Chapter 2

ZnO Based Schottky and Heterojunction Devices: A General Review

2.1. Introduction

The literature review is an integral part of a thesis. After introducing the importance of ZnO thin films and their devices in the form of Schottky [Schottky (1938), Sze (1981), Rhoderick and Williams (1988)] and heterojunction diodes [Anderson (1962), Choi *et al*. (2010),Chirakkara and Krupanidhi (2012)] for electronic and optoelectronic applications [Liang *et al*. (2001), Wang (2004), Lu *et al*. (2006), Jagadish and Pearton (2006), Zhai *et al*. (2009)] and the barrier height inhomogeneity (BHI) at metal/ZnO interfaces [Werner and Güttler (1991), Tung (1992), Schmitsdorf *et al*. (1997)] in Chapter-1, we will now present the review of some key state-of-the-art works in the present chapter in order to justify the scopes of the present thesis outlined in the last section of Chapter-1. The literature survey carried out in this chapter mainly deals with some important findings reported in the literature related to the electrical characteristics of ZnO based Schottky and heterojunction diodes with or without using a seed layer. Some state-of-the-art works on the effects of barrier height inhomogeneity (BHI) [Werner and Güttler (1991), Schmitsdorf *et al*. (1997)] and seed layer on the electrical and UV detection characteristics of ZnO based Schottky diodes have also been discussed. The layout of the present chapter is summarizes as follows.

Section 2.2 deals with a brief review of some important results on the electrical characteristics of ZnO based Schottky diodes. Some important literatures on the Schottky barrier inhomogeneity at metal/ZnO interface have been reviewed in Section 2.3. While the Section 2.4 mainly includes the review of some key results related to the effects of different seed layers on the device characteristics of ZnO thin film based Schottky diodes, Sec. 2.5 presents a brief review on the UV detection characteristics of the ZnO based Schottky diodes. Section 2.6 describes some important results on the electrical characteristics of ZnO based heterojunction diodes. Finally, Sec. 2.7 includes the summary and concluding remarks of the present chapter.

2.2. Electrical Characteristics of ZnO Based Schottky Contacts

In 1874, Braun [Braun (1874)] first reported the rectifying properties of metal-semiconductor contacts. He [Braun (1874)] first observed that the total resistance of a rectifying metal-semiconductor system is dependent on the polarity of the applied voltage and on the detailed surface conditions [Braun (1874), Sze (1981)]. The application of metal-semiconductor based point-contact rectifiers in different forms was started with the remarkable invention of J.C. Bose in 1904 [Schottky (1938), Sze (1981)]. In 1929, Schottky and Deutschmann [Schottky and Deutschmann (1929)] confirmed the existence of a barrier layer at the metal-semiconductor junction from measurements of the differential capacitance as a function of applied voltage [Sze (1981), Mönch (1990)]. Finally, in 1938, Schottky [Schottky (1938)] and Mott [Mott (1938)] explained the rectifying properties of the metal-semiconductor contacts in terms of a space charge region on the semiconductor side of the contact due to the depletion of majority charge carriers. The band bending in this space-charge region was characterized in terms of a barrier height, which was defined as the energy distance between the Fermi level and the edge of the respective majority-carrier band right at the interface. Because of this breakthrough research, the rectifying metal-semiconductor junctions are also named ***Schottky contacts*** or Schottky diodes and the energy barrier at the metal-semiconductor interface is also called ***Schottky Barrier*** in the honour of W. Schottky [Schottky (1938)]. In 1947, Bardeen [Bardeen (1947)] also proposed a theory for explaining the rectification characteristics of the metal-semiconductor contacts in term of llocalized states (Tamm levels) at the semiconductor interface with energies between the filled band and the conduction band distributed in the "forbidden" region.

The ZnO material started to become interesting to the electronic industry after its introduction as a compound semiconductor in 1940s [Bunn (1935), Brown (1957), Klingshirn (2007), Lee (2008), Janotti and Walle (2009), Biswas (2010)]. The first metal Schottky contacts on ZnO semiconductor were discovered by Mead and his co-workers during 1965-1970s [Mead (1965), Mead (1966), Neville and Mead (1970)]. Since then, a significant amount of works have been reported on ZnO based Schottky diodes.

In recent years, Schottky diodes based on ZnO thin films have been the subject of many investigations due to their possible applications in ultraviolet photodetectors [Zhai *et al*. (2009), Liu *et al*. (2010)], gas sensors [Kyoung and Jang (2010)], piezoelectric nanogenerators [Wang and Song (2006)], thin film transistors [Nomura *et al*. (2003), Fan and Lu (2006)] and solar cells [Chopra *et al*. (2004)] etc. In general, Schottky diodes with a large barrier height and small leakage current at the metal–semiconductor junction are desirable for practical applications. Thus, large work function based metals such as Pt (5.65) [Sze (1981), Brillson and Lu (2011)], Pd (5.12) [Sze (1981), Wenckstern *et al.* (2006)], Au (5.1) [Sze (1981), Lajn *et al*. (2009)] and Ag [Gür *et al*. (2007), Lajn *et al*. (2009)] are normally used for the Schottky contacts on ZnO thin films.

The electrical characteristics of ZnO based Schottky diodes are often influenced by various non-idealities such as the interface states and interfacial oxide layer, interface fixed charges and series resistance [Brillson and Lu (2011)]. The series resistance (R_s) is one of the important parameter, which causes the electrical characteristics of Schottky diodes to be non-ideal [Norde (1979), Sato and Yasumura (1985), Cheung and Cheung (1986)]. To determine the value of series resistance of ideal Schottky diodes (i.e. η=1), Norde [Norde (1979)] proposed a method by introducing a voltage function, called Norde's function. After that, Sato and Yasumura [Sato and Yasumura (1985)] modified the Norde's approach for Schottky diodes with $1 < \eta < 2$, and used two experimental I-V data measured at two different temperatures to extract the values of barrier height, ideality factor, and series resistance from the forward bias measured I-V characteristics of a particular Schottky diode. Later on, Cheung and Cheung [Cheung and Cheung (1986)] reported the estimation of barrier height, ideality factor and series resistance of the Schottky diodes by using a single forward current density-voltage (J-V) measurement of Schottky diode.

A number of works have been reported on the estimation of the electrical parameters of the ZnO based Schottky contacts using different metals and deposition techniques. The review of some important literatures related to electrical characteristics of ZnO based Schottky diodes are discussed below:

Sheng *et al***.** [Sheng *et al*. (2002)] fabricated the Silver Schottky contacts on *n*-ZnO epilayers grown on *R*-plane sapphire substrates by MOCVD method. They [Sheng *et al.*

(2002)] estimated the respective flat band barrier height as ~0.89eV and 0.92 eV from the I-V and C-V measurements, and the ideality factor of 1.33 from the I-V measurements.

Allen *et al***.** [Allen *et al*. (2007)] developed a method for fabricating silver oxide based highly rectifying contacts on *n*-type ZnO using hydrothermal and melt grown ZnO materials. They [Allen *et al*. (2007)] observed that the silver oxide based diodes on hydrothermal ZnO possessed lower ideality factor, lower reverse current, higher series resistance, and larger surface-polarity related differences in barrier height than those of the diodes grown on melt ZnO.

Nakano *et al*. [Nakano *et al*. (2007)] fabricated the conducting polymer based Schottky contacts on a single crystal ZnO (0001) by depositing a layer of conducting polymer, poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) on the ZnO by the spin-coating method. They [Nakano *et al*. (2007)] observed an excellent rectifying behavior with a typical ideality factor of 1.2 in their reported devices.

Young *et al*. [Young *et al*. (2008)] fabricated and characterized the Schottky diodes by growing iridium (Ir) contact electrodes on ZnO thin films. They [Young *et al*. (2008)] determined the Schottky barrier height at Ir/ZnO interface as 0.824 ± 0.04%, 0.837 ± 0.04% and 0.924 ± 0.04% eV by using the thermionic emission model, the Norde model [Norde (1979)] and the conventional capacitance–voltage measurement [Sze (1981)] respectively.

Allen and Durbin [Allen and Durbin (2008)] fabricated the Ni, Ir, Pd, Pt, and silver oxide Schottky contacts on the Zn-polar face of hydrothermally grown bulk ZnO. They [Allen and Durbin (2008)] studied the relationship between the barrier height of the Schottky contact and the free energy of formation of its "metal" oxide. The dominating influence of oxygen vacancies (V_O) could pin the ZnO Fermi level close to the V_O (+2, 0) defect level at approximately 0.7 eV below the conduction band minimum.

Li *et al*. [Li *et al*. (2008)] studied the effects of crystallinity and native defects of ZnO films on the performance of large area Pt/Ti/ZnO/Pt/SiO2/Si Schottky diodes of an inverted vertical MSM type structure. They [Li *et al*. (2008)] reported a barrier height of 0.88 eV and a reverse leakage current of 4.25×10^{-8} Acm^{-2} at −2V bias voltage for their Schottky devices.

Ali *et al*. [Ali *et al*. (2010)] investigated the interface properties and junction behavior of Pd Schottky contacts on ZnO thin films deposited by vacuum evaporation method on p-Si substrates. The value of the electrical parameters, such as the ideality factor, leakage current, resistance-area-product, carrier concentration and barrier height were extracted from their I-V measurements.

Klason *et al*. [Klason *et al*. (2008)] investigated the electrical characteristics and stability of Pd and Au Schottky contacts on ZnO nanorods grown on glass substrate. The nanorods were grown using the aqueous chemical growth method. They [Klason *et al*. (2008)] reported the best possible values of the ideality factor and barrier height of their as-deposited Pd/ZnO contacts as 1.74± 0.43 and 0.67 ± 0.09 eV respectively.

Periasamy and Chakrabarti [Periasamy and Chakrabarti (2009)] reported the fabrication and characterization of Al and Pt metal contacts on ZnO thin films grown on ITO coated glass substrates using thermal evaporation technique. While the Pt contact on the vacuum deposited ZnO thin films showed a rectifying nature with a barrier height of 0.72 eV by scanning tunnelling microscopy (STM), the Al contact on the ZnO films showed the ohmic characteristics.

