Chapter 7

Conclusion and Future Scope

7.1. Introduction

The basic objective of thesis is to present a detailed analysis of the electrical characteristics of some ZnO nanostructures based Schottky and heterojunction devices grown on Si substrates. The present chapter has been devoted to summarize and conclude the major observations presented in the various chapters of this thesis. We have also tried to outline some scope for future works related to the areas considered in the present thesis.

7.2. Chapter-Wise Summary of Major Contributions

Chapter-1 presents some general aspects of ZnO as a semiconductor material. It is observed that the ZnO nanostructures are better than their bulk counterpart due to their improved physical properties such as high surface area to volume ratio and carrier and photon confinement effects. The various synthesis techniques of ZnO thin films on various substrates including the Si have been discussed. It is also discussed that ZnO thin film based devices are very useful for fabricating nanodevices for UV detection, gas and bio sensing, piezoelectronic, and spintronic applications. The working principles of different material and thin film characterization techniques such as the field emission scanning electron microscopy (FESEM), atomic force spectroscopy (AFM), X-ray diffraction (XRD) and Photoluminescence (PL) spectroscopy have been discussed. The general electrical characteristics of ZnO based Schottky contacts and heterojunction diodes using thermionic emission theory have been presented. The barrier inhomogeneity phenomenon at the metal/semiconductor and at any heterojunction interface has been introduced. The estimation techniques of different parameters, such as the reverse saturation current, ideality factor, barrier height and the Richardson constant of the Schottky diodes have also

been outlined. The generalized modelling technique for including the effects of barrier inhomogeneity on the electrical parameters of the Schottky diodes by assuming a Gaussian function for the random barrier height distribution across the metal/semiconductor interface of the Schottky diodes have also been presented. The metal/ZnO based Schottky diodes for UV detection applications have also been discussed in details. Finally, the scopes of present thesis have been outlined at the end of this chapter.

Chapter-2 includes the review of some important state-of-the-art works reported on the electrical characteristics of ZnO thin film based Schottky and heterojunction diodes. A detailed literature survey on the reported current-voltage, capacitance-voltage and temperature-dependent current-voltage (I-V-T) characteristics of ZnO thin film based Schottky diodes as well as heterojunction diodes has been presented. The literature reviews on UV detection characteristics of ZnO thin film based Schottky diodes have also been studied. Some important findings based on which the scopes of the thesis have been outlined in the Chapter-1 may be summarized as follows:

- Among various synthesis techniques, both the thermal evaporation and the sol-gel methods are considered to be cost effective methods for fabricating ZnO nanostructure. However, the thermal evaporation can be considered to be a better technique than the sol-gel due to its better controllability on the thickness of the films grown on a particular substrate than that of the sol-gel method.
- Although a number of works have been reported on the analysis of temperature-dependent electrical characteristics of metal/ZnO based Schottky diodes, however, no significant work on the metal/ZnO thin film based Schottky diodes grown on Si substrates has been reported. Since, the use of Si substrates can provide the flexibility of integration of the ZnO thin film based sensors and detectors with the modern day's CMOS technology, the Schottky diodes on Si substrates can be special interests to the researchers.
- The barrier height and ideality factor of any Schottky diode as well as heterojunction have been reported to be highly sensitive to the operating temperature due to the random distribution of the barrier height across the metal/semiconductor and heterojunction interfaces respectively. The phenomenon is commonly known as the barrier inhomogeneity. However, no significant

investigation of the effects of barrier inhomogeneity on the electrical parameters, such as the barrier height, ideality factor, and Richardson constant of the ZnO thin film based Schottky diodes on Si substrates and n-ZnO/p-Si heterojunctions has been reported in the literature.

- Electrical characteristics of Schottky diodes are influenced by various non–idealties, such as the interface states, formation of interfacial oxide layer and series resistance due to bulk substrate. However, no significant study has been reported on the estimation of the series resistance of Pd/ZnO thin film based Schottky diodes fabricated on Si substrates.
- In literature, various methods such as the Cheung's function, Norde's method, Sato and Yasumura method or modified Norde's approach are reported for determination of the series resistance of any Schottky diode. However, the investigation on the suitability of a particular method for the Pd/ZnO Schottky diodes has not been well explored.
- Richardson constant is a fundamental parameter of any Schottky as well as heterojunction diodes. However no significant work has been reported so far on the estimation of this important parameter for any ZnO thin film based Schottky as well as heterojunction diodes fabricated on the Si substrates.
- Effects of different seed layers on the surface morphology, crystalline structure and optical properties of ZnO thin films are well studied. However, the effects of seed layers on the electrical parameters, such as the rectification ratio, reverse saturation current, barrier height and ideality factor of the ZnO thin film based Schottky and heterojunction diodes have not been well explored.
- ZnO thin film based Schottky photodetectors can be of great interests for the UV detection applications due their large surface-to-volume ratio with the carrier and photon confinements in two dimensions, superior stability owing to high crystallinity and possible surface functionalization with target-specific receptor species. However, only a limited amount of works have been reported so far on the ZnO nanostructures based Schottky UV photodetectors.

