Chapter 4

Effects of ZnO, Sn and Zn Seed Layers on the Electrical Characteristics of Pd/ZnO Thin Film Schottky Contacts Grown on n-Si Substrates

4.1 Introduction

The literature survey presented in Chapter-2 shows that high quality of ZnO thin films grown on Si substrates is difficult to achieve due to the large density of intrinsic defects in the ZnO thin films [Sheng *et al*. (2002), Allen *et al*. (2007), Hwang *et al.* (2013a)] owing to the large mismatching between lattice coefficients of ZnO and Si [Fu *et al.* (1998), Shen *et al*. (2006), Wang *et al*. (2007)]. It is also observed from the discussions of Chapter-2 that a seed/buffer layer of suitable material can be used on the Si substrates prior to the deposition of ZnO thin film to improve the surface morphology, crystalline structure and optical properties of ZnO thin films [Fu *et al*. (1998), Shen *et al*. (2006), Wang *et al*. (2007), Song and Lim (2007), Wu *et al.* (2012)]. Keeping this in view, the Chapter-4 has been designed to study the effects of three different seed layers of ZnO, Sn and Zn on the electrical characteristics of Pd/ZnO thin film Schottky diodes grown on n-Si substrates by thermal evaporation method. The outline of the present chapter is as follows:

Section 4.2 presents the fabrication details of Pd/ZnO Schottky diodes on n-Si substrates with the assistance of ZnO, Sn and Zn metal seed layers. The results and discussions related to the characterizations of the ZnO films (grown on a particular seed layer) and Pd/ZnO diodes have been presented in Section 4.3. Finally, Section 4.4 includes the summary and conclusion of the present chapter.

4.2 Fabrication Details of Pd/ZnO Thin Film Schottky Diodes on ZnO, Sn and Zn Seed Layer Coated n-Si Substrates Using Thermal Evaporation Method

Initially, n-Si substrates (of ~380 μm thickness) of resistivity ρ = 1- 6 Ω cm, is cleaned properly by piranha-HF method as discussed in Chapter-3. After cleaning, three batches of n-Si substrates have been prepared for deposition of ZnO, Sn and Zn seed layer using the thermal evaporation system (model no. 12A4D of HINDVAC, India) discussed in Chapter-3. Unless otherwise stated separately, the various growth conditions, such as the base pressure (10^{-3} mPa), distance between the source and substrate (18 cm), boat material (molybdenum) etc. in the evaporation unit have been maintained same as discussed in Chapter-3.

The first batch of n-Si substrates was placed in the thermal evaporation unit for deposition of a thin film of Zn metal (of thickness ~ 50 nm) at a base pressure of 10^{-3} mPa for duration of 55 minutes. The Zn filings (99.99 %) from the MERCK Ltd, Mumbai India were used as the source material for Zn deposition. The Zn thin film coated substrates was then put in the muffle furnace for optimized duration of 60 minutes at 600 °C in the O_2 gas atmosphere for complete oxidation of Zn into ZnO [Khanlary *et al*. (2012)]. The oxidized Zn (i.e. ZnO) seed layer coated n-Si substrates were cooled down to room temperature for film characterization and fabrication of Pd/ZnO Schottky diode under study.

The second and third set of the cleaned n-Si substrates were also processed subsequently for the growth of the respective seed layer (of ~ 50 nm thickness) of Sn and Zn metals on the n-Si substrates by the thermal evaporation method under the same growth conditions inside the evaporation unit as used for the Zn deposition discussed above. High purity Sn granules (99.99 %) from the Anala R, BDH Chemicals Ltd, England and Zn filings (99.99 %) from the MERCK Ltd, Mumbai, India were used as source materials for the deposition of Sn and Zn seed layers respectively. The thickness of the all the seed layers was monitored by the in-built digital thickness monitor attached to the evaporation unit used for our work.

All the three sets of samples of ZnO, Sn and Zn seed-layer coated n-Si substrates were placed in the thermal evaporation unit for deposition of ZnO thin films (~of 300 nm thickness) following the same method as described in Chapter 3 for the ZnO thin film deposition on the bare-n-Si substrates. The ZnO pallets of 10 mm diameter made from ultrapure ZnO powder (99.99 %) from the MERK-Chemical Ltd, Mumbai, India discussed in Chapter-3 were also used as the source material for the ZnO film deposition on the seed layer coated n-Si samples.

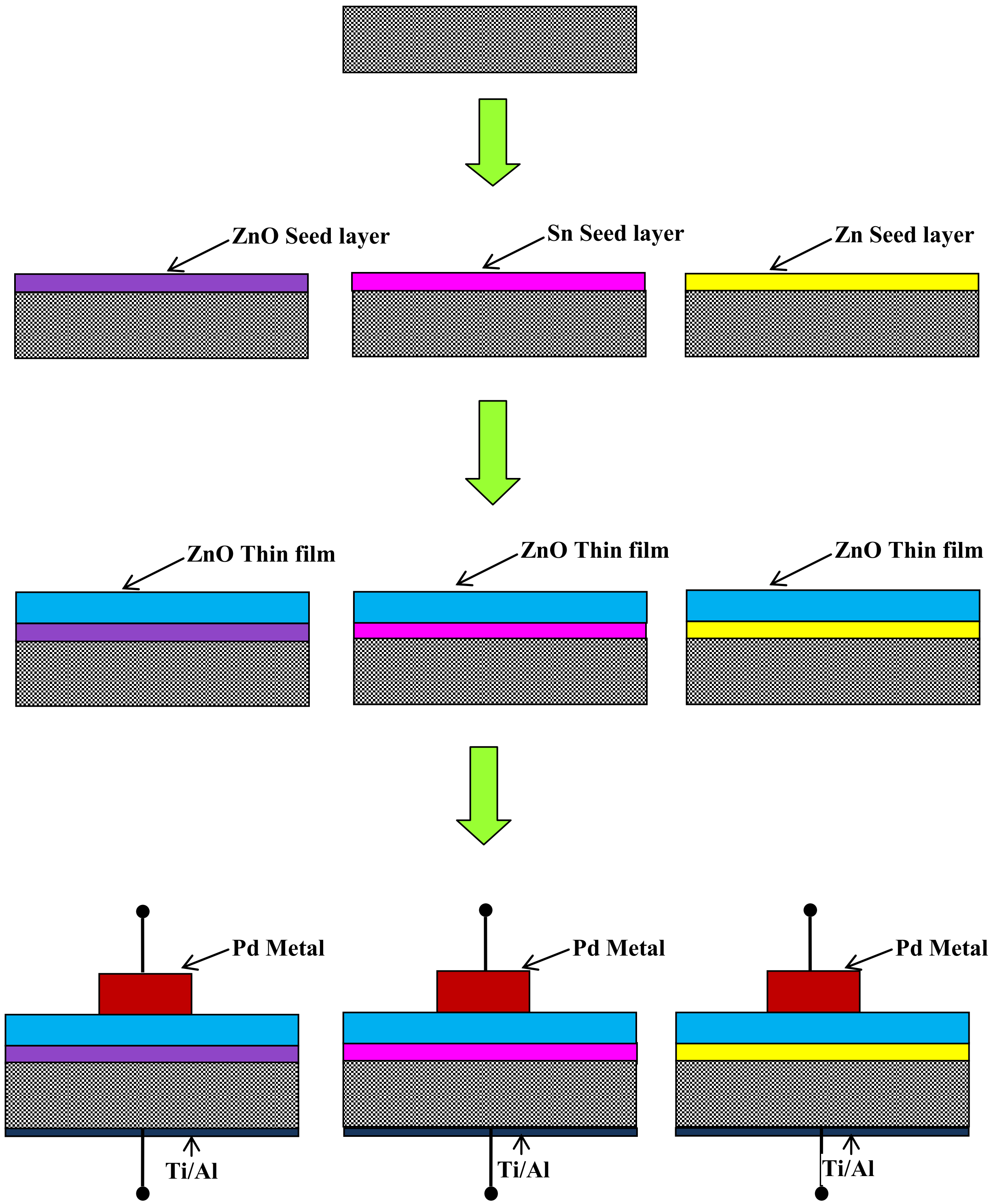

Figure 4.1: Schematic diagram for fabrication of Pd/ZnO Schottky diodes grown on n-Si substrates with assistance of ZnO, Sn and Zn seed layer

After the deposition of the ZnO films on the ZnO, Sn and Zn seed layer coated n-Si substrates, all the 3-set of samples were then processed for rapid thermal annealing treatment in the N_2 gas atmosphere for 30 minutes at temperature of 550 °C. Following the similar method followed in Chapter-3, Pd metal dots (of ~100 nm thickness and area (A) ~0.785×10^{-2} cm^{-2}) and Ti/Al (80/70 nm) layers were deposited for fabricating the Schottky contacts and ohmic contacts on the ZnO films and entire backside of the n-Si substrates of all the three sets of samples respectively. Finally, the fabricated vertical Schottky diode structures in the form of Pd/ZnO thin film/seed layer (ZnO, Sn or Zn)/ Ti/Al were processed for annealing in the N_2 gas atmosphere at 550 ^{o}C for 7 minutes to improve electrode quality as discussed in Chapter-3. The sequential fabrication details of the three Schottky device structures are described in Fig.4.1.