Mtangi *et al***.** [Mtangi *et al*. (2011)] fabricated the Pd/ZnO Schottky contacts using electron beam evaporation and resistive/thermal evaporation techniques. They [Mtangi *et al*. (2011)] studied and compare the electrical properties of the Pd/ZnO Schottky diodes using I-V and conventional deep level transient spectroscopy (DLTS) measurements.

It is well known that the substrates on which the ZnO thin films are grown play significant roles in determining the structural, morphological, electrical and optical characteristics of the films. In general, the substrates should be lattice matched with the material to be grown on it. Unfortunately, no suitable substrate is available which is closely lattice matched with ZnO. Despite the above fact, researchers have explored, sapphire [Sheng *et al*. (2002)], ITO [Periasamy and Chakrabarti (2009)], glass [Klason *et al*. (2008)], p-Si [Ali *et al.* (2010)], SiO_2/Si [Li *et al*. (2008)] etc. as substrates for fabricating ZnO thin film based Schottky devices. As discussed in Chapter-1 that Si substrates are of great interests for ZnO based devices for their additional flexibility of integration with the modern day's Si-based CMOS technology for achieving the future generation ZnO thin film based smart systems. However, since ZnO is naturally an n-type material, an n-Si substrate can be preferred over the p-Si to minimize the p-Si/n-ZnO heterojunction related effects on the performance of ZnO based Schottky devices. In this direction, Aydoğan *et al*. [Aydoğan *et al.* (2009)] measured the room temperature I-V and the capacitance–

voltage/frequency (C/V-F) characteristics of the Au/n-ZnO Schottky contacts on n-Si substrates. They [Aydoğan *et al.* (2009)] estimated various characteristic parameters, such as barrier height, ideality factor and series resistance of the Schottky diodes from the I-V measurements. They [Aydoğan *et al.* (2009)] also used the Cheung functions [Cheung and Cheung (1986)] and Norde method [Norde (1979)] to extract the electrical parameters of the device. Tsiarapas *et al.* [Tsiarapas *et al.* (2014)] investigated the electrical characteristics of Pd Schottky contacts on ZnO films by I-V and C-V measurements at different temperatures. ZnO films of two different thicknesses of 400 nm and 1000 nm were grown by DC-magnetron sputtering on the n-Si substrates. They [Tsiarapas *et al.* (2014)] compared the electrical parameters of the two devices and obtained better results for the 1000 nm-ZnO Schottky diodes than those of the 400 nm devices.

A number of experimental investigations show that the interface behavior of the metal-ZnO contact largely depends on the method of surface treatments, such as oxygen plasma treatments [Coppa *et al.* (2003), Mosbacker *et al.* (2007), Angadi *et al.* (2007)], UV–ozone treatment [Ip *et al.* (2004)], and H_2O_2 treatment [Kim *et al.* (2005), Gu *et al.* (2007), Schifano *et al.* (2007), Schifano *et al.* (2009), Lee *et al.* (2010)] usually performed on the ZnO surface prior to making a junction. In few reports, researchers [Krajewski *et al.* (2011), Lee *et al.* (2012)] used an interlayer of a different material between ZnO and Schottky metal to improve the performance of diodes. Here we discuss some of the important observations reported in the literature in the following.

Coppa *et al.* [Coppa *et al.* (2003)] fabricated 100-mm-diameter gold Schottky contacts on as-received, *n*-type ZnO wafers and those exposed for 30 min to a remote 20% O_2/80% of He plasma at 525±20 °C and cooled either in vacuum from 425 °C or the unignited plasma gas and reverse bias I-V have been determined. Plasma cleaning resulted in highly ordered, stoichiometric, and smooth surfaces.

Ip *et al.* [Ip *et al.* (2004)] investigated the effect of UV ozone cleaning of the ZnO surface on the characteristics of Pt contacts on n-type bulk single-crystal ZnO. The contacts were observed to be ohmic for samples not exposed to ozone prior to the Pt deposition, whereas an excellent rectifying behavior was observed for the Pt contacts grown on the ozone cleaned ZnO surface. The barrier height of the ozone treated Pt/ZnO Schottky contacts were estimated from the I-V measurements as 0:70 ±0:04 eV at 25 °C with an ideality factor of 1.49 and a saturation current density of 6.17×10^{-6} A cm^{-2}.

Kim *et al*. [Kim *et al*. (2005)] reported the formation of good Pt Schottky contacts on the Zn-terminated *n*-type ZnO (0001) surfaces (2×10^{17} cm^{-3}) using H_2O_2 solution based surface treatment method. The Pt contacts on organic solvent-cleaned ZnO (0001) showed leaky behavior with a high leakage current of −0.05 A under −5 V reverse bias voltage, whereas the H_2O_2-treated contacts showed the rectifying behavior with a very low leakage current of -6.5×10^{-8} A under −5 V reverse bias voltage.

Schifano *et al*. [Schifano *et al*. (2007)] investigated the formation of Pd Schottky barrier contacts on the H_2O_2 treated ZnO. They [Schifano *et al*. (2007)] observed the ohmic nature of the Pd contacts grown on the organic solvent cleaned O face $\left(000\bar{1}\right)$ ZnO surface and the rectifying characteristics of the Pd contacts grown on the H_2O_2 treated O face ZnO. They [Schifano *et al*. (2007)] reported a ninth order of magnitude in the rectification ratio of the current for H_2O_2 treated O face ZnO measured in bias voltages between -2 and +2 V.

Gu *et al*. [Gu *et al*. (2007)] systematically studied the conversion of the Au/*n*-ZnO contact from ohmic to rectifying with H_2O_2 pretreatment using I-V measurements, X-ray photoemission spectroscopy, positron annihilation spectroscopy, and deep level transient spectroscopy. H_2O_2 treatment did not affect the carbon surface contamination or the $E_C - 0.31\text{eV}$ deep level, but it resulted in a significant decrease of the surface OH contamination and the formation of vacancy-type defects close to the surface.

Angadi *et al*. [Angadi *et al*. (2007)] studied the effects of oxygen plasma treatment of the surface of ZnO thin films grown by molecular beam epitaxy (MBE) on the characteristics of the Au–ZnO–In junctions. They [Angadi *et al*. (2007)] observed that the ohmic characteristics of the Au–ZnO–In junctions prior to the oxygen plasma treatment gradually changed to the rectifying characteristics with the increase in oxygen plasma treatment time. However, no significant changes were observed in the crystallinity and surface microstructure after the plasma treatment

Mosbacker *et al.* [Mosbacker *et al.* (2007)] fabricated metal contacts of Au, Al, Ni, Pt, Pd, Mo, Ta, and Ir on the single crystal remote oxygen (20%O_2/80% He) plasma-treated ZnO $\left(000\bar{1}\right)$ surfaces purchased from different vendors and measured their Schottky barriers, ideality factors, and reverse currents. Using low-temperature nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS) under the metals, they [Mosbacker *et al*. (2007)] identified the presence of defect transitions at 2.1 eV, 2.5 eV, and 3.0 eV which were observed to be dependent on the process steps and choice of metals.

Lee *et al*. [Lee *et al*. (2010)] fabricated the Au/ZnO Schottky contacts using H_2O_2-treated unintentionally doped ZnO epilayers. They [Lee *et al*. (2010)] observed an abnormal behavior (i.e. the background carrier density-dependent trade-off relation between the barrier height and the ideality factor) in their transport properties attributed to the different background carrier concentrations of different ZnO epilayers used for the device fabrication.

Krajewski *et al*. [Krajewski *et al*. (2011)] fabricated ZnO/Ag Schottky junctions by the low temperature atomic layer deposition process. By introducing a thin layer (of 1.25 to 7.5 nm) of hafnium dioxide (HfO_2) between the ZnO and Ag Schottky metal, they [Krajewski *et al*. (2011)] observed an improvement in the rectification ratio from $\sim 10^2$ (for ZnO/Ag Schottky junctions without any HfO_2 layer) to $\sim 10^5$ at 2V. They [Krajewski *et al*. (2011)] attributed this effect to the passivation of ZnO surface accumulation layer reported for the ZnO thin films.

Lee *et al*. [Lee *et al*. (2012)] successfully fabricated the lateral Schottky diodes with a thin MgZnO layer inserted between the ZnO and Schottky contact metal layers using Ti/Au for ohmic contacts on the Mg0:3Zn0:7O thin film layer, and Ag, Au, and Pd for the Schottky contacts on the ZnO films. The Ag based Schottky diodes showed a rectification ratio of as high as $\sim 10^3$ at a bias voltage of ±1 V, an ideality factor of 2.37 and a work function of 0.73 eV.

After reviewing some important literatures related to the effects of an interlayer between metal and ZnO as well as surface treatment methods on the electrical characteristics of metal-ZnO contacts, we will now review some important reported works related to the investigation of the effects of barrier height inhomogeneity on the performance of the metal-ZnO Schottky diodes in the following section.

2.3. Effects of Barrier Height Inhomogenities (BHI) on the Electrical Characteristics of Metal/ZnO Schottky Junctions

Analysis of the room-temperature electrical characteristics of the metal/semiconductor Schottky barrier diodes (SBDs) does not provide us the complete information about the current-conduction process and the nature of the barrier formed at the metal/ semiconductor interface. A number of different studies [Lajn *et al*. (2009), Mtangi *et al.* (2009), Schmitsdorf *et al*. (1997), Sarpatwari (2009), Sarpatwari *et al.* (2011)] suggests that the measurements of I-V characteristics over a wide temperature range are essentially required to understand the different aspects of barrier height and current-conduction mechanisms at the Schottky junction interface. It is observed that barrier height and ideality factor of any Schottky diode are the functions of the operating temperature of the diodes [Werner and Güttler (1991), Chand and Kumar (1997), Mtangi *et al.* (2009), Lajn *et al*. (2009)]. While the barrier height of Schottky diodes is observed to be increased with the temperature, the ideality factor is reported to be decreased with increase in the temperature [Werner and Güttler (1991), Chand and Kumar (1997), Mtangi *et al.* (2009)] due to the barrier height inhomogeneity (BHI) phenomenon discussed in Chapter-1. According to the BHI phenomenon [Werner and Güttler (1991)] instead of having a constant barrier height at the metal-semiconductor junction, the barrier height is randomly distributed over the cross sectional area of the metal-semiconductor interface. As a result, the current of the Schottky diodes at lower temperatures is assumed to be contributed by the electrons surmounting the patches of lower Schottky barrier heights due to their smaller kinetic energy [Dökme *et al*. (2006), Yildiz *et al*. (2008)]. As the operating temperature of the device is raised, the electrons gain larger kinetic energy to surmount higher barrier heights thereby contributing currents in the device. This results in the higher values of the measured barrier heights and lower values of the ideality factor of a Schottky diode at higher temperatures.