The above observations can easily justify the scopes of the thesis defined in Chapter-1.

Chapter-3 presents the detailed analysis of the temperature dependent electrical characteristics of Pd/ZnO thin film Schottky diodes grown on n-Si substrates by thermal evaporation method. The analysis has been carried out with and without considering the barrier inhomogeneity phenomenon. The analysis of the FESEM image and XRD pattern confirms that the ZnO thin films grown on the n-Si substrates are of nanocrystalline nature with hexagonal wurtzite phase of ZnO. The PL spectrum analysis shows a strong near band edge (NBE) emission at wavelength of ~380 nm due to the excitonic transition between the valance band and conduction band. The I-V characteristics of Pd/ZnO thin film Schottky diodes have been analyzed by taking effect of series resistance into account. The value of different electrical parameters such as the barrier height $(\phi_{B,eff})$, ideality factor (η) and series resistance (R_s) are calculated from thermionic emission model, Cheung's function and Norde's methods. The value of R_s (~30.983×10^3 Ω) obtained from the Norde's function is observed to be much higher than 5333 Ω and 4734 Ω estimated by using the conventional thermionic emission model and Cheung's approach respectively. The above large discrepancy in the value of R_s is attributed to the non-suitability of the Norde's model for Schottky diodes with the ideality factor $\eta > 1$. Further, the measured temperature-dependent I-V characteristics of Pd Schottky contacts on ZnO thin films grown on n-Si<100> substrates have been analyzed over a temperature range 300-423 K by considering the effect of the barrier inhomogeneity phenomenon. The values of the zero-bias mean barrier height and effective Richardson constant are calculated as 1.41 eV and $19.54 Acm^{-2}K^{-2}$ respectively under the assumption of a Gaussian function for barrier height distribution at the Pd/ZnO interface. The estimated value of the effective Richardson constant is believed to be the first reported value for the Pd/ZnO thin film Schottky diodes. However, further improvement is required to obtain the Richardson constant closer to its theoretical value of $32 Acm^{-2}K^{-2}$. The integration capability of the proposed device structure with the Si based modern day's CMOS technology is believed to be useful for achieving future generation ZnO thin film based smart and intelligent nano-devices for gas sensing and optoelectronic applications.

Chapter-4 investigates the effects of ZnO, Sn and Zn seed layers on the structural and morphological characteristics of thermally deposited ZnO films on the seed layer coated n-Si substrates as well as on the electrical characteristics of the Pd/ZnO thin film Schottky

diodes fabricated on different seed layer coated n-Si substrates under consideration. The ZnO seed layer was grown by first depositing a thin metallic Zn layer on the n-Si substrate followed by thermal oxidation of metallic Zn layer in the O_2 gas atmosphere at 600 ^{0}C for the duration of 60 minutes. However, the Zn and Sn metal seed layers are deposited directly on the n-Si substrates by thermal evaporation method. Finally, three types of Pd/ZnO thin film/(ZnO, Zn or Sn) seed layer/n-Si Schottky diodes have been fabricated using three different types of seed layer discussed above. The analysis of the FESEM images has been used to confirm that the surface morphology of the ZnO thin films grown directly on the n-Si substrates has the nanocrystalline structure while the surface morphology of the ZnO films grown on the ZnO seed layer is observed to be of nanorods structure. The respective values of the rectification ratio (I_F / I_R), $\phi_{B,eff}$ and η of the Pd/ZnO thin film Schottky diodes have been observed to be improved from 113 to 2456, from 0.67eV to 0.81 eV and from 2.36 to 1.46 when the substrate used for the ZnO film synthesis is changed from the bare n-Si to the ZnO seed layer coated n-Si substrate. Similarly, the effects of Sn and Zn seed layers on the electrical characteristics of Pd/ZnO thin film/(Sn or Zn) seed layer/n-Si Schottky diodes have also been studied in this chapter. The surface morphologies of the ZnO thin films are observed to be changed from the nanocrystalline to nanoparticles, and from nanocrystalline to nanowires structures when the substrates for the ZnO film deposition are changed from the bare n-Si to Sn seed layer-coated n-Si and from bare n-Si to Zn seed layer-coated n-Si substrates respectively. A dramatic enhancement in the I_F / I_R of Pd/ZnO Schottky diodes is observed 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 the Sn seed layer coated n-Si substrates and to a value of 7.561×10^3 for the Zn seed layer coated device. The respective values of the $\phi_{B,eff}$ at the Pd/ZnO interface are 0.78 eV and 0.81 eV for the diodes using Zn and Sn coated n-Si substrates for ZnO deposition whereas the same is 0.67eV for the Schottky diodes using the ZnO films directly deposited on the bare n-Si substrates.

