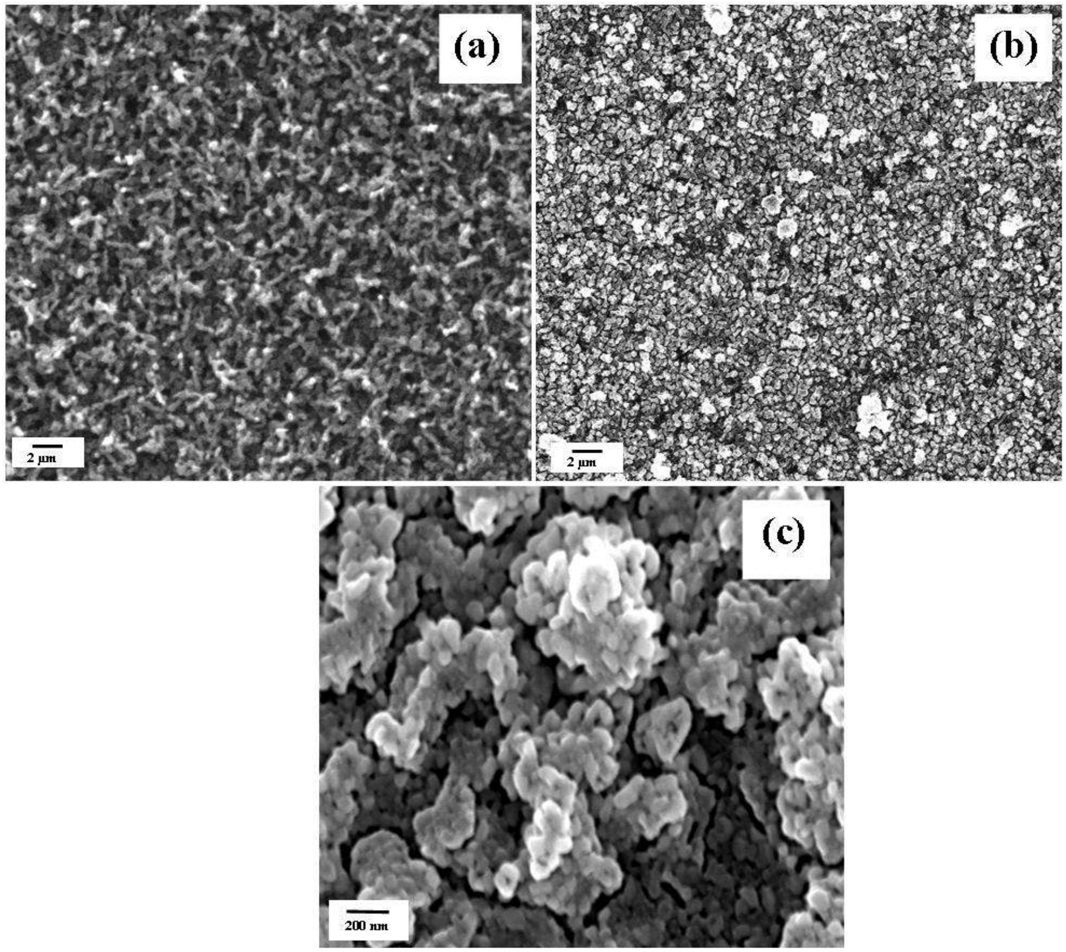

Figure 5.2: Typical FESEM image (top view) of ZnO thin film grown on **(a)** n-Si substrates **(b)** Sn seed layer coated n-Si substrate **(c)** high resolution image of ZnO NPs