It is discussed in Chapter-1 that the Richardson constant, an important parameter for modelling the I-V characteristics of any Schottky diode using thermionic emission model [Crowell (1965), Sze (1981), Tung (1992)], can only be estimated by measuring the I-V characteristics over a range of temperatures [Lajn *et al*. (2009), Mtangi *et al.* (2009), Sarpatwari *et al*. (2009), Sarpatwari *et al.* (2011)]. The estimation of the zero-bias mean barrier height described in Chapter-1 can be used to describe the thermionic model based I-V characteristics of the Schottky junction diodes. Thus, values of these parameters estimated from the measured I-V characteristics over a certain temperature range are important parameters for characterizing the Schottky diodes in general and metal/ZnO Schottky diodes in particular. A number of experimental investigations show that the values of the barrier height and Richardson constant estimated from the temperature-dependent analysis of the measured I-V characteristics of the metal/ZnO Schottky contacts differ significantly from their respective theoretically predicted values [Wenckstern *et al.* (2006), Allen *et al.* (2009), Lajn *et al.* (2009)]. The discrepancies between the experimentally estimated values and theoretically predicated values of the barrier height and Richardson constant can be optimized by taking the phenomenon of barrier height inhomogeneities into consideration. However, the barrier height inhomogeneities at the metal/semiconductor Schottky interface can be addressed by using two different approaches:

- The first one is based on the model proposed by **Werner and Güttler** [Werner and Güttler (1991)] who described the spatial barrier inhomogeneities as a random variable with some assigned probability distribution function such as the Gaussian [Werner and Güttler (1991), Chand and Kumar (1997), Allen *et al.* (2009), Lajn *et al.* (2009), or log-normal [Horvath (1992)] type. However, the Gaussian distribution function is the most widely accepted distribution nature of the barrier height used by many researchers to explain the difference in barrier heights observed from C-V and I-V measurements [Wenckstern *et al.* (2006), Gür *et al.* (2007), Lajn *et al.* (2009)].

- The second method is proposed by **Tung** [Tung (1992)] in 1992 which is based on the assumption of the presence of a locally non-uniform regions or patches with relatively lower or higher barriers with respect to an average barrier height. The interaction of the high barrier and the low barrier is described with the help of the so-called ‘saddle point’. These patches are taken to be small relative to the size of the depletion region so that the interaction of the patch with the surrounding depletion region causes a pinch-off or saddle point in the potential barrier away from the interface. This model is well known as the *Tung’s model* and is also used by the researchers for modeling the barrier inhomogeneity in the Schottky diodes [Tung (1992), Sullivan *et al.* (1991), Schmitsdorf *et al.* (1997), Sarpatwari *et al.* (2009), Sarpatwari *et al.* (2011)].

As mentioned earlier that barrier inhomogeneitiy phenomenon exists in all types of Schottky junction irrespective of the metals and semiconductors used for it. However, due to the increased importance of the metal/ZnO Schottky contacts for electronic, gas sensing and optoelectronic applications, the study of the effects of barrier inhomogeneity on the electrical characteristics of metal/ZnO Schottky contacts (using the Gaussian distribution function for the barrier height at metal/ZnO interface to determine the value of mean barrier height and Richardson constant) has been a subject of interests for many researchers during last more than a decade [Wenckstern *et al.* (2006), Allen *et al.* (2009), Lajn *et al.* (2009), Sarpatwari *et al.* (2009), Sarpatwari *et al.* (2011]. Reviews of some important literatures in this regard are discussed in the following:

Mönch [Mönch (1999)] explained for moderately doped semiconductors, current transport across Schottky contacts occurs by the thermionic emission model. They [Mönch (1999)] observed differences in effective barrier height and ideality factor from one diode to another due to the lateral barrier height inhomogeneities. They [Mönch, (1999)] then compared with the theoretical predictions for ideal Schottky contacts. Data of Si, GaN, GaAs, and CdTe Schottky contacts reveal that the continuum of metal-induced gap states is the fundamental mechanism that determines the barrier heights.

Chand and Kumar [Chand and Kumar (1997)] reported a numerical simulation based study for the investigation of the I-V characteristics of a Schottky diode using the thermionic emission-diffusion transport mechanism and assuming the Gaussian distribution function for the spatial barrier height with linear bias dependence relations for both the mean and standard deviation. The metal-semiconductor system in their study was observed to behave like a single Schottky diode of apparently a low zero-bias barrier height and a high ideality factor.

Wenckstern *et al.* [Wenckstern *et al.* (2006)] investigated the temperature dependence of the barrier height of high-quality Pd Schottky contacts on (0001)-oriented ZnO thin films by temperature dependent I-V and C-V measurements over the temperature range of 210 to 300K. The effective Schottky barrier height was estimated from the I-V measurements by considering the Gaussian barrier height distribution with a standard deviation around a mean barrier height. They [Wenckstern *et al.* (2006)] reported the mean barrier height as (1.16±0.04) eV which agreed well with the value of 1.14 eV determined from their C-V measurements.

In order to understand the temperature-dependent characteristics of the of Ag/n-ZnO Schottky contacts, Gür *et al*. [Gür *et al*. (2007)] carried out the I-V measurements over 200–500 K temperature range. They [Gür *et al*. (2007)] reported a Schottky barrier height of 0.82 eV and an ideality factor of 1.55 at room temperature. They [Gür *et al*. (2007)] also estimated the barrier height of 0.74 eV and Richardson constant of 0.248 A K^{-2} cm^{-2} from the Richardson plot showing a nearly linear characteristic without using BHI concept at Ag/n-ZnO Schottky contacts.

Lajn *et al*. [Lajn *et al*. (2009)] fabricated highly rectifying Ag, Au, Pd, and Pt Schottky contacts on heteroepitaxial ZnO-thin films grown by heteroepitaxial pulsed- laser deposition method. They [Lajn *et al*. (2009)] estimated the ideality factor and the effective barrier height from the I-V measurements over the temperature range of 20 to 310K of all the diodes. They [Lajn *et al*. (2009)] also used C-V and temperature-dependent I-V measurements for determining the bias dependent mean barrier height and the standard deviation of the devices by taking the lateral fluctuations of the barrier height into consideration.

Mtangi *et al*. [Mtangi *et al.* (2009)] performed the temperature-dependent I-V measurements on Pd/ZnO Schottky barrier diodes in the range of 20–300K. From the temperature-dependent forward bias I-V characteristics, the apparent Richardson constant was found to be 8.60×10^{-9} A $K^{-2}cm^{-2}$ in the 60–160 K temperature range, and mean barrier height of 0.50 eV in the 180–300K temperature range. After barrier height inhomogeneities correction, the Richardson constant and the mean barrier height were obtained as 167 A K^{-2} cm^{-2} and 0.61eV in the temperature range 80–180K, respectively.

Allen *et al*. [Allen *et al*. (2009)] studied the temperature-dependent I-V characteristics of ZnO Schottky diodes over the temperature range of 40–423 K. They observed a nearly ideal value of the ideality factor of ~1.09 at 300 K. They [Allen *et al*. (2009)] fabricated the planar geometry devices on the Zn-polar face of hydrothermally grown bulk ZnO single crystal wafer with a low electron concentration of $n = 1 \times 10^{14}$ cm^{-3}. They [Allen *et al*. (2009)] observed that the current transport could be dominated by the thermionic emission for the temperatures between 293 and 423 K when the ZnO surface was exposed to air. They estimated an experimental Richardson constant of 10 ± 6 Acm^{-2} K^{-2}.

Sarpatwari *et al*. [Sarpatwari *et al*. (2009)] proposed a method to include the effects of Schottky barrier height inhomogeneities on the Richardson constant extracted from the I-V-T measurements using Tung approach [Tung (1992)].As a case study, they [Sarpatwari *et al*. (2009)] applied their method to the temperature-dependent I-V measurements performed on the $IrOx/n$-ZnO Schottky diodes. They [Sarpatwari *et al*. (2009)] reported a homogeneous Richardson constant value of 27±7 $Acm^{-2}K^{-2}$ which was in close agreement with the theoretically expected value of 32 $Acm^{-2}K^{-2}$ for *n*-type ZnO.

Temperature-dependent electrical properties of Ag Schottky contacts on *a*-plane bulk ZnO single crystal in the temperature range of 100–300 K were investigated by Kim *et al.* [Kim *et al.* (2010)]. They divided the entire temperature region of 100–300 K into two sub-regions of 200–300K and 100–180K and used two different Gaussian distribution functions for the above two temperature regions to describe the lateral barrier inhomogeneity of the diodes. They [Kim *et al.* (2010)] reported the Richardson constant value of 29 A $cm^{-2}K^{-2}$ estimated from the modified Richardson plot in the temperature range of 200–300.

Das *et al.* [Das *et al.* (2010a)] analyzed the temperature-dependent I-V and X-ray photoelectron spectroscopy (XPS) measurements of the Au/ZnO single nanowire based Schottky diodes. The calculated barrier height of the Schottky diodes by using the thermionic emission model was observed to be in good agreement with the value obtained from the XPS measurements but lower than the theoretically predicted value.

