

Chapter 1

Introduction

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Introduction

Transition metal oxides like ZnO, TiO₂, SnO₂, NiO, In₂O₃ are a class of advanced ceramic materials that are technologically important with fascinating structures and properties [Wollenstein *et al.* (2003); Sundaresan *et al.* (2006); Jang *et al.* (2015); Trotochaud *et al.* (2012); kwon *et al.* (1995); Behr *et al.* (1995); Garzella *et al.* (2000)]. The unique magnetic, electrical and optical properties of these oxides are central to technological advances in various technologies based on superconductivity electronics, sensors, ultra high-density magnetic data storage and more recently in spintronics. Among the above transition metal oxides, zinc oxide (ZnO), II-VI binary compound semiconductor, has been received much interest over the past years due to its wide range of properties depending on doping, including a range of conductivity from metallic to insulating, high transparency, piezoelectricity, wide-bandgap semiconductivity, huge magneto-optic and chemical-sensing effects [Hadis Morkoc and Umit Ozgur (2009)]. In theoretical studies, ZnO is expected to be a promising candidate for achieving room temperature ferromagnetism after doping [Liu *et al.* (2005)]. Some optoelectronic applications of ZnO overlap with those of GaN, which is another important semiconductor with band gap $E_g \sim 3.4$ eV and exciton binding energy ~ 25 meV; generally used for fabrication of green, blue-ultraviolet, and white light-emitting devices [Pearson *et al.* (2003)]. However, due to quite availability of high-quality ZnO and a large exciton binding energy of ~ 60 meV, it gains advantage over GaN. The single crystals and epitaxial thin films of ZnO can be grown much easily which makes the technology required for the production of ZnO-based devices available relatively at lower cost. For example, GaN grown on sapphire possess exceptionally high concentration of defects (10^6 – 10^9 cm⁻²) due to large lattice mismatch ($\sim 16\%$). This degrades the device performance [Nakamura *et al.* (2000)]. However, epitaxial ZnO films grown on native substrates lead to the reduction of concentration of defects and show better

performances in electronic and photonic devices [Look *et al.* (2001); Ozgur *et al.* (2005); Ogale *et al.* (2005); Nickel *et al.* (2005); Jagadish *et al.* (2006)]. The other advantage of ZnO over GaN is that ZnO is amenable to wet chemical etching. This is particularly important in the device design and fabrication. The stability of ZnO against high energy radiation makes it a suitable candidate for space applications. Other favourable features of ZnO are low power threshold for optical pumping, and biocompatibility. Collectively, these properties of ZnO make it an ideal contender for the production of different devices ranging from sensors to ultra-violet laser diodes and nanotechnology-based devices.

1.1 Crystal Structure of ZnO

In nature, ZnO possesses three crystal structures such as wurtzite, zinc blende, and rocksalt (or Rochelle salt). The schematic diagram of these crystal structures are shown in Figure 1.1. Only the wurtzite structure of ZnO (space group $P6_3mc$) is found thermodynamically stable at ambient conditions. The other two structures are metastable. Zinc blende structure of ZnO (space group $F\bar{4}3m$) can be stabilised only by growth on cubic substrates and rocksalt structure (space group $Fm\bar{3}m$) may be obtained at relatively high pressures