5.3.2 XRD Patterns

We will now examine the suitability of the ZnO films deposited on the Sn seed layer coated n-Si substrates by analyzing the XRD data already considered in Chapter-4. The details of the XRD patterns (18 kW Cu-rotating anode, model: XDMAX, PC-20, Rigaku, Tokyo, Japan) of the ZnO films gown on n-Si substrates with and without the Sn seed layer have been shown in Fig. 5.3 (a) and 5.3 (b) respectively. All the observed diffraction peaks (002), (100), (101), (102) and (110) are well matched with the JCPDS data card no- 36-1451 of the ZnO material [JCPDS (1977), Talam *et al*. (2012)]. However, as per the JCPDS card no.05-0390, the presence of (220) peak in the XRD spectrum of the film grown on Sn seed layer refers to the presence of the Sn metal on the Si substrates [JCPDS (1977)]. Further, as per the Chapter-4, the preferred orientation of ZnO film is observed to be changed from (101) to (002) plane when the ZnO thin film is grown on Sn seed layer coated n-Si substrates in place of growing directly on bare n-Si substrates without using the seed layer. The (002) growth plane of the ZnO films deposited on the Sn seed layer indicates that the film can be explored for the UV detection applications [Liu *et al*. (2010), Ali and Chakrabarti (2010), Periasamy and Chakrabarti (2011)].

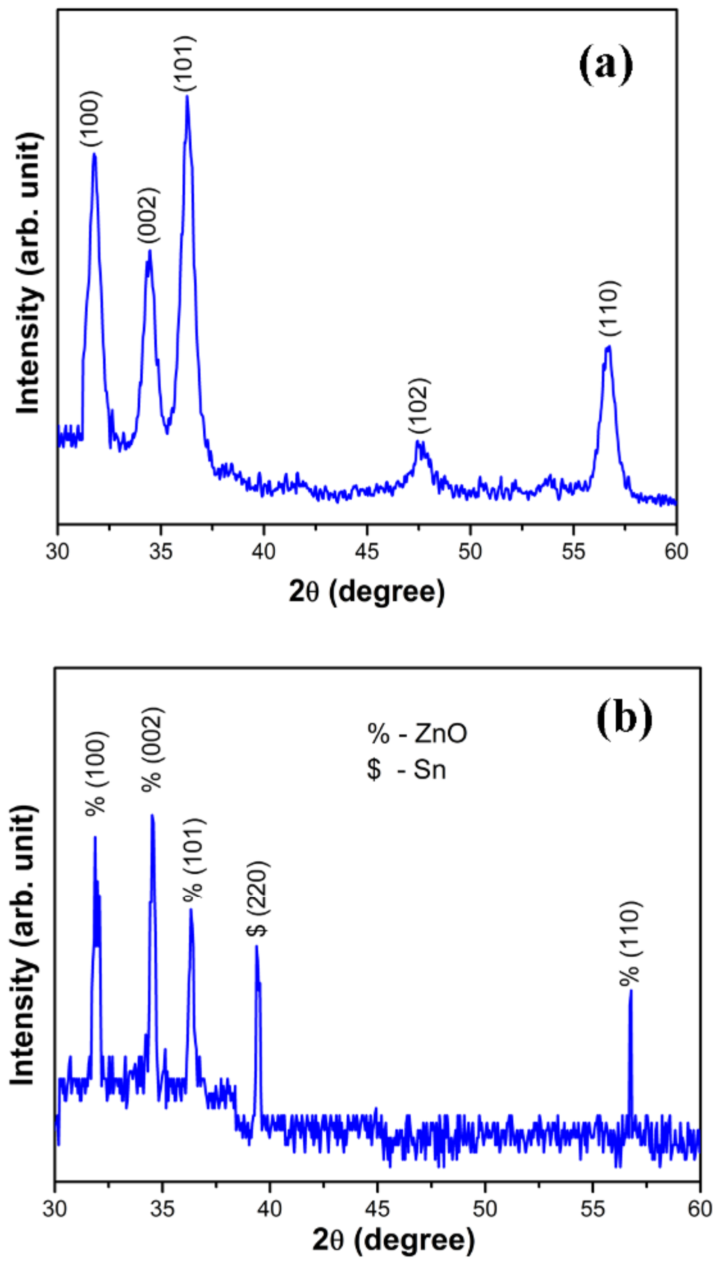

Figure 5.3: Typical XRD pattern of ZnO thin film grown on **(a)** n-Si substrates **(b)** Sn seed layer coated n-Si substrate