Yıldırım *et al.* [Yıldırım *et al.* (2011)] employed the Successive Ionic Layer Adsorption and Reaction (SILAR) method for the first time in the literature to prepare the Zn/ZnO/n-Si/Au–Sb sandwich structures. They [Yıldırım *et al.* (2011)] investigated the effect of sample temperature on the I-V characteristics of the Zn/ZnO/n-Si/Au–Sb structure over the temperature range of 80–320 K with step of 20 K. They [Yıldırım *et al.* (2011)] observed that the ideality factor and series resistance were decreased while the barrier height was increased with increasing temperature of the device.

Hussain *et al.* [Hussain *et al.* (2012)] fabricated the Au/ZnO nanorod (NR)/n-SiC Schottky diodes and investigated their interface traps and electrical properties by studying the I-V, C-V, capacitance-frequency (C-f) and conductance-frequency measurements of the diodes. They [Hussain *et al.* (2012)] observed a higher capacitance at low frequencies and concluded that the excess capacitance was a result of the interface states in equilibrium in the ZnO which could follow the alternating current signal.

Hussain *et al.* [Hussain *et al.* (2013)] presented an in-depth analysis of the temperature-dependent I-V characteristics of the Au/ZnO nanorods Schottky diodes. They [Hussain *et al.* (2013)] estimated the ideality factor and the barrier height taking the barrier inhomogeneity into consideration. They [Hussain *et al.* (2013)] suggested that, in addition to the barrier inhomogeneities at the Au/ZnO nanorods interface the tunneling, Fermi level pinning, and image force lowering could also contribute to the barrier height lowering of Au/ZnO nanorods Schottky diodes.

Table.2.1 Temperature-dependent Electrical parameters of different ZnO based Schottky diodes by taking phenomenon of barrier inhomogeneity into account

ZnO thin film /bulk	Growth Technique	Metal electrode	Standard deviation (eV)	Mean barrier height (I-V-T) (Temperature range) eV	Mean barrier height (C-V) eV	Richardson constant ($Acm^{-2}K^{-2}$)	References
ZnO thin film/Al_2O_3	PLD	Pd Al:ZnO	0.134±.01	1.16±0.04 eV (210-300K)	1.14	-	Wenckstern *et al*. (2006)
a-plane bulk ZnO single crystal	HT	Ag Ti/Au	0.16	(200-300K)	1.44	29	Kim *et al.* (2010)
ZnO thin film/Al_2O_3	PLD	Pt/Al:ZnO Pd/Al:ZnO Au/Al:ZnO Ag/Al:ZnO	0.14 0.15 0.14 0.14	1.27 1.23 0.96 1.04	1.34 1.20 1.22 1.35	- - - -	Lajn *et al.* (2009)
Bulk ZnO wafer	Melt grown	IrOx		0.91±0.01	-	27±7	Sarpatwari *et al*. (2009)
Bulk ZnO wafer		Pd Ti/Al/ Pt/Au		0.61 (80-180K)	-	167	Mtangi *et al.* (2009)
Bulk ZnO wafer	HT	Pt, capped, Ag_2O (400µm) & Ti/Al/Pt		(40-423K)	-	10±6	Allen *et al.* (2009)
ZnO thin film n-Si	sol-gel	Pd & Ti/Al	0.18	1.39 (294 - 443K)	1.34	31.67	Yadav *et al.* (2014)

Yadav *et al.* [Yadav *et al.* (2014)] reported the temperature-dependent analysis of the measured I-V characteristics of Pd/ZnO thin film based Schottky diodes grown on n-Si (100) substrates by sol–gel method. Assuming a Gaussian distributed barrier height at the Pd/ZnO interface with a standard deviation (σ_0) around a mean barrier height, the analysis estimated the value of Richardson constant of ~31.67 Acm^{-2}K^{-2}, which is not only very close to its theoretical value of ~32 Acm^{-2}K^{-2}, but also the best result reported so far for ZnO-based Schottky contacts.

It is already discussed that the Gaussian function can be used as the probability distribution function with a zero-bias mean barrier height and a standard deviation for describing the barrier height inhomogeneity at the metal/semiconductor interface described in Chapter-1. We now summarize some important results reported in the literature for the mean barrier height, standard deviation, and Richardson constant of metal/ZnO Schottky contacts in Table 2.1.

2.4. Effects of Different Seed Layers on Electrical Characteristics of ZnO Thin Film Based Schottky Diodes

As discussed in Chapter-1 that the growth of high-quality ZnO thin films on Si substrates can be of great interests to the researchers due to the flexibility of integration of the ZnO based electronic and optoelectronic devices with the modern CMOS technology for achieving ZnO thin film based smart circuits and systems for future generation applications. However, the easy oxidation of silicon surface, the formation of silicides at room temperature and most importantly the large mismatching between the respective values of the lattice constant and thermal expansion coefficients of ZnO and Si [Fu *et al.* (1998), Shen *et al.* (2006), Wang *et al.* (2007), Song and Lim (2007), Hwang and Chen (2012)] restrict the quality of the ZnO films on the Si substrates. Thus, appropriate interface engineering, such as the prevention of Si surface from oxidation and/or deposition of a buffer layer before the ZnO growth becomes necessary for improving the quality of the ZnO thin films on Si substrates as already mentioned in Chapter.1. Several researchers have proposed the use of the seed/buffer layers of different materials to engineer the ZnO/Si interface and have also investigated their effects on morphology, crystallinity and optical properties of the ZnO thin films grown on these seed/buffer layers [Fu *et al.* (1998), Nakamura *et al.* (2002), Zhang *et al.* (2004), Xiao and Kuwabara (2005), Teng *et al.* (2006), Shen *et al.* (2006), Wang *et al.* (2007), Cao *et al.* (2007), Lee *et al.* (2008), Cha *et al.* (2008), Zhao *et al.* (2009), Lee *et al.* (2011), Ghayour *et al.* (2011)]. The reviews of some important literatures related to the effects of seed/buffer layers of different materials (grown on Si as well other substrates) on the quality of the ZnO films (synthesized on the seed layers) are discussed in the following:

Fu *et al.* [Fu *et al.* (1998)] have investigated the effect of Zn buffer layer on growth and luminescence properties of ZnO thin films deposited on Si substrates. According to X-ray diffraction analysis and cathodoluminescence spectra, it is found that the Zn buffer layer plays an important role for improving crystal quality of films and for getting intense cathodoluminescence.

Nakamura *et al.* [Nakamura *et al.* (2002)] studied the influence of a pre-deposited homo-buffer layer on the ZnO film quality grown by the pulse laser deposition method on sapphire (0001) substrates as functions of temperature and duration of pre-deposition. The observed improvements in the surface morphology and flatness are due to the introduction of the seed layer. They [Nakamura *et al.* (2002)] reported that the buffer layer could relax the strain caused by the lattice mismatch between ZnO and sapphire by about 18%, which, in turn, could improve the crystallinity of the ZnO films.

Zhang *et al.* [Zhang *et al.* (2004)] investigated the effects of the ZnO buffer layer on the crystallinity, surface morphology and optical properties of ZnO films grown on c-plane sapphire substrates using XRD, SEM and PL spectroscopy measurements. The c-axis oriented ZnO films were grown on sapphire by low-pressure MOCVD at the temperature of 600 ºC with different ZnO buffer layer thicknesses between 5 and 55 nm. They [Zhang *et al.* (2004)] observed that the surface morphology, structural and optical properties of the films were dependent on the thickness of the buffer layer. They [Zhang *et al.* (2004)] reported that ZnO films with good structural and optical properties could be grown on the ZnO buffer layers of ~15 nm thickness.

Xiao and Kuwabara [Xiao and Kuwabara (2005)] investigated the effects of the ZnO seed layer on the orientation of the sol-gel derived ZnO thin films deposited on Si substrates. Prior to the growth of the sol-gel derived ZnO films, the sol-gel spin coating method was also used to grow a seed layer of ZnO on the substrate by using a precursor of lower concentration than that used for the ZnO thin film preparation. They [Xiao and

Kuwabara (2005)] concluded that the seed layer could be used to improve the orientation of the finally prepared ZnO films on the thin ZnO seed layer. They [Xiao and Kuwabara (2005)] further noted that the baking temperature, baking time and precursor concentration of the seed layer material could also affect the final ZnO film quality grown on the seed layer.

Teng *et al.* [Teng *et al.* (2006)] studied the optical properties of the RF sputtered ZnO thin films on Si and glass substrates with and without using an indium tin oxide (ITO) buffer layer prepared under different oxygen partial pressures in the sputtering gas. They [Teng *et al.* (2006)] observed that the photoluminescence (PL) characteristics of the ZnO thin films were dependent on the oxygen partial pressure and substrate. Further, the peaks in the ultraviolet region of the PL spectra of the ZnO films on the glass and Si substrates with the ITO buffer layer were observed to be red-shifted with the increase in the excitation intensity.

Shen *et al.* [Shen *et al.* (2006)] reported the successful growth of high quality ZnO thin films on the γ-Al_2O_3 buffer layer coated Si (100) substrates by using the MOCVD method. The properties of the ZnO films on the Al_2O_3 buffer layer were found to be improved in comparison with those of as-grown ZnO films directly on the Si substrates without a buffer layer. They [Shen *et al.* (2006)] observed that the ZnO films gown on the γ-Al_2O_3 buffer grown (on Si (100) substrates) possessed a highly-preferential *c*-axis (0002) orientation with a very narrow (0002) peak, smooth surface morphology and better PL spectral properties. They [Shen *et al.* (2006)] reported that the use of γ-Al_2O_3/Si as substrate could be beneficial for high quality ZnO film deposition due to the smaller residual stress in ZnO films than that in the films grown directly on the bulk Si substrates.

Wang *et al.* [Wang *et al.* (2007)] engineered the ZnO (0001) / Si (111) interface by using a three-step technique involving low-temperature Mg deposition, oxidation, and MgO homoepitaxy. The double heterostructure of MgO(111)/Mg(0001)/Si(111) formed at -10 °C was used to prevent the Si surface from oxidation. Based on the *in situ* reflection of high-energy electron diffraction and *ex situ* characterizations by the transmission electron microscopy, X-ray diffraction, and photoluminescence measurements they [Wang *et al.* (2007)] reported that the double heterostructure could serve as an excellent template for the growth of single-domain ZnO thin films.