4.3 Results and Discussion

This section has been divided into two parts:

(i) The first part includes only the effect of the ZnO seed layer on the morphological, structural and optical properties of vacuum deposited ZnO thin films and on the electrical characteristics of Pd/ZnO thin film Schottky diodes grown on ZnO seed layer coated n-Si substrates. We have kept it in a separate subsection due to the same characteristics of the seed layer material ((i.e. ZnO) and the films of the material (i.e. ZnO) deposited on it for making the Pd/ZnO Schottky devices.

(ii) The second subsection presents the effects of Sn and Zn seed layers on the various properties of the ZnO films and the electrical characteristics of the Pd/ZnO thin film Schottky diodes grown on the seed layer coated n-Si substrates. Since Sn and Zn are the metallic seed layers of the same group, they have been discussed in this separate subsection.

It is already mentioned that the ZnO films are inherently of n-type semiconductors, thus the n-Si/n-ZnO [Kim *et al*. (2001)], Sn/ZnO [Sze (1981), Reddy *et al*. (2007)] and Zn/ZnO [Sze (1981)] junctions are, in general, ohmic in nature. The effects of the ZnO, Sn and Zn seed layers on the properties of ZnO thin films deposited on them have been investigated by analyzing the FESEM, XRD and EDS data in the similar manners as considered in Chapter-3. Further, the n-Si/n-ZnO [Kim *et al*. (2001)], Sn/ZnO [Sze (1981), Reddy *et al*.

(2007)] and Zn/ZnO [Sze (1981)] junctions are ohmic in nature, the vertical Pd/ZnO/(Sn or Zn) seed-layer/n-Si/Ti/Al and Pd/ZnO/n-Si/Ti/Al structures represent the desired Schottky diodes structures under consideration.

4.3.1 ZnO Seed Layer Based Pd/ZnO Thin Film Schottky Diodes

In this subsection, we have first investigated the effects of ZnO seed layer on surface morphology, crystalline structure and chemical composition of ZnO thin films by analyzing the FESEM images, XRD patterns and EDS spectra. Then, we have discussed the effects of ZnO seed layer on different electrical parameters such as rectification ratio, reverse saturation current, barrier height, ideality factor and series resistance of Pd/ZnO thin film Schottky diodes under consideration.

4.3.1.1 Surface morphology study of ZnO thin films by FESEM images

The FESEM images (model no.FEI QUANTA 200, FESEM) of the ZnO thin films directly grown on the n-Si substrates, ZnO seed layer and the ZnO thin films grown on the ZnO seed layer have been shown in Figs. 4.2 (a), (b) and (c) respectively. While the FESEM images of Fig. 4.2 (a) and (b) show the nanocrystalline nature of both the directly deposited ZnO film (on bare n-Si substrate) and ZnO seed layer (obtained by oxidizing the metallic Zn deposited on the n-Si substrate), the surface morphology of the vacuum deposited ZnO thin films on the ZnO seed layer consists of the arrays of nanorods (NRs). The as-grown ZnO nanorods are uniformly grown on the whole n-Si substrates with growth direction perpendicular to the substrates surface. It is clear from Figs. 4.2 (a), (b) and (c) that the thermally oxidized Zn i.e. ZnO seed layer changes the nature of the vacuum deposited ZnO thin films from the nanocrystalline to nanorods (NRs) structure.

4.3.1.2 AFM images of ZnO nanorods

The surface topographical analysis of the seed-layer assisted ZnO thin films i.e. nanorods (NRs) have been studied by using AFM (Model No. P47 from NT-MDT Co.,Russia) images. The probes used were NSG10 series in tapping mode also from NT-MDT Co., Russia. The parameters of the probe used for this measurement includes the elastic constant =11.5 N/m; resonance frequency =255 kHz; length = 100 mm; width = 35 mm; thickness = 2.3 mm; tip radius = 10 nm and tip angle = 22º. The AFM images as shown in Fig 4.3 (a)

& (b) clearly demonstrate that well-aligned vertical ZnO nanorods arrays with excellent surface morphology can be grown on the ZnO seed layer coated n-Si substrates by thermal evaporation method.

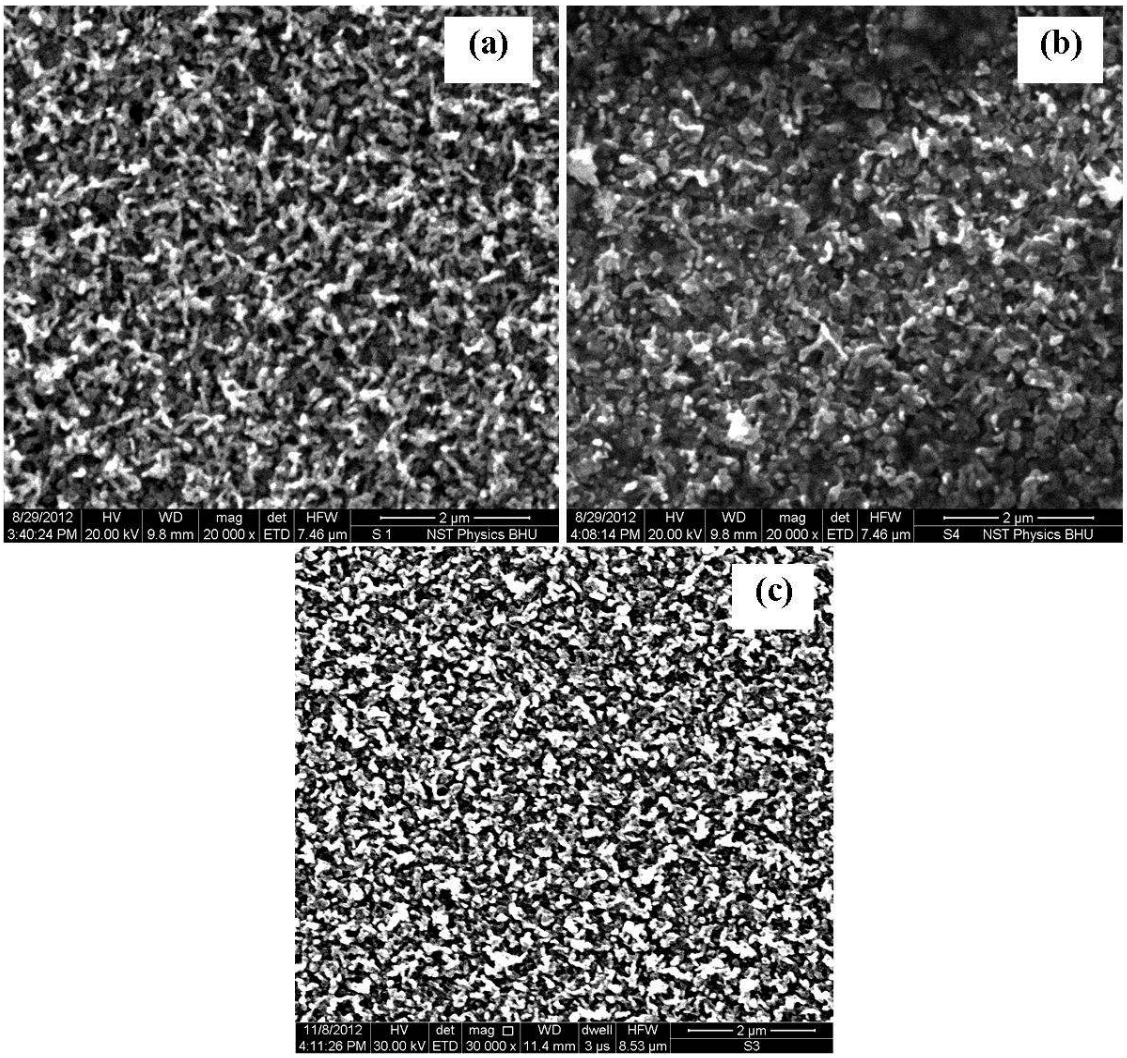

Figure 4.2: FESEM image (top view) of **(a)** ZnO thin film grown on bare n-Si substrate; **(b)** ZnO seed layer **(c)** ZnO seed layer assisted ZnO thin film grown on n-Si substrates by thermal evaporation method