5.3.3 Photoluminescence Spectrum

The optical properties of ZnO NPs have been studied by the photoluminescence (PL) spectrum (RPM 2000, Accent Optics, USA) with excitonic wavelength of 266 nm at room temperature as shown in Fig. 5.4. The main peak in the PL spectrum appearing at ~355 nm is due to the excitonic transition between the valance band and conduction band [Djurišic *et al*. (2007), Liu *et al*. (2010)]. A number of other peaks also observed in the PL spectrum may belong to various kinds of zinc and oxygen related defects [Gong *et al*. (2007), Djurišic *et al*. (2007), Bayan and Mohanta (2011)]. The small peak at ~375.84 nm corresponds to the near band edge emission [Bayan and Mohanta (2011)]. The luminescence peak at ~436 nm corresponds to the Zn vacancies and the peaks from 443 nm to 450 nm may represent the single ionized Zn interstitials (Zn^{+}) [Wang *et al*. (2006), Djurišic *et al*. (2007), Selim *et al*. (2007)]. Two other peaks at ~483 and ~527 nm observed in the PL spectrum correspond to the single ionized oxygen vacancy (V_O^{+}) and oxygen interstitial defects (O_i) [Gong *et al*. 2007), Bayan and Mohanta (2011)].

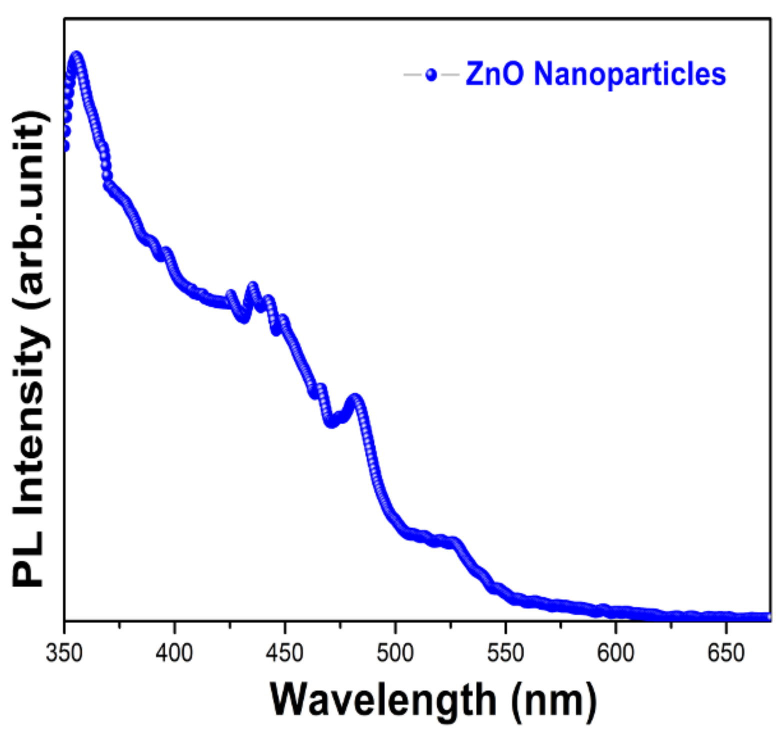

Figure 5.4: Photoluminescence Spectrum of ZnO NPs grown on Sn coated n-Si substrates