Cao *et al.* [Cao *et al.* (2007)] reported the optical and field emission properties of a simple ZnO seed-layer assisted electrochemical deposition (ECD) route for the synthesis of different ZnO nanostructures on Si substrates. The ZnO seed layer is prepared by simple RF sputtering method. They [Cao *et al.* (2007)] observed that simple ZnO films, nanowires, and nanosheets could be prepared in a rational way by just controlling the ECD current density. Except for ZnO nanosheets, both the room-temperature and low-temperature photoluminescence measurements of the ZnO films and nanowire arrays showed strong excitonic emissions in the UV region.

Song and Lim [Song and Lim (2007)] investigated the effects of ZnO seed layers on the growth of ZnO nanorods using hydrothermal method. They [Song and Lim (2007)] used the RF sputtering for the growing the ZnO seed layer on Si substrates. It is observed that the morphology of the ZnO nanorods was strongly influenced by the thickness and crystal size of the seed layer. The surface area of ZnO nanorods was found to be improved with the decrease in the thickness of the ZnO seed layer due to the decrease in the crystal size of the seed layer. They [Song and Lim (2007)] also reported that the orientation of the ZnO seed layer could significantly affect the crystallinity of the nanorods.

Cha *et al.* [Cha *et al.* (2008)] demonstrated a novel synthesis and growth method for achieving vertically aligned ZnO nanowires on a SiO_2 coated Si substrate. The growth direction of the ZnO nanowires was determined by the crystal structure of the ZnO seed layer formed by the oxidation of a DC-sputtered Zn film. They [Cha *et al.* (2008)] achieved the preferred growth direction of the seed layer as (002) under the optimized conditions of the Zn film thickness and thermal treatment.

Zhao and Hu [Zhao and Hu (2009)] prepared the ZnO thin films with and without using a homo-buffer layer on Si (111) substrates by pulse laser deposition (PLD) method under various growth conditions. The photoluminescence (PL) measurements showed an dramatic improvement in the optical properties of the ZnO thin films prepared by introducing oxygen into the growth chamber. As compared to the films grown on the substrates without a buffer layer, the buffer layer assisted ZnO films exhibited an aligned spotty reflection high-energy electron diffraction (RHEED) pattern and a stronger near-band-edge emission (NBE) with a smaller full-width at half-maximum (FWHM) of 98 meV.

Ghayour *et al.* [Ghayour *et al.* (2011)] deposited ZnO seed layers of 20 nm, 40 nm, 160 nm and 320 nm thickness on Si (100) substrates by rf-magnetron sputtering and then synthesized ZnO nanorods on the seed layer at 95°C for 2 h by hydrothermal method. They [Ghayour *et al.* (2011)] studied the effects of the seed layer thickness on the alignment, diameter, density and growth rate of nanorods. It is observed that the alignment of nanorods might depend on the crystallinity, grain size and roughness frequency of the sputtered seed layer. They [Ghayour *et al.* (2011)] observed an improvement in the crystallinity of the ZnO nanorods with the increase in the seed layer thickness.

So far we have considered the literatures dealing with the effects of seed layers on the ZnO film properties. It is clearly observed that the use of a suitable seed layer can reduce the lattice mismatching between the substrates and the ZnO thin films grown on it thereby proving better structural and optical characteristics of the films. We will now review some literatures related to the effects of seed layer on the electrical characteristics of ZnO based Schottky diodes as well as heterojunction diodes mainly reported by a single research group as discussed in the following:

Hwang and Chen [Hwang and Chen (2012)] systematically investigated the effects of pre-annealing of the hydrothermal deposited ZnO seed layer on the material properties of ZnO nanorods (NRs) and on the rectifying behavior of the ZnO NRs/p-Si heterojunction diodes. They [Hwang and Chen (2012)] observed that ZnO NRs could not be grown on the un-annealed seed layer deposited on the Si substrates. With the increase in the annealing temperature of the seed layer in the oxygen environment prior to the growth of ZnO NRs could lead to better crystallization with fewer defect-centres in the ZnO NRs due to the oxygen-vacancy-related defects. However, at a high pre-annealing temperature, the characteristics of ZnO NRs degraded due to the evaporation of oxygen atoms, resulting in more oxygen-vacancy-related defects. They [Hwang and Chen (2012)] reported an extremely high rectification ratio of 1.8×10^5 in their ZnO NR/p-Si based heterojunction diodes.

In an another work, Hwang *et al.* [Hwang *et al.* (2013a)] fabricated non surface-treated ZnO Schottky diodes on Si substrates using one of two different seed layers prepared by the sol-gel and hydrothermal (HT) methods. The ZnO films were grown on the seed layer by the HT method and the Au/ZnO Schottky diodes were fabricated to study the effects of different seed layers on the electrical characteristics of the diodes. They [Hwang *et al.* (2013a)] observed that the Schottky diodes grown on the hydrothermal based seed layer showed a very good rectifying behavior with a rectification ratio as large as 8000 at a bias voltage of ±2 V due to Zn vacancies. In contrast, an ohmic behavior was observed in the Schottky diodes with ZnO films grown on the sol-gel derived seed layers due to oxygen vacancies..

Later in 2013, Hwang *et al.* [Hwang *et al.* (2013b)] fabricated different types of seed layers on Si substrates using the sol–gel or hydrothermal method and they synthesized the ZnO nanocrystal on the seed layers by hydrothermal process. They [Hwang *et al.* (2013b)] observed a large numbers of Zn vacancies near the interface of Au/ZnO with a hydrothermally grown seed layer. The Zn vacancy played an acceptor-like role to raise the barrier height of the Au/ZnO diodes to 0.79 eV with a rectifying ratio of more than 8000. On the other hand, for Au/ZnO with a sol-gel based seed layer showed the presence of oxygen vacancies near the Au/ZnO interface. As a consequence, they [Hwang *et al.* (2013b)] observed a significant reduction in the barrier height of Au/ZnO contacts due to the donor-like role of O vacancy in ZnO films which had led to an ohmic behavior in the I–V characteristics.

2.5. Schottky Ultraviolet Photodiodes

As discussed in Chapter-1 that, ZnO has drawn a significant amount of interests of the researchers [Özgür *et al*. (2005), Jagadish and Pearton (2006), Das *et al.* (2010b)] in recent times for UV detection applications because of its low material cost, easy availability, low-cost fabrication methods, environment-friendly and bio-compatible characteristics in addition to its inherently large direct band-gap of 3.37 eV and high excitonic binding energy of 60 meV at room temperature. A number of ZnO-based UV detector structures including p-n junction photodiodes both in the homojunction [Lopatiuk-Tirpak *et al.* (2006)] and heterojunction forms [Park *et al*. (2003), Alivov *et al.* (2005), Ismail *et al.* (2008), Chen *et al*. (2008), Zhu *et al*. (2008)], photoconductors [Basak *et al.* (2003), Mandalapu *et al.* (2007), Chang *et al*. (2009)], metal-semiconductor-metal (MSM) photodiodes [Lin *et al*. (2005),Young *et al*. (2006), Li *et al*. (2006), Ali and Chakrabarti (2010)], and Schottky photodiodes [Liang *et al*. (2001), Oh *et al*. (2006), Endo *et al*. (2007), Nakano *et al*. (2008), Wenckstern *et al*. (2010)] have been reported in the literature. Among the ZnO based p-n junction photodiodes, while a significant amount of interests have been shown on the n-ZnO/p-Si heterostructures for UV detection, the works reported on the n-ZnO/p-ZnO homojunction [Lopatiuk-Tirpak *et al.* (2006)] and p-ZnO/n-Si heterojunctions [Dutta and Basak (2008)] are very much limited possibly due to the difficulties in achieving stable and controllable p-type ZnO thin films [Look and Claflin (2004), Look (2006), Liu *et al.* (2010)]. On the other hand, the major drawback of the n-ZnO/p-Si heterojunction based UV detectors is that devices may not be suitable for operation under a visible light background due to an obvious presence of photoresponse to visible light absorption in the depletion region of the p-Si side of the n-ZnO/p-Si heterojunction [Liu *et al.* (2010)]. Different photoconductor based UV photodetectors using different materials (e.g. Au, Pt, Al/Au, Ni/Au, ITO etc.) [Liu *et al.* (2000), Basak *et al.* (2003), Mandalapu *et al.* (2007), Chang *et al.* (2009)] for ohmic contacts on ZnO as electrodes and different techniques such as pulse laser deposition (PLD) [Özgür *et al.* (2005)], MOCVD [Liu *et al.* (2000)], RF Sputtering [Moon *et al.* (2005)], Molecular Beam Epitaxy (MBE) [Alivov *et al.* (2005), Mandalapu *et al.* (2007)], and sol-gel [Basak *et al.* (2003), Dutta *et al.* (2008),] for the synthesis of ZnO films have been reported in the literature. Although, the photoconductor based ZnO detectors can provide high internal gain to result in a large photoresponsivity at room temperature and can work without any amplifying device, the sub-linear relations of the internal gain with the incident power, poor UV/visible contrast, and persistent photoconductive effects put challenges in optimizing the parameters of detectors for practical applications [Liu *et al.* (2010)]. Researchers have also explored the ZnO based MSM UV detector structures due to its simple structure, ease of fabrication and integration techniques, and low capacitance per unit area. Various methods such as the MOCVD [Liu *et al.* (2000)], laser assisted molecular beam deposition (LAMBD) [Li *et al.* (2006)], RF sputtering [Moon *et al.* (2005)], atomic layer deposition (ALD) [Shan *et al.* (2009)], MBE [Alivov *et al.* (2005)] and vacuum deposition [Ali *et al.* (2010)] have been used for the fabrication of ZnO MSM-UV photodetectors. Despite the inherently fast nature due to the low capacitance per unit area, the poor responsivity of the MSM photodiodes due to the small active light collecting region caused by the shadowing of electrode metallization is the major drawback of the MSM based photodetectors. In place of MSM using two metal-semiconductor Schottky contacts, the single metal-ZnO based Schottky photodiodes, in general, are reported to have higher quantum efficiency, lower dark current, and higher UV/visible contrast [Razeghi and Rogalski (1996), Nakano *et al.* (2008)]. Further, the ZnO Schottky photodiodes is simpler in structure with higher expected photoresponse than the MSM photodetectors [Özgür *et al.* (2005), Liu *et al.* (2010)]. Moreover, Schottky type UV photodetectors have high speed and low noise performance [Liang *et al*. (2001)]. However, only a limited amount of works [Fabricius (1986), Endo *et al*. (2007), Nakano *et al*. (2008)] has been reported on the ZnO thin film based Schottky UV photodetectors. The review of some important literatures related to the ZnO based UV Schottky photodiodes are discussed in the following.