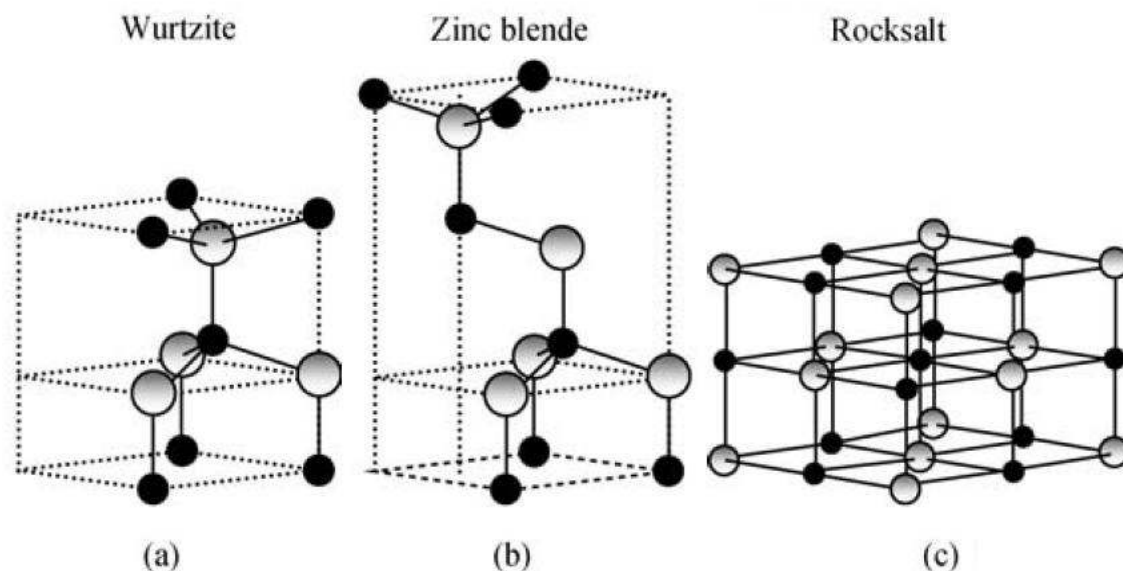


Figure 1.1: Stick and ball representation of ZnO crystal structures: (a) hexagonal wurtzite, (b) cubic zinc blende, and (c) cubic rocksalt. The shaded gray and black spheres denote Zn and O atoms, respectively [after Hadis Morkoc and Umit Ozgur (2009)].

(~10 GPa), similar to the case of GaN [Leszczynski *et al.* (1999)]. The ideal wurtzite structure is formed by two interpenetrating hexagonal close-packed (hcp) sublattices, each of which consists of one type of atom (either group II atom or group VI atom). These sublattices are displaced with respect to each other along the three fold c-axis by the amount of $u = 3/8 = 0.375$. Each sublattice includes four atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron. The lattice parameters for wurtzite structure are, $a = b$ and c , where the ratio of $c/a = \sqrt{8/3} = 1.633$. In a real ZnO crystal (shown in Figure 1.2), the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio or the u value [Kisi *et al.* (1989)]. This deviation occurs such that the tetrahedral distances are kept roughly constant in the lattice. The experimentally observed c/a ratio is found to be smaller than the ideal value. Experimentally, for wurtzite ZnO, the real values of u and c/a were determined in the range of 0.3817-0.3856 and 1.593-1.6035, respectively [Reeber *et al.* (1970)].

In ZnO, Zn atoms are surrounded by four O atoms at the corners of a tetrahedron, and vice versa. The d-electrons of zinc hybridise with p-electrons of oxygen. Due to the tetrahedral coordination, the bond distances of 4 nearest neighbours and 12 next-nearest neighbours become equal. The tetrahedral coordination is typically of sp^3 type covalent bonding, however, due to the large electronegativity difference in between Zn and O, this material also show a substantial ionic character. Therefore, the bonding nature of Zn^{2+} ions (empty 4s orbital) and O^{2-} ions (completely filled 2p shell) in ZnO resides inbetween covalent and ionic compound semiconductor. The ionicity of ZnO is 0.616 on the Phillips ionicity scale. On the basis of the Pauling electronegativity scale, the Zn-O bond has a significant, 60%, ionic nature instead of being considered as a covalent compound. Considering a ZnO molecular unit lattice and representing Zn and O as a lattice point, it can be noticed that along the [0001] axis, the alternate layer formation is similar to *ABAB* arrangement of atoms. This molecular arrangement further represents a hcp lattice and implies that the