5.3.4 Pd/ZnO NPs based UV Schottky Photodiodes

The electrical characteristics have already been investigated in Chapter-4. In this section, we will investigate the effect of Sn seed layer on the UV detection properties of the Pd/ZnO NPs based Schottky diodes under consideration. In view of the above, the room-temperature I-V characteristics measured under dark and UV illuminated conditions have been shown in Fig. 5.5 (a) and (b) for the as-fabricated Pd/ZnO NPs/Sn/n-Si (i.e. with Sn seed layer) and Pd/ZnO/n-Si (i.e. without Sn seed layer) Schottky diodes respectively. While Fig. 5.5 (a) shows a very good UV detection property of the Pd/ZnO NPs/Sn/n-Si device in the reverse bias operation, the result of Fig. 5.5 (b) shows the UV light detection capability of the Pd/ZnO/n-Si Schottky diodes in its forward bias region. The current of ~2.4221×10^{-7}A under dark condition is observed to be increased to a value of ~1.3112×10^{-4} A at corresponding bias voltage -3V when the Pd/ZnO NPs/Sn/n-Si Schottky diode is illuminated by the UV radiation. Alternatively, the current of 2.7210×10^{-3}A is observed under dark condition and increased to a value of 8.8211×10^{-3}A at corresponding forward bias voltage +3V in the device without a Sn seed layer.

We will now present different UV detection parameters such as the contrast ratio, quantum efficiency, responsivity, resistance area product and detectivity of the Pd/ZnO NPs/Sn/n-Si structure based Schottky photodiodes at room temperature in the following.

(a) Contrast ratio

The contrast ratio or sensitivity is an important figure of merit of an UV detector and is defined as the ratio of the current under UV illumination (I_{ph}) to the dark current (I_{dark}). For the Sn seed layer based Schottky diodes at -3V bias voltage, the contrast ratio or sensitivity is estimated as ~541.34 whereas the same obtained for the device without the seed layer is only ~3.24 at 3V forward bias voltage. Clearly, a dramatic improvement in the contrast ratio is obtained by introducing the Sn seed layer between the ZnO film and the Si substrate in the device.

(b) Quantum efficiency

The quantum efficiency basically represents the optical-to-electrical conversion efficiency of any photodetector. For the Pd/ZnO NPs/Sn/n-Si Schottky photodiode, the quantum efficiency η_{QE} can be defined as [Ali and Chakrabarti (2010), Su *et al*. (2010)]

$$\eta_{QE} = \frac{I_{ph}}{P_{opt}} \times \frac{h\nu}{q} \tag{5.3}$$

where I_{ph} is the photocurrent, P_{opt} is the incident optical power, h is the Planck's constant, ν is the frequency of the light and q is the elementary charge. The quantum efficiency of the device determined from Eq. (5.3) is ~68 % at -3V and ~365 nm wavelength of the UV radiation.

(c) Responsivity

Besides the quantum efficiency, the responsivity also represents an important figure of merit of the photodetectors. To determine the responsivity (R) of the Pd/ZnO NPs Schottky photodiodes, we may use the following expression [Liang *et al*. (2001), Young *et al*. (2008)]:

$$R = \eta_{QE} \times \frac{q\lambda}{hc} \tag{5.4}$$

By putting value of the quantum efficiency in Eq. (5.4), we get the value of responsitivity as ~0.20 A/W.

The estimated values of the responsivity and quantum efficiency for the Pd/ZnO NPs Schottky diodes grown on the Sn seed layer coated n-Si substrates in the present study are remarkably higher than those achieved with conventional Pd Schottky contacts on ZnO nanocrystalline thin films fabricated on bared Si substrates prepared by vacuum evaporation and sol-gel methods as reported by Ali and Chakrabarti (2012). They [Ali and Chakrabarti (2012)] reported the values of the responsivity and quantum efficiency of ~0.08 A/W and 23% for vacuum deposited ZnO film based devices and 0.17 A/W and 62 % for sol-gel derived ZnO film based devices. The measured responsivity of our proposed Schottky photodiodes is even larger than another result of ~ 0.18 A/W at 300 nm and -2V reverse bias voltage reported by Lin *et al.* [Lin *et al.* (2008)] for ZnO nanorod/polyfluorene p-n heterojunction based UV photodiodes fabricated by solution processes at low temperature. The measured responsivity is even better than the (0001) ZnO single crystal based Schottky ultraviolet photodiodes reported by Endo *et al.* [Endo *et al.* (2007)] by using the hydrothermal growth method.