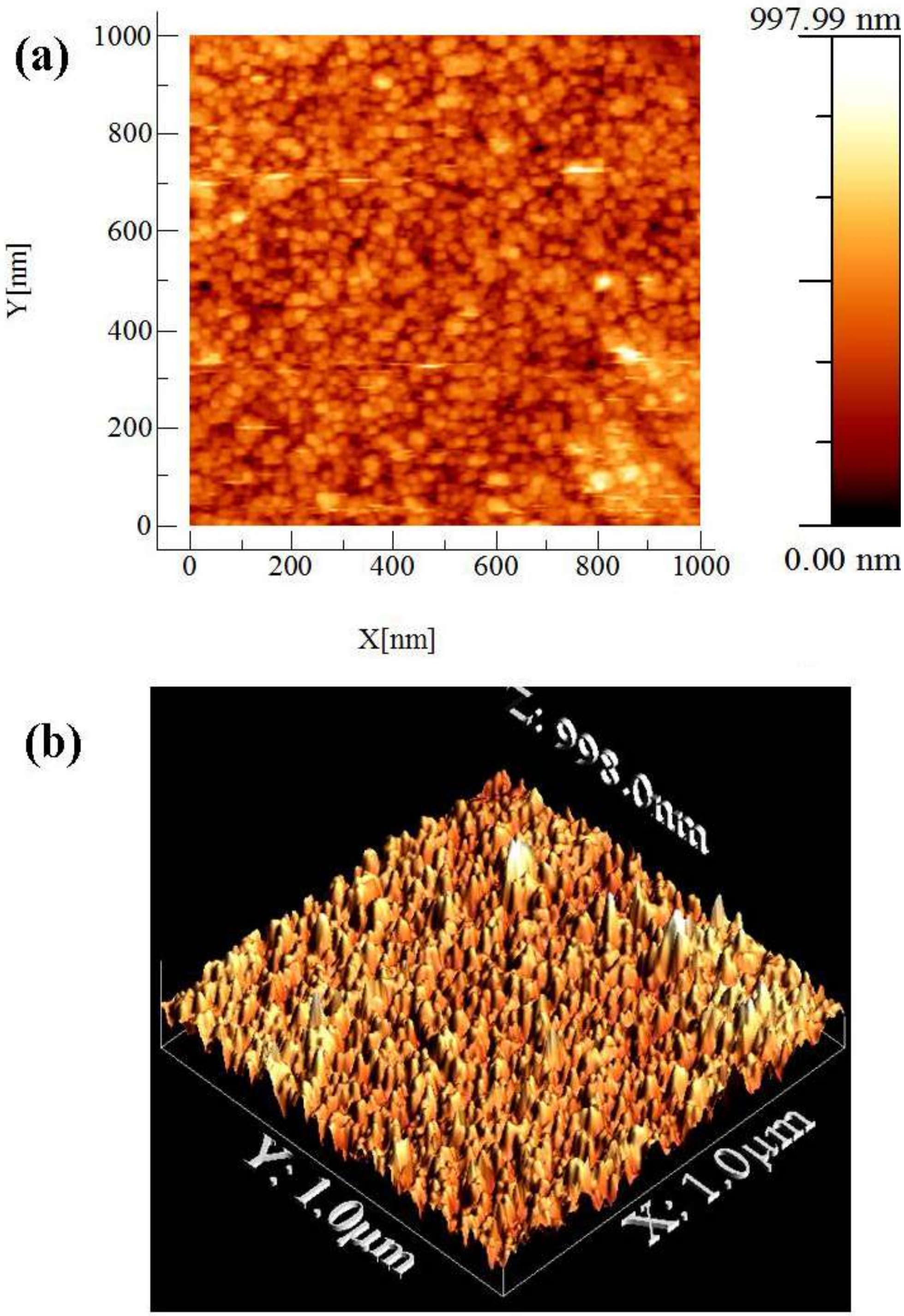

Figure 4.3: **(a)** Two dimension (2D) **(b)** three dimension (3D) AFM image of ZnO nanorods obtained in tapping mode grown on n-Si substrates with assistance of ZnO seed layer

4.3.1.3 EDS spectra

The chemical composition of ZnO thin films grown on the ZnO seed layer coated n-Si substrates have been compared with ZnO thin films grown directly on the bare n-Si substrates. A good amount of Zn and O elements are observed in the EDS spectra as shown in Fig 4.4 (a) and (b). The peak of Si is also observed in the EDS spectra due to silicon substrates. When we have compared both the EDS spectra, it is clear that peak of Si is reduced by a high order when the substrates changes from bare n-Si to ZnO seed layer coated n-Si substrates. It implies that the density of ZnO thin film is increased due to the presence of the ZnO seed layer on the n-Si substrates.

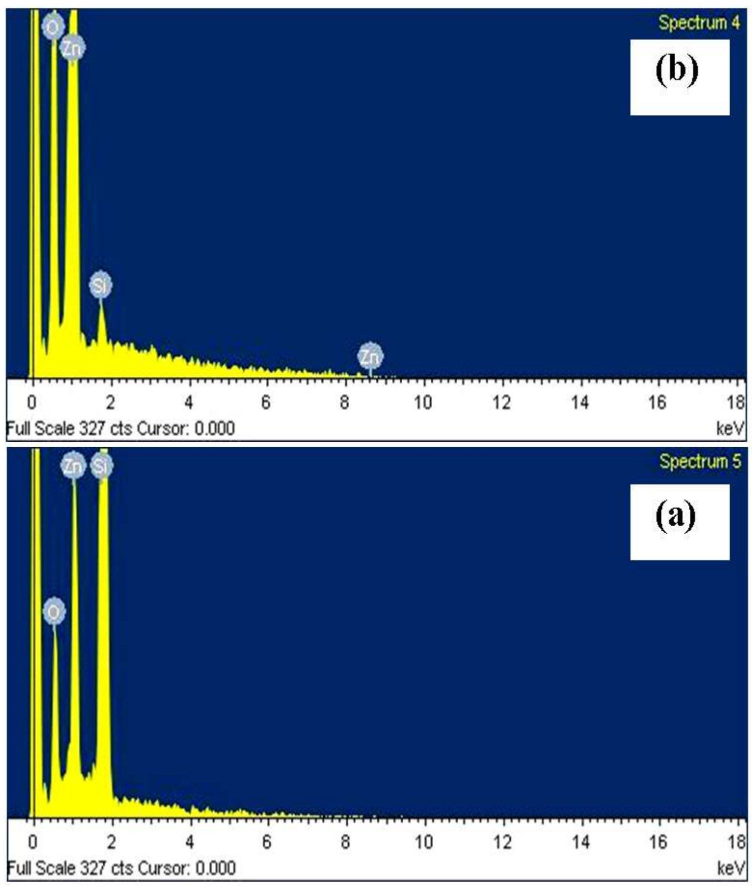

Figure 4.4: Typical EDS spectra of **(a)** ZnO thin films grown on bare n-Si substrates **(b)** ZnO thin film grown on ZnO seed layer coated n-Si substrates by thermal evaporation method

4.3.1.4 XRD pattern of ZnO thin films

The XRD pattern (18 kW Cu-rotating anode, model: XDMAX, PC-20, Rigaku, Tokyo, Japan) of the ZnO thin films directly grown on the n-Si substrates, ZnO seed layer and the ZnO seed layer assisted ZnO thin films (i.e. ZnO nanorods (NRs)) have been shown in Figs. 4.5 (a), (b) and (c) respectively. All the observed peaks i.e. (100), (002), (101), (102), (110) are well matched with JCPDS data card of ZnO (JCPDS no-36-1451). Clearly, all the as-grown ZnO thin films shown in Fig.4.5 have hexagonal wurtzite structure with (101) diffraction plane as the dominant preferential growth direction. However, Fig.4.5 (c) shows that the intensity of diffraction planes of the ZnO film grown on the ZnO seed layer coated n-Si substrates is observed to be the highest among the three types of ZnO films considered in Fig.4.5. This implies that the quality of the ZnO thin films (i.e. ZnO NRs) deposited on the seed layer coated n-Si substrates is better than that of the films directly grown on the bare n-Si substrates.