Chapter-5 In this chapter, Pd/ZnO NPs based Schottky photodiodes have been fabricated on the Sn-seed layer coated n-Si (100) substrates by using the low-cost thermal evaporation method. The Pd/ZnO NPs Schottky contacts exhibit good diode characteristics with I_F / I_R of ~1309 at ± 3 V, $\phi_{B,eff}$ ~0.75 eV and η ~2.67. When the Schottky diode is

illuminated by a UV radiation of 650 μW power at 365 nm wavelength, the diodes have exhibited an excellent contrast ratio of ~ 541 with a quantum efficiency of ~68% at room temperature. The values of responsivity, detectivity and zero bias resistance-area product of Pd/ZnO NPs Schottky diodes are determined as 0.20A/W, 6.53×10^{9} $mHz^{1/2}W^{-1}$ and17.66 $\Omega.m^{2}$ respectively. The large surface area of the ZnO NPs is believed to promote oxygen adsorption and desorption at the NPs surfaces thereby enhancing the UV detection properties of the vacuum deposited ZnO NPs on the Sn seed layer. Based on the comparison of various performance related parameters of the proposed photodiodes and other UV detector structures, the proposed Pd/ZnO NPs based Schottky photodiodes are believed to be extremely suitable for the UV detection applications.

Chapter-6 presents a detailed analysis of the temperature-dependent electrical characteristics of n-ZnO NWs/p-Si heterojunction diodes by taking the barrier inhomogeneity phenomenon into consideration. The ZnO NWs have been synthesised on AZO coated p-Si substrates by thermal oxidation of vacuum deposited Zn in O_2 gas atmosphere at 600 ºC for the duration of 60 minutes. The ZnO NWs are found to be highly crystalline in nature with a hexagonal wurtzite structure confirmed by the XRD measurement. The PL spectrum of the as-grown ZnO NWs exhibits a peak near band edge (NBE) emission at wavelength of 397 nm. The electrical characteristics of the n-ZnO NWs/p-Si heterojunction diodes have been investigated in terms of room temperature C-V and temperature dependent I-V characteristics over the temperature range of 300-423 K. The $\phi_{B,eff}$ estimated from the C-V measurement is found to be 0.75 eV which is very close to its theoretical value of 0.72 eV. The temperature dependent measured I-V characteristics have been analyzed to express $\phi_{B,eff}$ and η as functions of temperature as well as bias voltage by considering the barrier inhomogeneity across the n-ZnO/p-Si heterojunctions as a Gaussian distributed function with a zero-bias standard deviation σ_0 around a mean barrier height $\phi_{B0,m}$ at $T = 0°K$. The value of $\phi_{B,eff}$ is estimated to be 0.715 eV at room temperature which is very close to its theoretical value of 0.72 eV. The estimated value of the Richardson constant is observed to be improved from an unrealistic value of $\sim 9.75\times10^{-8}\,Acm^{-2}K^{-2}$ to a more realistic value of $\sim 49\,Acm^{-2}K^{-2}$ after taking barrier inhomogeneity phenomenon into consideration. The value of the interface state density is observed to be decreased from 3.18×10^{13} eV^{-1} cm^{-2} to 4.59×10^{11} eV^{-1} cm^{-2} with

an increase in $E_c - E_{ss}$ from 0.10 eV to 0.63 eV below the conduction band edges at interface of n-ZnO NWs/p-Si heterojunction diodes. This trend clearly shows that the density of interface states near the middle of the band gap of ZnO semiconductor is nearly negligible as compared that near the bottom of the conduction band.

7.3. Future Scope of the Work

This thesis presents some investigations on the electrical characteristics of some ZnO thin film based Schottky contacts and heterojunction diodes for optoelectronic applications. Since, no research work is complete in all aspects; there are also some limitations in the work presented here. Based on the constraints and limitation of the works carried out in this thesis, we will discuss some future scopes of works as given below:

- The deep level defects analysis of metal/ZnO Schottky junction can be carried out by using temperature-dependent charge transport, deep level transient spectroscopy (DLTS), Kelvin probe force microscopy (KPFM) and depth resolved cathodoluminescence spectroscopy (DRCLS) techniques.
- Capacitance vs. voltage analysis at various high and low frequancies can be done for further analysis of interface states at Schottky as well as heterojunction diodes.
- The nano-composites of ZnO with different polymers can be explored for ZnO based UV photodetectors.
- Fabrication and characterization of ZnO nanostructures based Schottky ultraviolet photodiodes on flexible polymer substrates can be studied.