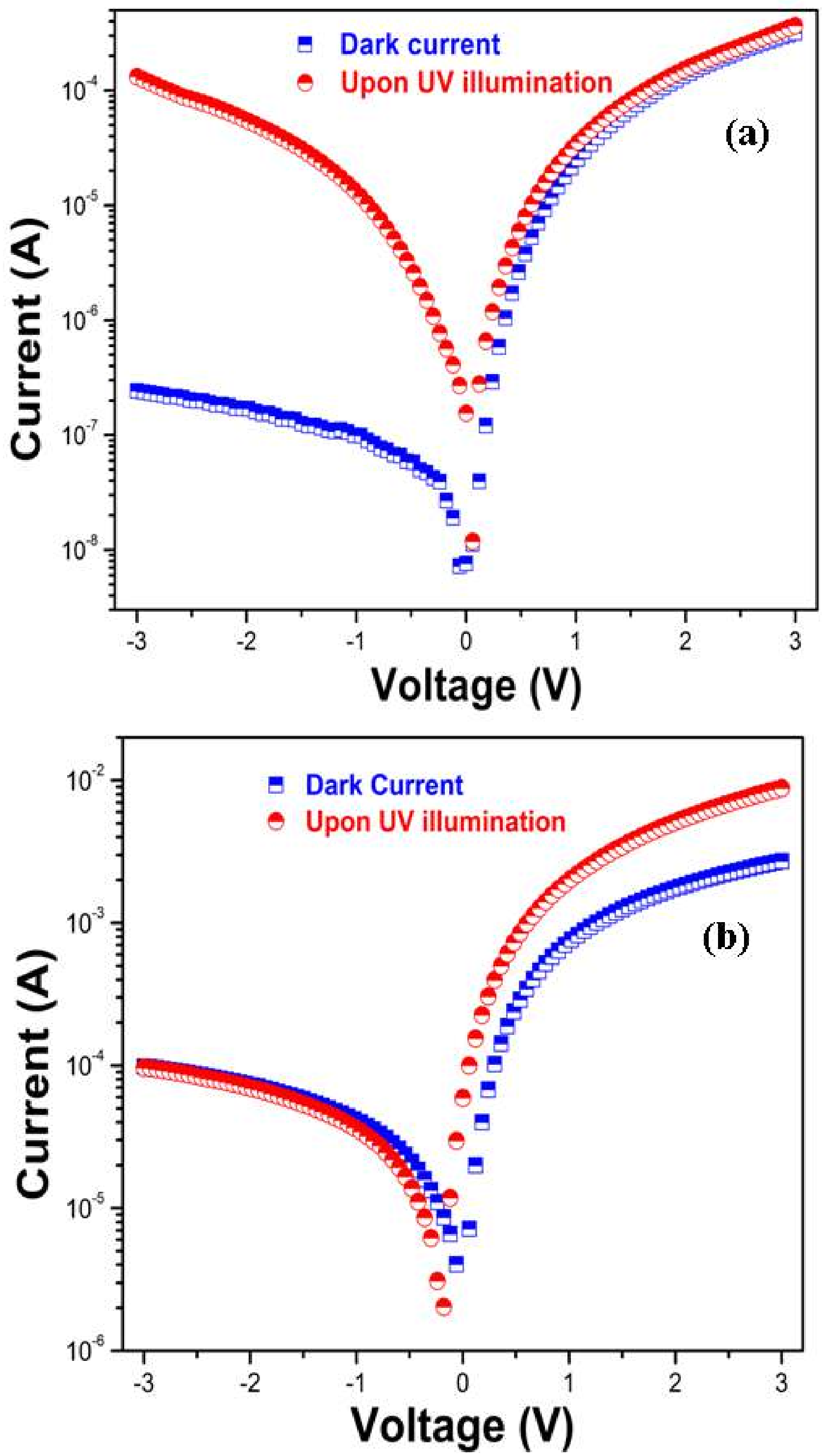

Figure 5.5: UV detection characteristics of Pd/ZnO NPs based Schottky diodes with **(a)** Sn seed layer **(b)** without Sn seed layer