It should be mentioned that the ZnO has hexagonal wurtzite structure with lattice constants a =3.252 Å, c = 5.213 Å whereas the Si has cubic diamond structure with lattice constant a =5.4301 Å [Jagadish and Pearton (2006)]. Now, the lattice mismatching [Lee *et al.* (2004)] between ZnO and Si substrates is defined by $\frac{(a_{ZnO} - a_{Si})}{(a_{Si})} \times 100$ where a_{ZnO} and a_{Si} is the plane spacing of ZnO and Si substrates respectively. For the ZnO films grown on the bare Si substrates, the lattice mismatching between the Si and ZnO is calculated as ~40.1% [Lee *et al.* (2004), Teng *et al.* (2006)]. This large lattice mismatching may degrade the quality of the ZnO thin films directly grown on Si substrates. On the other hand, the use of ZnO seed layer between the ZnO and Si substrates minimizes the lattice mismatching from 40.1% to 0.28% [Lee *et al.* (2004)], which subsequently improves the crystalline quality of ZnO thin films (ZnO NRs) grown on seed layer coated n-Si substrates as observed from Fig. 4.5 (c).

Table.4.1 Lattice mismatching between ZnO and substrate materials

Substrate materials	Lattice mismatch with ZnO (%)
Si	40.3
Si/ZnO(seed layer)	0.28

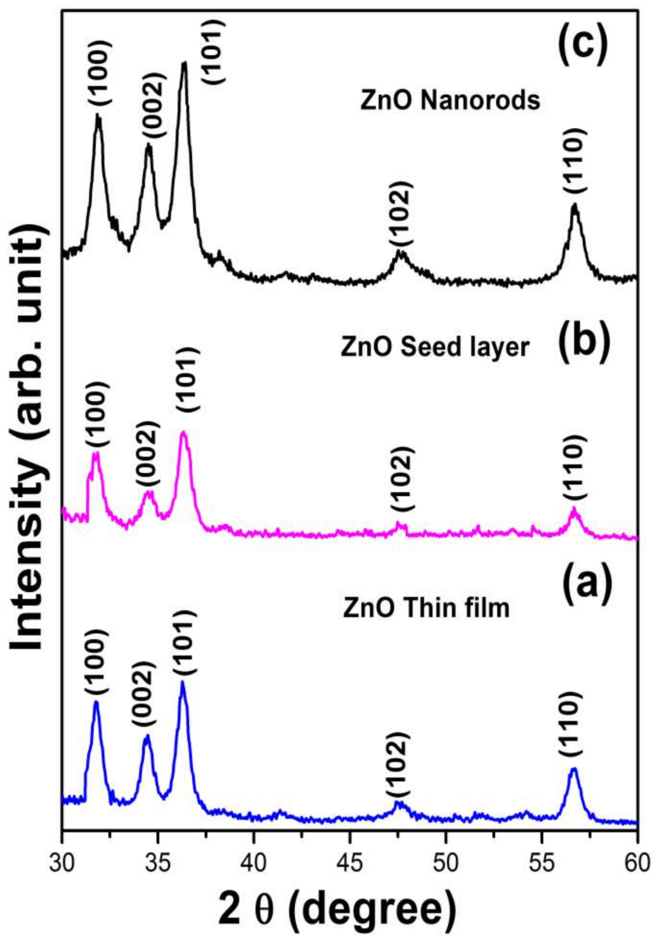

Figure 4.5: Typical XRD pattern of **(a)** ZnO thin films grown on bare n-Si substrates **(b)** ZnO seed layer **(c)** ZnO seed layer coated ZnO thin film

4.3.1.5 Growth mechanism of ZnO nanorods (NRs) on ZnO-seed layer coated n-Si substrates

Various steps for the possible growth mechanism of the as-grown ZnO NRs on the ZnO-seed layer coated n-Si substrates are schematically described in Fig.4.6. Since no metal-catalyst is used in the synthesis of ZnO NRs, the growth mechanism of ZnO NRs can be explained by the vapour–solid (VS) approach [Yi *et al*. (2005)]. When the oxidation of Zn layer (~50 nm) takes place in O_2 gas atmosphere at temperature of 600 °C (which is much greater than the melting point (419 °C) of the Zn) [Jagadish and Pearton (2006)], the Zn metal is melted and the oxygen in the inlet flow is believed to be absorbed by the Zn metal on the surface till formation of some Zn/ZnOx seeds occurs. As the ZnO thin film (~300 nm) is deposited on the ZnO seed layer (formed by the thermal oxidation of Zn as mentioned above), the Zn/ZnOx seeds act as nucleation sites for the growth of nanostructures and promote the aligned growth of ZnO NRs on the n-Si substrates. The growth of ZnO NRs is started after the formation of the ZnO seeds and continues as long as nucleation sites are available. Since no nucleation site is available when the ZnO films are deposited directly on the bare Si substrates, no NRs-type structure is formed as evidenced from the FESEM images.

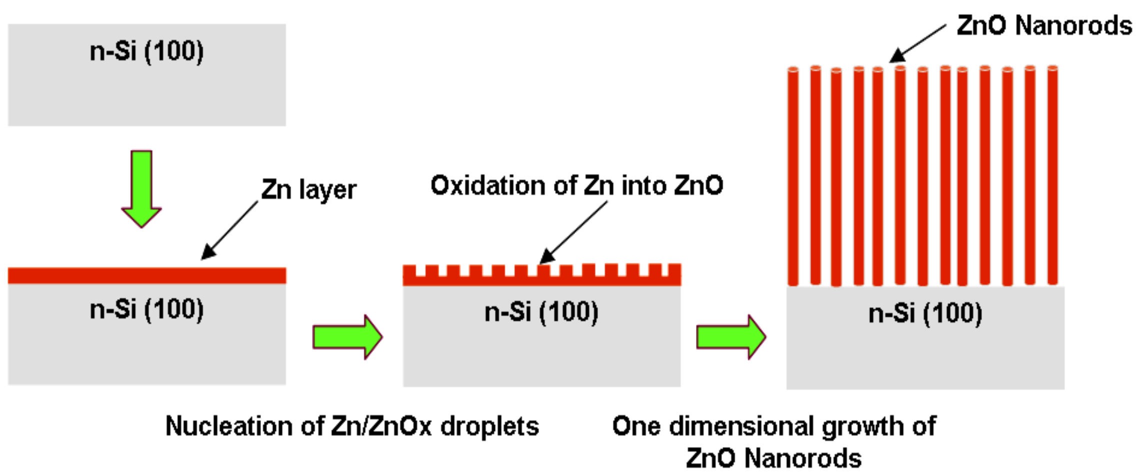

Figure 4.6: Schematic diagram for the possible growth mechanism of ZnO nanorods grown on n-Si substrates by ZnO seed layer assisted thermal evaporation method

4.3.1.6 Electrical characteristics of Pd/ZnO thin film Schottky diodes with and without a ZnO seed layer

The current-voltage (I-V) characteristics of the Pd Schottky contacts grown on the seed layer assisted ZnO thin films (i.e. ZnO NRs) and directly deposited ZnO thin films on the bare n-Si substrates have been compared in Fig.4.7. The I-V characteristics have been measured in the voltage range between -2 to +2 V by using a semiconductor parameter analyzer (Agilent B1500A) at room temperature. For the Pd/ZnO thin film Schottky contact without ZnO seed layer, the I-V characteristic shows a very poor rectification ratio (I_F / I_R) (i.e. the ratio of the current I_F at a forward bias voltage of 2 V divided by the absolute value of the reverse current I_R at –2 V reverse bias) of ~ 113 whereas this value of I_F / I_R changes drastically and approaches the value ~2.456×10^3 (~21 times more without seed layer) for the Pd/ZnO thin film Schottky contacts grown on the ZnO seed layer assisted ZnO thin films. In other words, the Pd Schottky contacts grown on the seed layer assisted ZnO films possess superior rectifying characteristics at room temperature than the Schottky contacts grown on ZnO films without using a ZnO seed layer.

Following the discussion presented in Chapter-3, the measured I-V characteristics of Pd/ZnO thin film Schottky diodes is reproduced as [Bethe (1942), Mead (1965), Sze (1981), Rhoderick and Williams (1988)]

$$I = I_0\left\{= AA^*T^2\, exp\left(-\frac{q\phi_{B,eff}}{kT}\right)\right\}\left\{exp\left[\frac{q(V-IR_s)}{\eta kT}\right]-1\right\} \tag{4.1}$$

where q is the elementary charge, V is the applied voltage, η is the ideality factor (defined as $\eta = (q/kT)\{dV/d(ln I)\}$), k is the Boltzmann constant, R_s is the series resistance, T is the absolute temperature and I_0 is the reverse saturation current.