The UV photoresponse in ZnO thin films was first observed by Mollow in the 1940s [Mollow (1954), Liu *et al*. (2010)]. However, the research of ZnO based photodetectors started gradually since the 1980s. In 1986, Fabricius and coworkers [Fabricius (1986)] first fabricated a ZnO Schottky photodiode using sputtering system. The diode structure consisted of a glass substrate with a Mn electrode as the bottom contact material to the ZnO-Au diode. They [Fabricius (1986)] observed a very poor quantum efficiency of only ~1%.

Liang *et al.* [Liang *et al*. (2001)] fabricated the first n-ZnO epitaxial film based Schottky UV photodetectors grown on the R-plane sapphire substrates by MOCVD method by using Ag as Schottky contact metal and Al as ohmic contact metal. They [Liang *et al*. (2001)] compared their results with the Al/n-ZnO/Al photoconductors and reported a leakage current of the Ag/n-ZnO/Al Schottky photodiodes approximately 5 orders of magnitude smaller than that of its photoconductive counterpart.

Oh *et al*. [Oh *et al*. (2006)] reported an Au/ ZnO: N (~10nm) / ZnO (~1000nm) Schottky type UV detector grown on (0001) GaN/Al_2O_3 substrates by plasma-assisted molecular-beam epitaxy and measured the photoresponsivity of ~1.5 A/W and the leakage current of ~1 nA at 5 V bias in their device. Although, they [Oh *et al*. (2006)] observed a large bandwidth of ~195 nm, but the structure was relatively a complex one as compared to others [Liang *et al*. (2001)].

Endo *et al*. [Endo *et al*. (2007)] reported a Pt/ZnO/Al Schottky ultraviolet photodiode structures using a (0001) single crystal grown by the hydrothermal growth method and observed a responsivity of ~0.185 A/W at a wavelength of 365 nm.

A transparent conducting polymer Schottky electrode based ZnO ultraviolet photodiode with quantum efficiency as high as unity in ultraviolet region and a visible rejection ratio of about 10^3 under zero-bias condition was reported by Nakano *et al.*

[Nakano *et al*. (2008)]. They [Nakano *et al*. (2008)] used ZnO (0001) bulk single crystal as UV detecting semiconductor and poly (3,4-ethylenedioxythiophene) poly

Wenckstern *et al*. [Wenckstern *et al*. (2010)] used selected ZnO thin films to investigate the impact of vacuum-activated surface conduction on the I–V measurements of Au/ZnO Schottky diodes. They [Wenckstern *et al*. (2010)] reported that the formation of vacuum-activated surface conduction path could significantly reduce the rectification of the Au/ZnO Schottky barrier diodes and the phenomenon could be completely suppressed by dielectric passivation of the Schottky diodes.

Ali and Chakrabarti [Ali and Chakrabarti (2012)] reported two Pd/ZnO thin film Schottky UV photodetectors grown on p-type Si substrates by the vacuum thermal deposition and sol-gel methods and measured the responsivity values of~ 0.08 A/W and ~0.17 A/W for the vacuum deposited and sol-gel derived ZnO films respectively. However, the individual contributions of the Pd/ZnO Schottky contact and p-Si/n-ZnO heterojunction photodiode [Park *et al.* (2003)] to the total measured photoresponse were not estimated by the authors [Ali and Chakrabarti (2012)].

Table 2.2 summarizes some important results on ZnO based photodetectors using different structures reported in the literature. The important detector parameters such as the detection wavelength, contrast ratio, responsivity, quantum efficiency, and detectivity of different photodetector structures have been compared in the table.

Table. 2.2 The comparison of UV detection properties for ZnO based various device structures

Device structure (Substrates)	**Growth Technique**	**Contrast Ratio**	**Responsivity (A/W)**	**Quantum efficiency (%)**	**Detectivity (mHz$^{1/2}$W^{-1})**	**Light of detection (Optical power)**	**References**
MSM (Sapphire)	MOCVD	-	1.5 at 5V	-	-	368nm (0.1 mW)	Liang *et al.* (2001)
MSM MISIM (p-Si<100>)	Sol-gel	12 904	0.056 at 3V 0.20 at 3V	19 70	1.28×10^{9} 6.50×10^{9}	365 nm (0.1mW)	Ali and Chakrabarti (2010)
Schottky contact (bulk ZnO)	HT	- -	0.185 at Zn face 0.09 at O face	62.8 31.0	- -	365 nm -	Endo *et al.* (2007)
Heterojunction (p-Si<100>)	TE	- -	0.18 at -3V 0.12 at -3V	- -	- -	365 nm (0.1 mW)	Periasamy and Chakrabarti 2011
MIS MSM (Sapphire)	MBE	3.2×10^{4} 2.9×10^{2}	0.0083 at 5V 0.089 at 5V	- -	- -	370 nm (250 W)	Young *et al.* (2007)
p-n diode (ITO)	ECD	-	0.18 at -2V		-	300 nm (1mW)	Lin *et al.* (2008)
MSM (PS-Si Quartz)	VLS	- - -	0.22 at 5V 0.073 at 5V 0.053 at 5V	85 28 20	- - -	365 nm (150W)	Abdulgafour *et al.* (2012)
Heterojunction (SiC)	MBE	-	0.045 at -7.5V	-	-	-	Alivov *et al.* (2005)
Heterojunction (p-Si<100>)	HT	-	22 at -20 V	-	-	363 nm	Shao *et al.* (2012)
Heterojunction (c-Si isotype)	CSP	-	0.1 at	-	-	375 nm (216 mW)	Ismail *et al.* (2008)

2.6. Electrical Characteristics of ZnO Based Heterojunction Diodes

It has been already discussed earlier that ZnO heterojunction based devices have drawn tremendous interests of the researchers for highly transparent electronic devices, blue or ultraviolet optoelectronic devices, UV photodetectors, photodiodes and surface acoustic wave devices [Özgür *et al.* (2005), Jagadish and Pearton (2006), Lu *et al.* (2006)]. In view of the advantages of electronic and optical confinements offered by heterojunction structures, n-type ZnO layer has been grown on various p-type semiconductors such as p-Si [Choi *et al.* (2010), Reddy *et al.* (2008), Dhananjay *et al.* (2007), Al-Heniti *et al.* (2011), Chirakkara and Krupanidhi (2012)], c-Si [Romero *et al.* (2004), Chen *et al.* (2006)], p-GaN [Wu *et al.* (2012), Abbasi *et al.* (2013)], p-AlGaN [Alivov *et al.* (2003)] and p-SiC [Alivov *et al.* (2005)], Diamond [Sang *et al.* (2012)] etc. It is already discussed earlier in Chapter-1 that p-Si/n-ZnO heterojunctions obtained by growing n-type ZnO on the p-Si substrates can be of special interests due to their technological advantage of natural integration with the modern day's Si based CMOS technology for achieving hybrid and smart sensors and detectors for future generation applications. However, the performance and efficiency of ZnO thin film based devices fabricated on the Si substrates are limited by the presence of defects levels and/or formation of silicides at the ZnO/Si interface [Dhananjay *et al.* (2007), Reddy *et al.* (2008), Al-Heniti *et al.* (2011)]. Thus, the controlling of the interfacial oxide layer and minimizing charge carrier recombination are the crucial issues for enhancing the performance of n-ZnO /p-Si based heterojunction diodes. In this section, we will now present the review of some important reported works on the electrical characteristics of various ZnO based heterojunctions diodes in the following.

Chen *et al.* [Chen *et al.* (2006)] fabricated the undoped and intentionally Nitrogen (N)-doped ZnO thin films on p-Si substrates for achieving n-ZnO/p-Si heterojunction diodes by plasma immersion ion-implantation deposition techniques respectively. The undoped and N-doped ZnO films were of *n* type (n~10^{19} cm^{-3}) and highly resistive (resistivity ~10^5 Ω cm) respectively. The I-V characteristics of the undoped-ZnO/*p*-Si heterojunctions was reported to be ohmic in nature for the applied forward bias voltage larger than ~0.4 V. For the N-doped-ZnO/ *p*-Si samples, they observed the ohmic nature of the heterojunctions for forward bias voltage of <1.0 V but then exhibited a relation $I \sim V^2$ for the bias voltage >2.5 V. They [Chen *et al.* (2006)] also explained transport properties of the undoped- ZnO/ *p*-Si and the N-doped-ZnO/ *p*-Si diodes in terms of the Anderson model and the space charge limited current model.

Dhananjay *et al*. [Dhananjay *et al*. (2007)] reported the growth of ZnO thin films on p-type Si substrates by thermal oxidation method. They [Dhananjay *et al*. (2007)] investigated the electrical transport properties of the n-ZnO/p-Si heterojunctions by the I-V and C-V measurements and observed a barrier height consistent with the energy difference between the work functions of Si and ZnO of their as-fabricated heterojunction diodes.

Ajimsha *et al*. [Ajimsha *et al.* (2008)] fabricated heterojunction diodes of *n*-type ZnO/*p*-type silicon (100) by pulsed laser deposition of ZnO films on *p*-Si substrates in oxygen ambient at different pressures. These heterojunctions were found to be rectifying in nature with a maximum forward-to-reverse current ratio of about 1,000 in the applied voltage range of −5 V to +5 V. The I-V characteristics and the variation of the series resistance of the *n*-ZnO/*p*-Si heterojunctions were found to be in line with the Anderson model and Burstein-Moss (BM) shift.