(d) Resistance-Area product

The resistance-area (RA) product of Pd/ZnO NPs Schottky photodiodes is calculated by following relation [Ali *et al*. (2010), Chakrabarti *et al.* (2003)]:

$$RA = \left(\frac{dJ}{dV}\right)^{-1} \tag{5.6}$$

The RA (i.e. resistance – area) product of the photodiode can be obtained from the slope of the current density (J) vs. voltage (V) characteristics. The calculated value of zero bias resistance–area product $(R_0 A)$ is ~17.66 Ω. m^2.

(e) Voltage dependent detectivity

The voltage dependent detectivity of the Schottky UV photodiodes is calculated by using the following relation [Chakrabarti *et al.* (2003), Ali *et al*. (2010), Dwivedi (2011)]:

$$D_{opt} = \frac{\lambda \eta_{QE} q}{hc}\left(\frac{RA}{4kT}\right)^{1/2} \tag{5.7}$$

By putting the value of RA from Eq. (5.6) in Eq. (5.7), the value of the detectivity for the Pd/ZnO NPs/Sn/n-Si Schottky photodiodes under consideration is computed as ~6.53×10^9 $mHz^{1/2}W^{-1}$. The detectivity is observed to be much larger than the typical ZnO based MSM UV photodetectors reported by Ali and Chakrabarti [Ali and Chakrabarti (2010)] and is as good as the value reported for the complicated MISIM structures by Ali and Chakrabarti [(Ali and Chakrabarti (2010)].

In Table 5.1, we have finally compared the different performance parameters determined for our proposed Pd/n-ZnO NPs/Sn/n-Si Schottky UV photodiodes with other UV photodetector structures reported in the literature. Clearly, the proposed Pd/ZnO NPs based Schottky structures could be well-explored for the UV detection applications.

Table 5.1: Comparison of different UV detection parameter of ZnO based various device structures with present study

Device Structure	Contrast ratio	Responsivity (A/W)	Quantum efficiency (%)	Detectivity ($mHz^{1/2}W^{-1}$)	Ref.
Schottky diode	541.34	0.20 at -3V	68	6.53×10^{9}	Present study
MSM	12	0.056 at 3V	19	1.28×10^{9}	Ali and Chakrabarti (2010)
MISIM	904	0.20 at 3V	70	6.50×10^{9}	Ali and Chakrabarti (2010)
MIS	3.2×10^{4}	0.0083 at 5V	-	-	Young *et al*. (2008)
p-n diodes	-	0.18 at -2V	-	-	Lin *et al*. (2008)

5.3.5 UV Detection Mechanism at the Surface of ZnO NPs Grown on Sn Layer

The excellent UV response of the Sn seed layer based Pd/ZnO NPs Schottky photodiodes may be attributed to the presence of excess oxygen related hole-trap states at the surface of ZnO NPs which may extend the lifetime of the holes by preventing charge-carrier recombination [Soci *et al*. (2007), Das *et al*. (2010b), Wu *et al*. (2011)]. The large surface area of ZnO NPs may also make the lifetime of photo carrier longer [Ali and Chakrabarti (2010), Das *et al*. (2010b)] thereby enhancing the UV photo response of the Schottky diodes under study. The photoconduction mechanism behind the UV detection at the surface of ZnO NPs is shown in Fig. 5.6, which may be described in the following manner:

- Under dark condition, oxygen molecule (O_2) capture electrons (e^-) from the surface of n-ZnO NPs and make adsorbed oxygen $(O_2(g)+e^- \rightarrow O_2^-(ads))$, which in turn, may lead to the formation of low-conductivity depletion region near the ZnO NPs surface.
- When UV light of wavelength $h\nu >> E_g$ enters into the ZnO material through the

inter-metal dot spacing and gets absorbed by ZnO NPs, the electrons (e^-) and hole (h^+) pairs are generated ($h\nu \rightarrow e^- + h^+$) in the ZnO films.