Following the conventional method already discussed in Chapter 1 and 3, we have calculated the values of the I_0, $\phi_{B,eff}$, and η of the Pd Schottky contacts grown on the ZnO seed layer assisted ZnO thin films (i.e. ZnO NRs) and listed in Table.4.2. The values of I_0 estimated for the Pd/ZnO thin film Schottky diodes with and without using ZnO seed layer are 4.97×10^{-10} A and 8.76×10^{-8} A respectively. Using the above values of I_0, we have calculated the values of $\phi_{B,eff}$ of the devices with and without using a seed layer as 0.81 eV and 0.67 respectively. The estimated value of η is observed to be improved significantly from a value of 2.36 to 1.46 when the ZnO seed layer is used in the device structure. This implies that the Pd/ZnO contact becomes more ideal in nature in case of the ZnO thin film grown on the seed layer than the ZnO thin films directly grown on the Si substrates. Wenckstern *et al*. [Wenckstern *et al*. (2006)] reported $\phi_{B,eff}$ = 0.81 eV and η = 1.49 at 290 K for Pd Schottky Contacts on n-type ZnO thin film grown on the glass substrate while Periasamy and Chakrabarti [Periasamy and Chakrabarti (2009)] reported the value of $\phi_{B,eff}$ = 0.72 eV and of η =1.52 at room temperature of the Pt/ZnO thin film Schottky Contacts on ITO coated glass. Thus, the estimated values of the barrier height and ideality factor are in good agreement with the reported results by Wenckstern *et al*.

[Wenckstern *et al*. (2006)] & Periasamy and Chakrabarti [Periasamy and Chakrabarti (2009)].

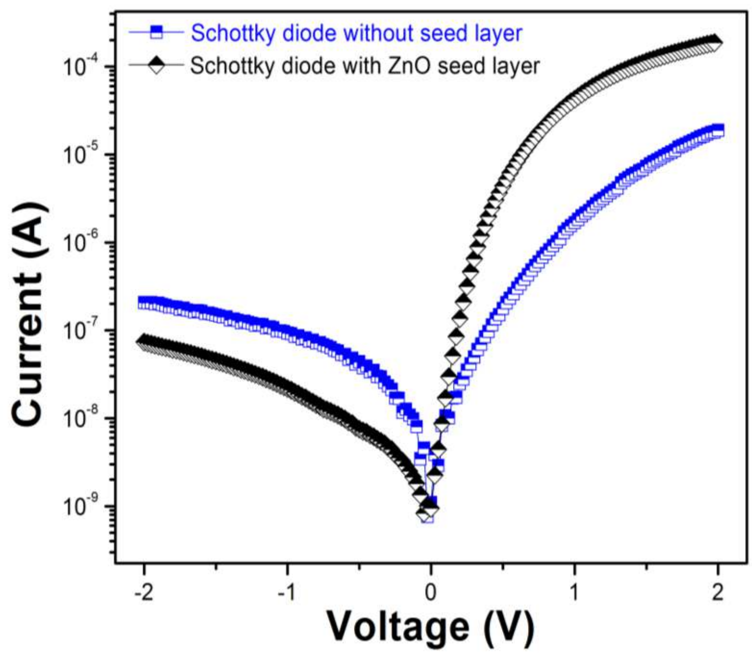

Figure 4.7: Room temperature ln I vs. V characteristics of Pd/ZnO thin film Schottky diodes with and without ZnO seed layer

To study the effect of ZnO seed layer on the series resistance (R_s) of the Schottky diode under consideration, we have used the following relations proposed by Cheung and Cheung [Cheung and Cheung (1986)] as discussed in Chapter-3:

$$\frac{dV}{d(ln\,I)} = \left(\frac{\eta kT}{q}\right) + IR_s \tag{4.3}$$

$$H(I)\left\{ = V - \left(\frac{\eta kT}{q}\right) ln\left(\frac{I}{AA^* T^2}\right)\right\} = \eta\phi_{B,eff} + IR_s \tag{4.4}$$

The plots of $dV/d(ln\,I)$ vs. I and $H(I)$ vs. I for Schottky diode structures with a ZnO seed layer under study have been shown in Fig.4.8. Note that R_s and η can be obtained from the slope and y-axis intercept of $dV/d(ln\,I)$ vs. I plot respectively. Similarly, the slope of $H(I)$ vs. I also represents R_s and its y-axis intercept can be used to estimate $\phi_{B,eff}$ as summarized in Table.4.2. However, since the effect of R_s is mainly dominant in the higher current region of the I-V characteristics, the values of η and $\phi_{B,eff}$ determined from the above described manner may differ significantly from those determined from the conventional method applicable for the low-current region (i.e. the region where the diode possesses the conventional exponential I-V characteristics described by Eq. (4.1) with $R_s = 0$). This can be attributed to the existence of the series resistance and interface states and to the voltage drop across the interfacial layer.

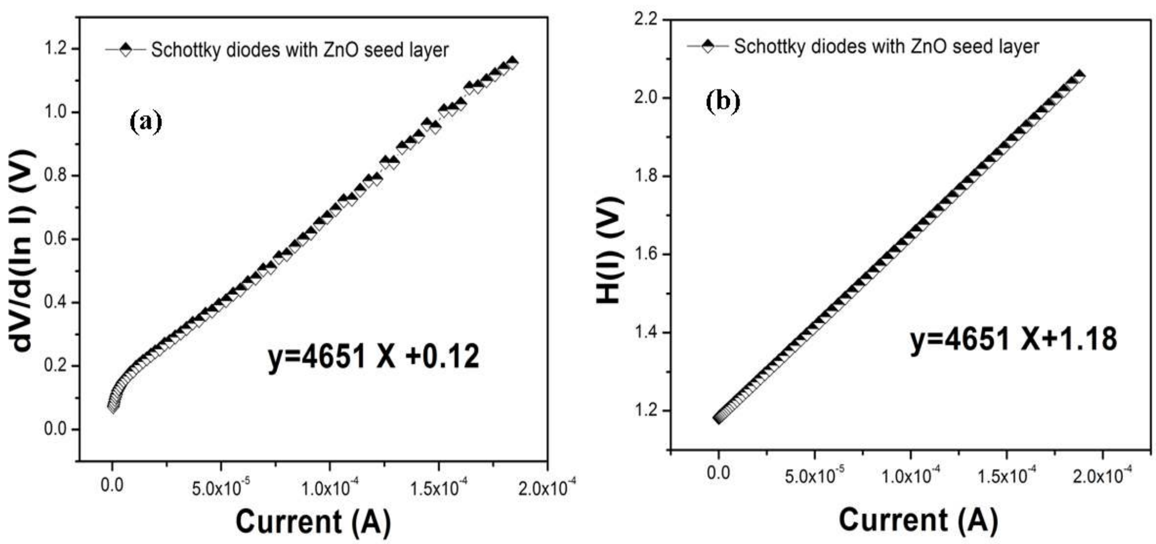

Figure 4.8: Calculation of series resistance by **(a)** dV/d(ln) vs. I plot **(b)** H(I) vs. I plot

Table.4.2 Different Electrical parameters of Pd/ZnO thin film Schottky diodes grown on n-Si substrates with and without ZnO seed layer

Pd/ZnO Schottky diode grown on n-Si substrates	**Thermionic emission (I-V)**			**Cheung– Cheung method**			
				dV/d (ln I) vs. I		H(I) vs. I	
	I_F / I_R	$\phi_{B,eff}$	η	R_s	η	R_s	$\phi_{B,eff}$
without seed layer	113	0.67	2.36	4734	5.79	4734	0.67
ZnO seed layer	2456	0.81	1.46	4651	4.61	4651	0.80

4.3.2 Effects of Sn and Zn Seed Layers on the Structural Properties of Vacuum Deposited ZnO Films and Electrical Characteristics of Pd/ZnO Thin Film/(Sn or Zn)/ Seed Layer Schottky Diodes

After discussing the effects of ZnO seed layer on the structural properties of the vacuum deposited ZnO films deposited on it and the electrical characteristics of the Pd/ZnO thin film/ZnO seed layer/n-Si/ Ti/Al Schottky diode structures, we will now discuss the same for the vacuum deposited ZnO films grown on the Sn and Zn seed layers and Pd/ZnO thin film/ seed layer (either Sn or Zn) /n-Si/ Ti/Al Schottky diode structures in the following.

4.3.2.1 Surface morphology

Figs. 4.9 (a), (b) and (c) shows the FESEM images (with magnification view of ~ 1μm) of the vacuum deposited ZnO thin films grown on bare n-Si, Sn seed-layer coated n-Si and Zn seed-layer coated n-Si substrates respectively. Clearly, the ZnO thin films grown on the bare n-Si substrates appear to be nanocrystalline (Fig. 4.9(a)) in nature whereas the films grown on Sn seed layer and Zn seed layer coated Si substrates have nanoparticles (Fig. 4.9 (b)) and nanowires structures (Fig. 4.9 (c)) respectively. It may be mentioned that the physical and optical properties of ZnO thin films grown on any substrate are very much affected by the matching of their lattice constants and thermal expansion coefficients [Shen *et al*. (2006), Wang *et al*. (2007)]. The ZnO thin films grown on bare n-Si substrates suffer from poor crystalline quality due to high lattice mismatching between ZnO and Si substrates, easy oxidation of silicon surface and the formation of silicides at room temperature [Wang *et al*. (2007)] as discussed in Chapter-3. As per the discussions of Chapter-2, a seed layer of a suitable material can be used to improve the quality of the films by minimizing the above difficulties [Wang *et al*. (2007)]. In the present work, in addition to the ZnO, Sn and Zn seed layers have been chosen due to the least mismatching of these metals with the ZnO as already reported by other researcher [Ding *et al*., (2004), Lee *et al*. (2008)]. The change in surface morphology (*from nanocrystalline to nanoparticles and nanowires*) is attributed to the improved structural characteristics of ZnO thin films grown on the Sn and Zn coated n-Si substrates as compared to the films grown on the bare n-Si substrates without using a seed layer.