Reddy *et al*. [Reddy *et al.* (2008)] fabricated well-aligned, low-resistive ZnO nanorods on ZnO-coated glass and p-Si substrates using a simple and economic solution method. They [Reddy *et al.* (2008)] investigated the device performance of ZnO nanorods by studying their I-V characteristics at room temperature. They reported the respective values of turn-on voltage and saturation current of ~2.25V and ~1.27μA with a diode quality factor of 1.9.

Lee *et al*. [Lee *et al*. (2010)] synthesized the n-ZnO and p-ZnO thin films on p-Si substrates by photo induced electro deposition method under illumination. They observed the good rectifying I-V characteristics of both the n-ZnO/p-Si and p-ZnO/p-Si heterojunctions with respective turn-on voltages of 0.56 V and 0.46V. From the analysis of temperature-dependent I-V characteristics, they [Lee *et al*. (2010)] concluded that while the transportation of charge carriers could be governed by the thermionic emission of the carriers over the barrier height at high forward bias voltages, however, the multi-step tunnelling-assisted carrier capture-emission mechanism could be responsible for the current conduction at low bias regions.

The fabrication of ZnO thin film/p-Si nanowires based heterojunction diodes were reported by Choi *et al.* [Choi *et al.* (2010)]. They [Choi *et al*. (2010)] deposited the ZnO thin films on vertically aligned p-Si nanowire arrays grown by electroless wet chemical etching of Si wafer. The junction properties were studied by measuring the I-V and C-V characteristics. They [Choi *et al*. (2010)] observed a well defined rectifying behavior with a turn-on voltage of 2.26 V and an ideality factor of 4.

Baydogan *et al*. [Baydogan *et al*. (2012)] deposited Al-doped zinc oxide (ZnO:Al) films with a 1.2 at.% Al concentration on p-type silicon wafers using a sol–gel dip coating technique. The films were annealed in vacuum at five different temperatures between 550 and 900 °C for 1 h. They [Baydogan *et al*. (2012)] observed a decrease in the resistivity of the films with the increasing annealing temperature. The ZnO films annealed at a temperature of 700°C were observed to provide the controlled current flow through the ZnO: Al/p-Si heterojunction up to 20 V [Baydogan *et al*. (2012)].

Hazra *et al*. [Hazra *et al*. (2013)] reported the electrical characteristics of Si/ZnO based heterojunction diodes at room temperature. They [Hazra *et al*. (2013)] deposited the ZnO films conformally on the p-Si substrates by ALD technique without using any buffer/seed layer. The junction properties were evaluated by measuring I-V and C-V characteristics. The I-V measurements showed the well defined rectifying nature with a rectification ratio of 127, turn-on voltage of 0.6 V, ideality factor of 2.72 and barrier height of 0.76 eV of the ZnO/Si heterojunction diode without a buffer layer.

All the literatures reviewed above did not consider the effect of barrier height inhomogeneity at the heterojunction interface similar to the phenomenon existing at the metal-semiconductor Schottky contacts already discussed earlier. Further, the above works do not address the effect of interface states on the heterojunction characteristics. We will now review some limited works reported in the literature related to the effects of barrier height inhomogeneity and the interface states on the electrical characteristics of the Si/ZnO heterojunction diodes in the following:

(a) Barrier height inhomogeneity correction at n-ZnO/p-Si heterojunction interface

It is already discussed that the temperature-dependent I-V measurements can only provide us the details of the information about the interface of the Schottky or any heterojunction. As defined earlier for Schottky diodes, the barrier inhomogeneity at the interface of any heterojunction refers to the non-uniform random distribution of the spatial barrier height across the heterojunctions. Since the thermionic emission model is used for describing of the I-V characteristics of the ZnO/Si heterojunction devices [Al-Heniti *et al.* (2011), Chirakkara and Krupanidhi (2012)] the similar methodology as discussed for the Schottky junctions can also be used for estimating the effects of the barrier inhomogeneity on the electrical parameters of the ZnO/Si heterojunction interfaces. Some important literatures related to modeling of barrier inhomogeneity phenomenon at the ZnO/Si heterojunction diodes have been reviewed in the following:

Majumdar and Banerji [Majumdar and Banerji (2009)] studied the I-V characteristics of the p-ZnO/n-Si heterojunction have been studied in the temperature range 140–300 K. They [Majumdar and Banerji (2009)] confirmed the presence of the barrier height inhomogeneity by observing increased barrier height and decreased ideality factor values with the increased temperature. They [Majumdar and Banerji (2009)] observed a linear plot of ln (I_0) versus $1/kT$ with an activation energy of 0.07 eV. It is suggested that the trap-assisted multistep tunneling could be the dominant carrier transport mechanism in their heterojunctions.

Al-Heniti *et al*. [Al-Heniti *et al.* (2011)] reported the temperature-dependent heterojunction characteristics of n-type ZnO nanowires/p-Si diodes over the temperature range of 25–130°C. The turn-on and breakdown voltage of the device were observed to be slightly decreased with the increase in the operating temperature of the heterojunction diodes. The effective potential barrier height and the saturation current were also found to be increased with the temperature. In an another work, Al-Heniti *et al*. [Al-Heniti *et al.* (2012)] reported the successful growth of the ZnO nanowire networks (NWsN) by simple thermal evaporation process by using metallic zinc powder in the presence of oxygen. The as-grown ZnO nanowire networks grown on Si substrate were then utilized to fabricate n-ZnO/p-Si heterojunction diodes. They [Al-Heniti *et al.* (2012)] investigated the temperature-dependent I–V characteristics of the fabricated heterojunction diodes for temperatures in the 77 K–477 K. They [Al-Heniti *et al.* (2012)] observed a large value of turn-on voltage of ∼5 V at different temperatures with a mean built-in-potential barrier of 0.84 eV.

Chirakkara and Krupanidhi [Chirakkara and Krupanidhi (2012)] fabricated the ZnO/Si heterojunctions by growing ZnO thin films on p-type Si (100) substrates by pulse laser deposition (PLD) method without using a buffer layer. The electrical properties of the junction were studied by temperature-dependent I-V measurements and room temperature C-V analysis. They [Chirakkara and Krupanidhi (2012)] observed a much lower value in Richardson constant of 5.19×10^{-7} $\mathrm{AK^{-2}cm^{-2}}$ than the theoretical value of 32

$AK^{-2}cm^{-2}$ for ZnO. They [Chirakkara and Krupanidhi (2012)] used a Gaussian distribution function for the barrier inhomogeneity with a standard deviation of σ^2 =0.035 V. They measured the values of barrier height and Richardson constant as 1.3 eV and 39.97 A K^{-2} cm^{-2} respectively after taking the barrier inhomogeneity phenomenon into consideration in the modified Richardson plot**.**

Hazra and Jit [Hazra and Jit (2014)] reported the temperature-dependent electrical parameters of p-Silicon nanowires (SiNWs)/n-ZnO thin film based core–shell heterojunction diodes fabricated by conformally deposited ZnO by ALD technique on metal-assisted chemically etched SiNWs. The temperature-dependent I-V characteristics of the device were estimated using the modified thermionic emission model using a Gaussian distributed barrier height function to include the effects of barrier inhomogeneity phenomenon at the p-Si NWs /n-ZnO heterojunction interface. It is observed that the value of the Richardson constant was changed from an impractical value of 1.989×10^{-6} $Acm^{-2}K^{-2}$ to a realistic value of 36.6 $Acm^{-2}K^{-2}$ once the barrier inhomogeneity phenomenon was taken into consideration in the analysis.

Ranwa *et al*. [Ranwa *et al.* (2014)] studied the I-V characteristics of ZnO NRs/Si heterojunctions in the temperature range of 120–300 K. The self-aligned ZnO nanorods (NRs) were grown on n-Si (100) substrates by RF sputtering techniques. Barrier height and ideality factor estimated from thermionic emission model were found to be highly dependent on the operating temperature of the heterojunctions. They [Ranwa *et al.* (2014)] observed a large deviation in the Richardson constant from its theoretical value of n-Si without considering the presence of barrier inhomogeneities at heterojunction interface.

(b) Distribution of interface states at heterojunction interfaces

Previous studies on the C-V characteristics of heterojunction devices were based on the pioneering work of Anderson [Anderson (1962)] without considering the effect of interface sates at the heterojunction interface. It has been found that the C-V characteristics of heterojunction diodes are very much sensitive to the interface state density and surface pinning effect caused by high density of interface states at the heterojunction interface [Donnelly and Milnes (1967), Sharma *et al*. (2013)]. However, only a limited amount of study has been reported in the literature in regard.

Chattopadhyay and Haldar [Chattopadhyay and Haldar (2001)] have also theoretically studied the C-V characteristics of an anisotype heterojunction including the effects of interface states and series resistance. It is observed that the C-V characteristics of any heterojunction are affected by the interface state density, doping concentration of the semiconductors making the heterojunction, temperature and series resistance [Chattopadhyay and Haldar (2001)].

Romero *et al*. [Romero *et al*. (2004)] have measured the electrical, structural and compositional properties of n-ZnO/c-Si heterojunctions fabricated by the chemical spray pyrolysis method. They [Romero *et al*. (2004)] used the C-V method and admittance spectroscopy over the temperature range of 223 K-373 K. Their as-fabricated n-ZnO/c-Si heterojunctions showed a barrier height consistent with the difference in energy of the work functions of Si and ZnO. [Romero *et al*. (2004)] also studied the C-V characteristics of the n-ZnO:Al/c-Si heterojunctions. They [Romero *et al*. (2004)] observed a more complex C-V characteristic possibly due to the defects at or near the n-ZnO:Al/c-Si interface. Some important results related to the temperature-dependent electrical characteristics of the p-Si/n-ZnO heterojunction diodes have been summarized in Table 2.3.

The estimated values of the barrier height and Richardson constant of various heterojunction configurations with/without a seed layer reported in the literatures have been include in this table.