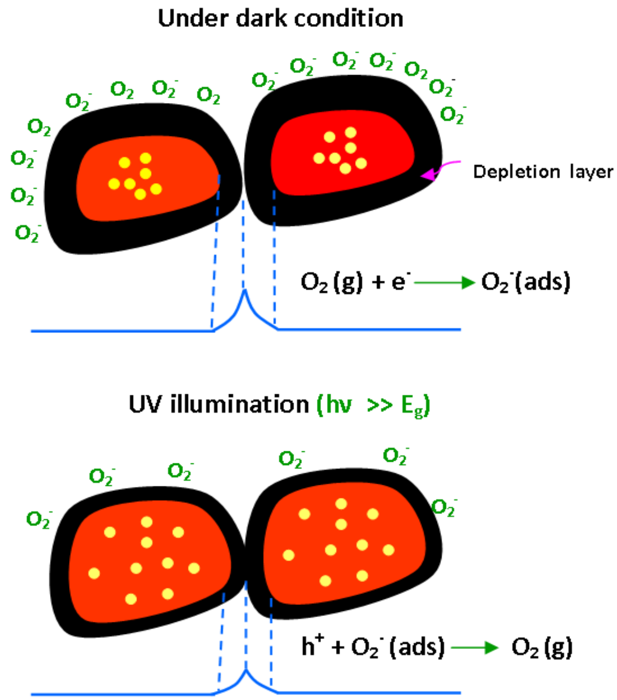

Figure 5.6: UV detection characteristics of Pd/ZnO NPs based Schottky diodes with and without UV illumination

- The photo-generated holes migrate towards the NPs surface along the potential produced by the band bending thereby neutralizing the negatively charged oxygen ions $\left(h^+ + O_2^-(ads) \rightarrow O_2(g)\right)$. This is the way by which oxygen is photo desorbed from the ZnO NPs surface [Soci *et al*. (2007), Wu *et al*. (2011)].

- At the same time, the photo-generated electrons significantly increase the conductivity of the NPs. As a result, the very large surface area of ZnO NPs can easily promote the oxygen adsorption and desorption at the NPs surfaces.

- The trapping mechanism involved in the oxygen adsorption/desorption makes the ZnO NPs under consideration a good material for the UV detection applications [Soci *et al*. (2007)].

5.4 Summary and Conclusion

In this chapter, the UV detection characteristics of Pd/ZnO NPs based Schottky diodes fabricated on Sn-seed layer coated n-Si (100) substrates have been investigated in details. Some of the important observations from the chapter are given as:

- ZnO NPs have been synthesized on Sn seed layer coated n-Si substrates by thermal evaporation method. The estimated diameter values of the as-grown ZnO NPs vary between ~30 nm to ~70 nm.

- The PL spectrum of as-grown ZnO NPs exhibits main peak at ~355 nm due to excitonic transition between valance band and conduction band. A number of other peaks are also observed in the PL spectrum which may belong to various kinds of zinc and oxygen related defects.

- Upon UV exposure, the as-fabricated Pd/ZnO NPs/Sn/n-Si Schottky diodes exhibit high contrast ratio of ~541 with excellent quantum efficiency of ~68% at room temperature.

- The value of responsivity, detectivity and zero bias resistance-area product for Pd/ZnO NPs Schottky diodes are determined as 0.68 A/W, 6.53×10^9 $mHz^{1/2}W^{-1}$ and 17.66 $\Omega. m^2$ respectively.

- The large surface area of ZnO NPs is believed to promote oxygen adsorption and desorption at the NP surfaces thereby enhancing the UV detection properties of the vacuum deposited ZnO NPs on the Sn seed layer coated n-Si substrates.

- Based on the comparison of various performance related parameters of the proposed photodiodes and other UV detector structures, it is concluded that the proposed Pd/ZnO NPs based Schottky photodiodes can be well explored for the UV detection applications.