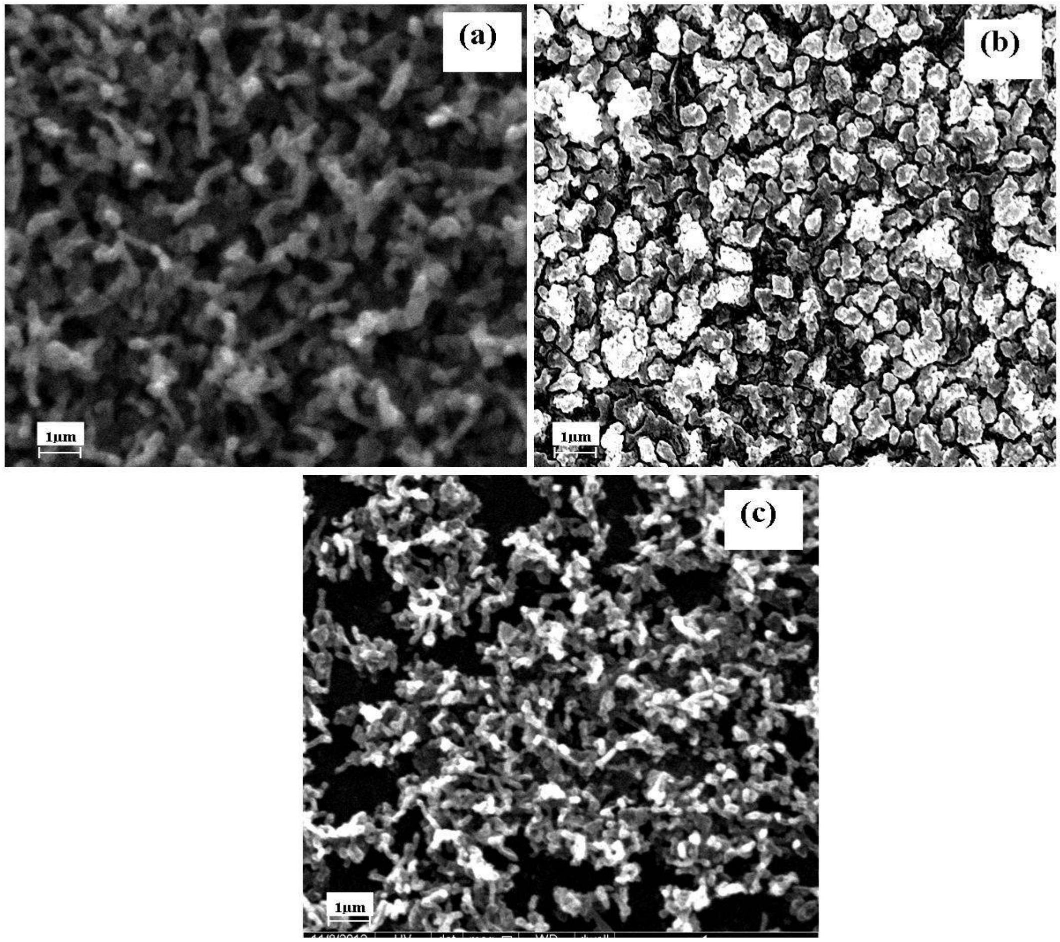

Figure 4.9: FESEM images of ZnO thin film grown on **(a)** bare n-Si substrates **(b)** Sn seed layer **(c)** Zn seed layer grown on n-Si substrates by thermal evaporation method

4.3.2.2 EDS spectra

The EDS spectra of the ZnO thin films grown on bare n-Si, Sn seed-layer coated n-Si and Zn seed-layer coated n-Si substrates have been shown in Figs 4.10 (a), (b) and (c) respectively. It is observed that a good amount of Zn and O elements in atomic ratio is present in the EDS spectra of all ZnO thin films. The peak of Si is also found in EDS spectra of all ZnO thin films due to Si substrates used for deposition of ZnO thin films. The presence of Sn is confirmed by the small peak of the Sn metal in the EDS spectra [Fig. 4.10 (b)] of the ZnO film grown on the Sn seed-layer coated n-Si due to Sn seed layer. No other peaks of any metal or impurities are detected from the EDS spectra of all the ZnO thin films. Thus, the above results demonstrate that the catalyst-free growth of ZnO nanoparticles and nanowires are possible on n-Si substrates by using the Sn and Zn seed layers respectively.

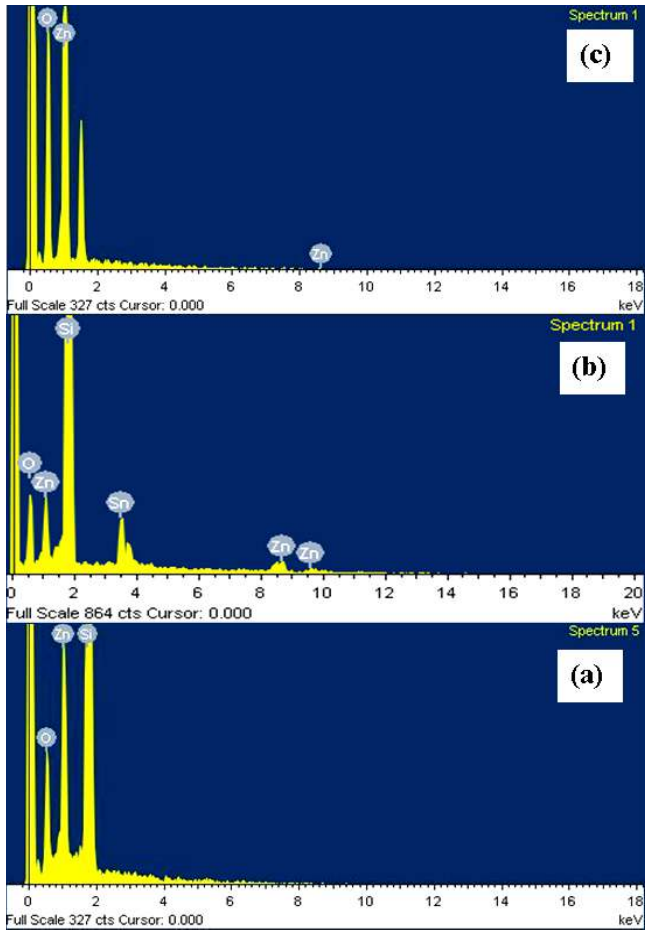

Figure 4.10: EDS spectrum of ZnO thin film grown on **(a)** bare n-Si substrates **(b)** Sn seed layer **(c)** Zn seed layer grown on n-Si substrates by thermal evaporation method

4.3.2.3 XRD patterns

The XRD patterns (18 kW Cu-rotating anode, model: XDMAX, PC-20, Rigaku, Tokyo, Japan) of the ZnO thin films grown on bare n-Si substrates, Sn seed layer coated n-Si substrates, Zn seed layer coated n-Si substrates have been shown in Figs.4.11. While the orientation of diffraction plane is changed from the (101) to (002) diffraction plane when the substrate is changed from the bare n-Si to the Sn seed layer coated n-Si, the orientation of diffraction planes is observed to remain unchanged for Zn seed layer coated n-Si substrates orientation of diffraction planes remain same for the change of substrate from the bare n-Si to the Zn seed layer coated n-Si.