Table.2.3 Highlighting the recent results on temperature dependent electrical characteristics of n-ZnO/p-Si heterojunction diodes

Heterojunction configuration	Growth Technique	Seed layer	Mean Barrier height (eV)	Richardson Constant (AK^{-2} cm^{-2})	References
Al/n-ZnO thin film/p-Si/Al	PLD	none	1.3 eV (300-390 K)	39.97	Chirakkara & Krupanidhi (2012)
Ag/n-ZnO NWs/p-Si/Al	TE	none	0.68 eV (298-403 K)	-	Al-Heniti *et al.* (2011)
Ag/n-ZnO NWsN/p-Si/Al	TE	none	0.84 eV (77- 477 K)	-	Al-Heniti *et al.* (2012)
Al/n-ZnO thin film/p-Si/Al	PLD	ZnO	(140-300 K)	-	Majumdar & Banerji (2009)
In/n-ZnO NRs/p-Si/Al	ALD	ZnO	(293-423 K)	-	Reddy *et al.* (2008)
Ti/Al/ n-ZnO thin film /p-Si NWs/Al	ALD	none	1.26 eV (303-423 K)	36.6	Hazra and Jit (2014)

2.7. Summary and Concluding Remarks

We have discussed so far some noteworthy state–of–art research on the electrical characteristics of ZnO based Schottky diodes, heterojunction diodes, and Schottky ultraviolet photodiodes in the present chapter. We may now summarize some important observations based on which the scopes of the thesis have been outlined in the last section of Chapter-1.

- ZnO is a wide band gap semiconductor material with many promising properties for blue/UV optoelectronics, transport electronics, spintronic devices, biomedical and sensing applications [Özgür *et al.* (2005), Jagadish and Pearton (2006), Wang and Song (2006), Xu *et al.* (2013)]. The lower cost and higher excitonic binding energy (~60 meV at room temperature) along with a wide bandgap energy (~3.37 eV) of the ZnO has made it a better choice over another wide bandgap semiconductor GaN for optoelectronic applications [Lee (2008), Janotti and Walle (2009), Biswas (2010)]. ZnO in the form of thin film as well as nanostructures are considered to be better than their bulk counterpart for various optoelectronic and other sensing applications due to their large surface area to volume ratio.

- The common substrates used for the synthesis of ZnO thin films and nanostructures are sapphire, ITO, glass and Si [Wang *et al*. (2007), Logeeswaran *et al*. (2011)]. Among them, Si has a special place in the semiconductor industry because of its low-cost and ease of availability, and flexibility of integration (of the ZnO based devices on Si substrates) with the modern day's CMOS technology for achieving future generation smart sensors and Si based optoelectronic integrated circuits (OEICs). However, it is always a challenging task to grow the high-quality of ZnO thin films/nanostructures on the Si substrates due to the large mismatching in the lattice constants and thermal expansion coefficients between the ZnO and Si materials. As a consequence of the above facts, it is difficult to achieve the desired electrical characteristics of ZnO based electronic devices such as Schottky diode, heterojunction diode and Schottky ultraviolet photodiodes grown on Si substrates. Thus, new fabrication techniques are required for improving the quality of ZnO thin films/nanostructures on Si substrates.

- Almost all the deposition techniques including the chemical vapor deposition (CVD), vapor phase transport (VPT), molecular beam epitaxy (MBE), pulse laser deposition (PLD), Radio frequency (RF) Sputtering, sol-gel and thermal evaporation (TE) methods [Smith (1994), Wang (2004), Özgür *et al*. (2006), Lu *et al*. (2006), Biswas (2010)] can be explored for the synthesis of ZnO thin films. While most of the methods are expensive, the sol-gel spin coating and thermal evaporation are considered to be the cost effective techniques for the ZnO deposition in various substrates including Si, ITO, glass and plastics.

- It is difficult to achieve the ZnO films of desired thickness using the sol-gel spin coating method due to the non-availability of thickness monitoring systems during the growth of a particular ZnO layer. On the other hand, the thickness of the ZnO films can be accurately controlled during deposition by attaching a digital thickness monitoring unit with thermal evaporation unit. Thus, thermal evaporation can be considered as a better inexpensive method for ZnO thin film deposition of a desired thickness than the sol-gel method.

- The ZnO based Schottky diodes have drawn considerable attention in recent times due to their possible applications in UV photodetectors, gas sensors and piezoelectric nanogenerators etc. However, the major difficulty in the ZnO based

Schottky diodes is their temperature-dependent barrier height and ideality factor due to the barrier inhomogeneity phenomenon at the metal/ZnO interface [Allen *et al*. (2009), Sarpatwari *et al*. (2009), Lajn *et al*. (2009)]. As a result, the electrical characteristics of ZnO based Schottky diodes are often observed to be affected by various non-idealities such as an interface states and interfacial oxide layer, interface fixed charges, and series resistance due to the bulk substrate [Werner and Güttler (1991), Tung (1992)].

- Among the ZnO based p-n junction photodiodes, while a significant amount of interests has been shown on the n-ZnO/p-Si heterostructures [Chirakkara and Krupanidhi (2012)], the works reported on the n-ZnO/p-ZnO homojunction and p-ZnO/n-Si heterojunctions are very much limited possibly due to the difficulties in achieving stable and controllable p-type ZnO thin films [Majumdar and Banerji (2009), Zhao *et al.* (2008)]. Since the ZnO is intrinsically an n-type semiconductor, most of the studies are confined to the n-ZnO based UV Schottky photodetectors grown on various *p*-type semiconductors, such as SiC, Si, AlGaN, InP, Si etc.
- In general, the n-ZnO/p-Si heterojunctions show the rectifying characteristics of a diode. However, the n-ZnO/n-Si heterojunctions may possess an ohmic characteristic [Kim *et al.* (2001)]. Thus, metal/ZnO Schottky diodes grown on n-Si substrates can be a better option than those grown on the p-Si substrates [Ali *et al*. (2010)]
- Although, p-Si/n-ZnO substrates are highly desirable, however, the easy oxidation of silicon surface, the formation of silicides even at room temperature and the big lattice mismatch between the ZnO and Si severely influence the quality of ZnO films grown on p-Si substrates [Fu *et al*. (1998), Shen *et al*. (2006), Wang *et al*. (2007)]. As a result, the fabrication of nearly a defect-free, oxide-free and strain-free n-ZnO layer on p-Si is still a challenge for the current researchers. In general, a seed/buffer layer of a suitable material with a lattice constant in between the Si and ZnO is normally grown on the Si substrates prior to the ZnO deposition to improve the quality of the ZnO films [Song and Lim (2007), Hwang and Chen (2012]
- In general, temperature-dependent current-voltage (I-V-T) measurements are analyzed to study the effects of barrier inhomogeneities at Metal/ZnO interface and heterojunction interface of the ZnO thin film based Schottky contact and

heterojunction diodes respectively [Werner and Güttler (1991), Sarpatwari *et al*. (2009), Lajn *et al*. (2009)]. Further, the thermionic emission model is used for describing the I-V characteristics of both the Schottky diodes and heterojunction devices [Sze (1981)]. The barrier height is increased and the ideality factor is decreased with the increase in the operating temperatures of both the Schottky and heterojunction diodes due to the barrier inhomogeneity phenomenon [Schmitsdorf *et al*. (1997), Chand and Kumar (1997)]. Most of the researchers [Lajn *et al*. (2009), Mtangi *et al*. (2009), Allen *et al*. (2009)] have assumed a Gaussian distribution function for the barrier height distribution across the entire interface with a standard deviation around a mean barrier height.

- The Richardson constant, mean barrier height and the ideality factor are the fundamental parameters required for characterizing the I-V models of the Schottky and heterojunction diodes based on the thermionic emission theory. In most of the cases, the value of Richardson constant obtained from temperature-dependent I-V measurements is significantly smaller than its theoretical value [Lajn *et al*. (2009), Mtangi *et al*. (2009), Allen *et al*. (2009)]. However, to the best of our knowledge, no significant work is reported so far on the estimation of the Richardson constant of any ZnO thin film based Schottky diodes fabricated by thermal evaporation technique.

- As mentioned earlier, the seed layer is generally used to improve the quality of ZnO thin films grown on various substrates. Seed layers of different materials, such as ZnO, Zn, MgO, Al_2O_3, ITO, and Zn have been used for studying their effects on the surface morphology and crystalline structure of ZnO thin films grown on the substrates [Fu *et al*. (1998), Shen *et al*. (2006), Wang *et al*. (2007)]. However, very limited works have been reported for studying the effect of a seed layer on the electrical characteristics of ZnO based Schottky and heterojunction diodes. Thus, there is enough space left for the researcher to work in this direction.

- ZnO nanostructures based photodetectors can be of great interests for the UV detection applications due to their large surface-to-volume ratio, carrier and photon confinements in two dimensions, superior stability owing to high crystallinity and, possible surface functionalization with target-specific receptor species [Zhai *et al*.

(2009), Liu *et al*. (2010)]. However, only a limited amount of works have been reported so far on the ZnO nanostructures based Schottky UV photodetectors.

- It is already mentioned that the flexibility of integration of the ZnO nanostructures based devices (grown on silicon (Si) substrates) with the well-developed Modern CMOS technology may be explored for achieving smart sensors and UV photodetectors for future generation sensing and detection applications. Since the use of a seed layer of a suitable material on the Si substrates can improve the quality of ZnO thin films/nanostructures deposited on Si, there are also enough scopes for studying the effects of different seed layer materials on the electrical and optical characteristics of the ZnO based Schottky contacts (grown on the seed layer coated Si substrates) for electronic and UV detection applications.

We will end the present chapter with the conclusion that there are enough scopes for studying the fabrication and electrical characterization of the ZnO thin films/nanostructures based Schottky diodes, heterojunction diode and Schottky ultraviolet photodiodes grown on Si substrates with and without using a seed layer. There are also scopes for investigating the effects of a particular seed layer on the ZnO films and electrical characteristics of the ZnO thin film based devices for electronic and optoelectronic applications. The scopes of the present thesis presented in the Chapter-1 have been derived from the observations described above.