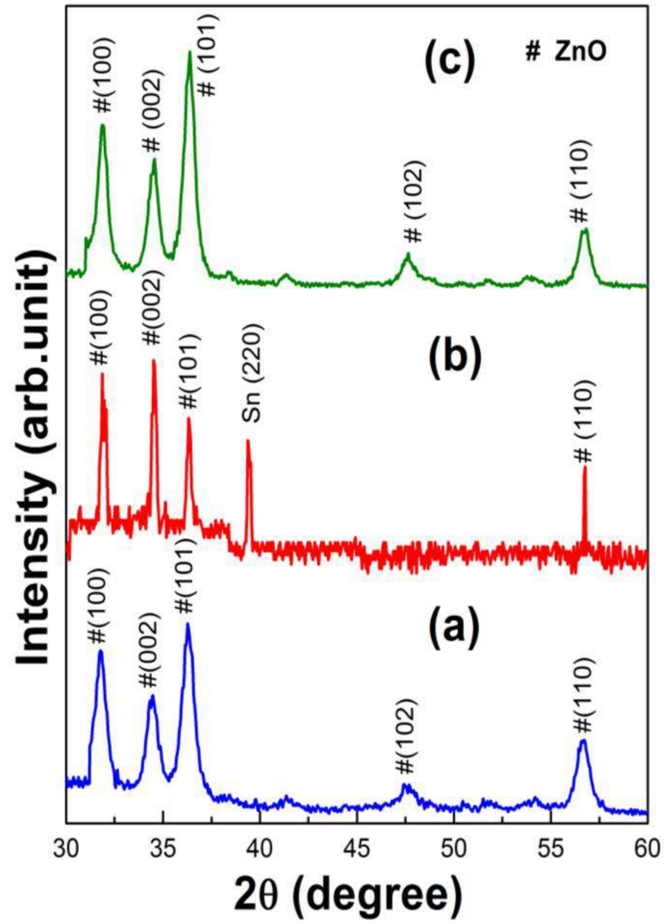

Figure 4.11: XRD pattern of ZnO thin film grown on **(a)** bare n-Si substrates **(b)** Sn seed layer **(c)** Zn seed layer grown on n-Si substrates by thermal evaporation method

4.3.2.4 Analysis of the I-V characteristics of Pd/ZnO thin film/(Sn or Zn)seed layer/n-Si/Al/Ti Schottky diodes

The room temperature ln (*I*) vs. *V* characteristics of the Pd/ZnO thin film Schottky diodes grown on bare n-Si substrates, Sn seed layer coated n-Si substrates, and Zn seed layer coated n-Si substrates have been compared in Fig. 4.12. The measured rectification ratio I_F / I_R at $\pm 2\text{V}$ of the Pd/ZnO thin film Schottky diodes without any seed layer is ~ 113 whereas the I_F / I_R ratio of the Schottky diodes grown on the Sn and Zn seed layer coated Si substrates are found as ~885 and ~7561 respectively. Clearly, the rectifying characteristics of Pd/ZnO thin film Schottky diodes are improved dramatically due to the use of Sn and Zn seed layers as compared to that of the device grown on the bare n-Si substrates. Assuming the thermionic emission model, the I-V characteristics of the Pd/ZnO

Schottky diodes grown on the Sn or Zn seed layer coated Si substrates can also be described by the Eq. (4.1) already discussed for the ZnO seed layer based Schottky diodes under study in this chapter. Following the conventional methodology described in Chapter-1 and Chapter-3, the estimated values of I_0, $\phi_{B,eff}$ and η are found to be decreased from 8.76×10^{-8} A to 1.32×10^{-9}A, increased from 0.67 eV to 0.78 eV and decreased from 2.36 to 2.10 respectively when the substrate is changed from the bare n-Si to Zn seed layer coated n-Si for the growth of ZnO films of the Schottky diodes. For the Schottky diodes with Sn seed layer, moderate values of I_0 = 5.41 $\times10^{-9}$A, $\phi_{B,eff}$ = 0.75 eV and $\eta = 2.67$ are observed.

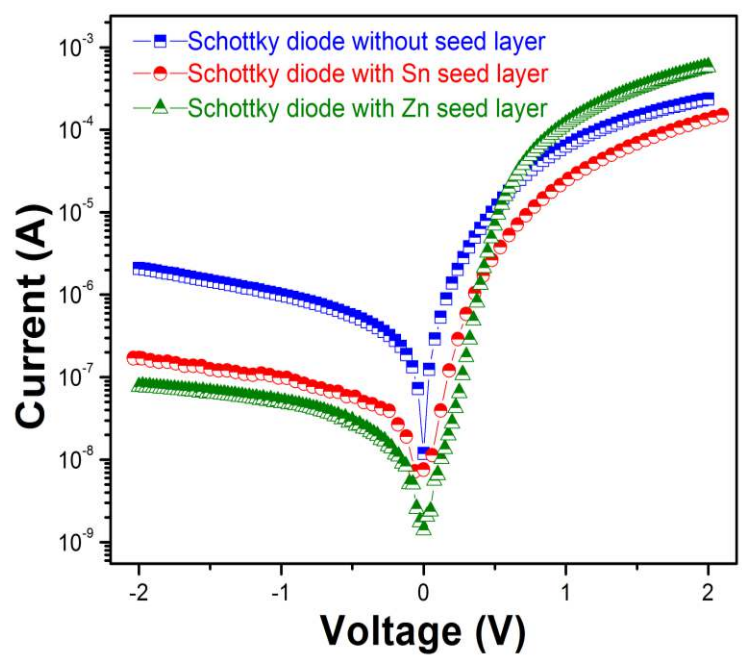

Figure 4.12: ln I vs. V characteristics of Pd/ZnO thin film Schottky diodes grown on **(a)** bare n-Si substrates **(b)** Sn seed layer coated n-Si substrates **(c)** Zn seed layer coated n-Si substrates

To study the effect of Sn and Zn seed layers on the series resistance (R_s) of the Schottky diodes under consideration, we can use the plots of $dV/d(ln I)$ vs. I and $H(I)$ vs. I shown in Fig. 4.13 for the Schottky diode structures with Sn and Zn seed layers as well as for the diode fabricated on the bare n-Si presented in Chapter-3. Following the method used for ZnO seed layer based Schottky diodes, the estimated values of η, $\phi_{B,eff}$ and R_s of the Sn and Zn seed layer based Schottky diodes are summarized in Table.4.3. Not that a very small change from 4734.5 Ω (i.e. of the Schottky diode without any seed layer) to 4637 Ω in the value of R_s has occurred when the Sn seed layer is used whereas R_s has been reduced from 4734.5 Ω to a very small value of 1677.7 Ω when the Zn metal seed layer has been used in the device.

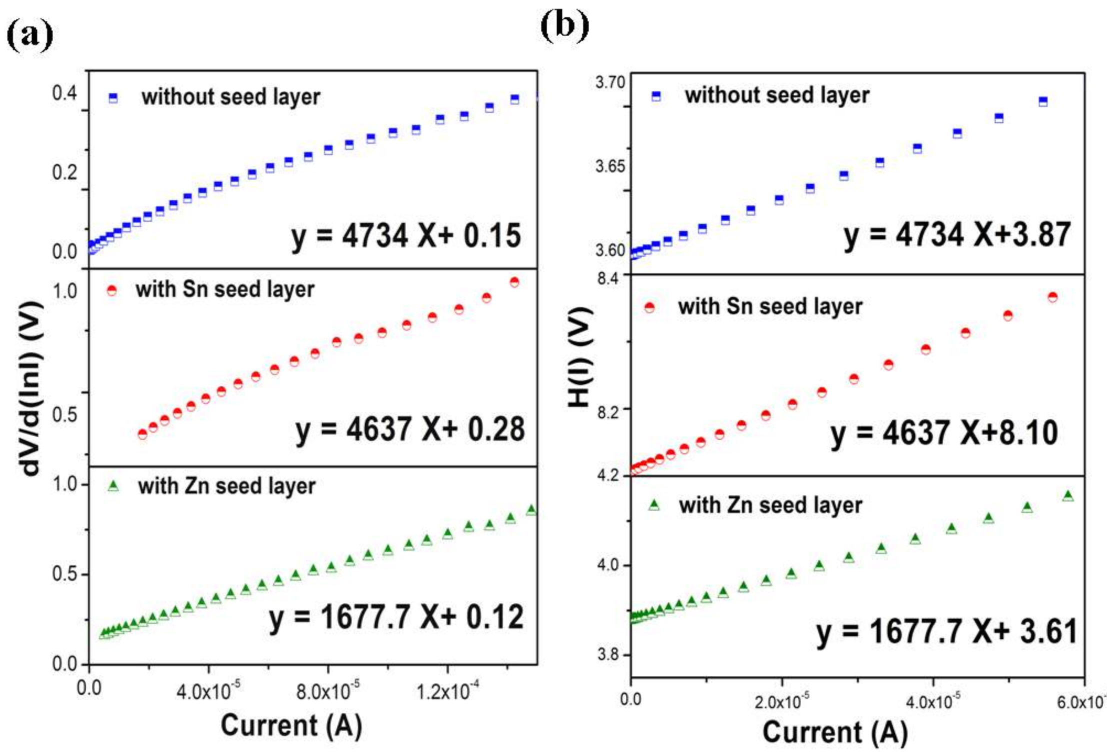

Figure 4.13: Determination of series resistance by Cheung-Cheung method **(a)** dV/d(ln I) versus I plot **(b)** H(I) vs. I Plot

Table. 4.3 Comparison of various electrical parameters of Pd/ZnO Schottky diodes grown on n-Si substrates with Sn and Zn metal seed layers

Pd/ZnO Schottky diode grown on n-Si substrates with	Thermionic emission (I-V)			Cheung – Cheung method			
				dV/d (ln I) vs. I		H(I) vs. I	
	I_F / I_R	$\phi_{B,eff}$	η	R_s	η	R_s	$\phi_{B,eff}$
No seed layer	113	0.67	2.36	4734	5.79	4734	0.67
Sn seed layer	885	0.75	2.67	4637	10.8	4637	0.76
Zn seed layer	7561	0.78	2.10	1678	4.63	1677	0.78

Now, the values of the rectification ratio of the Pd/ZnO Schottky diodes grown on n-Si substrates with ZnO, Sn and Zn seed layers have been compared with diodes grown on bare n-Si substrates by a bar diagram as shown in Fig.4.14.

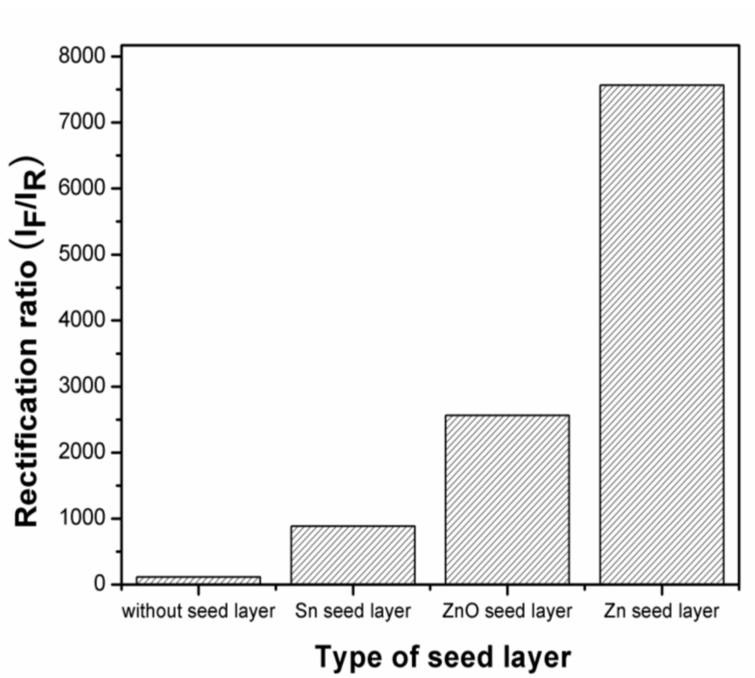

Figure 4.14: Variation of rectification ratio with different types seed layers

4.4 Current Transport Mechanism

Fig. 4.15 shows the ln (V) versus ln (I) plot for studying the carrier transport mechanism in the as-fabricated Pd/ZnO thin films Schottky diodes with Sn, Zn and ZnO seed layers under consideration. The linear I~V relation for V < 0.15 for all the four Pd/ZnO Schottky diodes shows a ohmic behavior of the device commonly attributed to the tunneling of charge carriers between the states at the interfaces [Sze (1981), Hwang *et al*. (2013a)]. The diodes with Sn, ZnO and without any seed layer nearly follow the I ~ exp (V) relation for $V > 1.5\,\text{V}$ possibly due to the recombination tunneling mechanism [Chen *et al*. (2006), Hwang *et al*. (2013a)]. However, the Schottky diodes with a Zn seed layer follows a linear I-V relation for V < 0.15V, an exponential relation I ~ exp (V) for $0.15\,\text{V} < V < 1\,\text{V}$ and a power law relation ($I \sim V^2$) for V >1V possibly due to the space charge limited current transport mechanism due to the trap levels at different energies within the band gap of the ZnO films [Sze (1981), Hussain *et al*. (2012), Hwang *et al*. (2013a)]. The current flow due to space-charge-limited (SCL) emission is well known and the associated current-voltage power law relationship can be observed in many materials, particularly in insulators and semiconductors [Sze (1981)]. Under an applied field, the space-charge effect occurs due to the carrier injection, and the resultant current due to the presence of the space-charge effect is referred to as the SCL current.

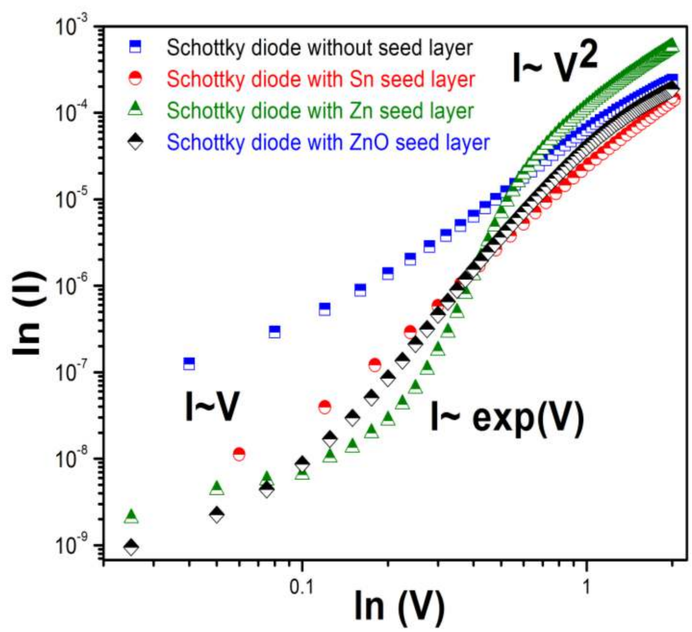

Figure 4.15: Current transport mechanism across all the Pd/ZnO thin film Schottky diodes under consideration

4.5 Summary and Conclusion

Three types of Pd/ZnO thin film Schottky diodes have been fabricated on three different types of seed layer materials namely ZnO seed layer, Sn and Zn metal seed layer deposited on the n-Si substrates prior to the growth of the ZnO films by thermal evaporation method. The effects of ZnO, Sn and Zn metal seed layers on the structural properties of the vacuum deposited ZnO films and the electrical characteristics of Pd/ZnO thin film Schottky diodes (grown on the seed layer) have investigated. Some of the significant observations from this chapter are given as follows:

- The surface morphology of the ZnO thin film is observed to be changed from the nanocrystalline to nanorods, nanocrystalline to nanoparticles, and nanocrystalline to nanowires structure when the substrates used for the ZnO film deposition are changed from the bare n-Si to ZnO seed layer-coated n-Si substrates, bare n-Si to Sn seed layer coated n-Si substrates and bare n-Si to Zn seed layer coated n-Si substrates respectively.
- The XRD spectra of the vacuum deposited ZnO films on the bare n-Si, ZnO seed layer-coated n-Si, Zn seed layer coated n-Si, and Sn seed layer coated n-Si substrates show that the preferred crystal orientation of the vacuum deposited ZnO thin films is the (101) plane in all cases except for the ZnO films grown on the Sn seed layer coated n-Si substrates for which (002) plane is the preferred crystal orientation.
- The rectification ratio of the Pd/ZnO Schottky diode is observed to be changed from a nominal value of 1.13×10^2 at ± 2 V for the device grown on the bare n-Si substrates to a large value of 8.85×10^2 for the device grown on Sn seed layer coated n-Si substrates, to 2.546×10^3 for the device grown on ZnO seed layer coated n-Si substrates and to a value of 7.564×10^3 for the Zn seed layer coated device.
- The value of the barrier height at Pd/ZnO interface is increased from 0.67 eV to 0.75 eV when the surface morphology of ZnO thin film is changed from nanocrystalline (for bare n-Si substrates) to nanoparticles structure (for the Sn seed layer coated n-Si substrates), from 0.67 eV to 0.78 eV when the surface morphology is changed from nanocrystalline (for bare n-Si substrates) to nanowires structure (for Zn coated n-Si substrates) and from 0.67 eV to 0.81 eV

when the film morphology is changed nanocrystalline (for bare n-Si substrates) to nanorods structure (for ZnO coated n-Si substrates).

- A nominal change is observed in value of the series resistance from 4734 Ω to 4651 Ω when the substrates used for ZnO film deposition is changed from the bare n-Si to ZnO seed layer coated n-Si substrates and from 4734 Ω to 4637 Ω the substrate is changed from bare n-Si to Sn seed layer coated n-Si substrates. However, a significant reduction *(*>3k*)* is observed for the Schottky diodes grown on the Zn seed layer coated Si substrates.