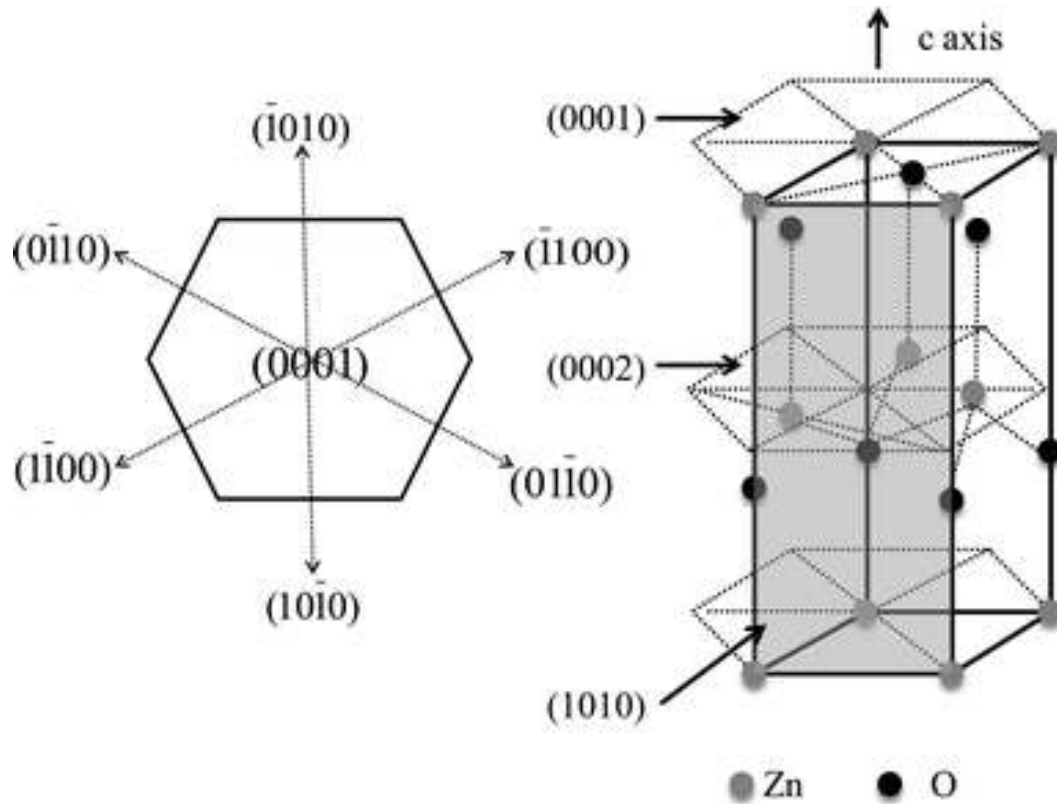


Figure 1.2: The hexagonal wurtzite crystal structure of ZnO. One unit cell is outlined for clarity [after Somnath *et al.* (2013)].

[0001] axis is a polar axis, referred to as the c-axis. The planes along the c-axis are neutral and contain as many Zn as O atoms. Due to the polar nature of c-axis, the anisotropy appear in the ZnO crystal structure which governs several significant consequences, i.e. unidirectional growth and chemical etching, the electro-mechanical (piezoelectricity) and opto-electronic properties. Along the c-axis, the face terminations of wurtzite ZnO takes place with the polar Zn terminated (0001) and O terminated (000 $\bar{1}$) faces. The next two most common faces of ZnO are non-polar (11 $\bar{2}$ 0) (*a*-axis) and (10 $\bar{1}$ 0) faces which both contain an equal number of Zn and O atoms. The O-terminated (000 $\bar{1}$) face possesses a slightly different electronic structure to the other three faces. Additionally, the polar surfaces and the (1010) surface are found to be stable, however the (11 $\bar{2}$ 0) face is less stable and generally has a higher level of surface roughness than its counterparts. The (0001) plane is also basal.

1.2 Physical Properties and Applications

ZnO possesses various physical properties such as piezoelectric, electrical, mechanical, optical and sensing. Furthermore, the above physical properties can be modified by doping it with different transition metal ions. The basic physical parameters of bulk ZnO are tabulated in Table 1.1. ZnO, with a tendency for unidirectional growth to form different nanostructures in highly oriented and ordered arrays, generate the great possibility for the development of future nanoscale devices. Some of the properties of ZnO and their scope in device formation are discussed below.

1.2.1 Piezoelectric Properties

The origin of the piezoelectricity in ZnO is due to the tetrahedral coordination of Zn and O atoms which gives rise to polar symmetry along the hexagonal axis (c-axis). In the presence of external pressure, lattice distortion takes place that induces local dipole moments, thus macroscopic dipole moment appears over the whole crystal and generate piezoelectricity. This polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and spontaneous polarization. Due to its moderately high (very high for a semiconductor) electromechanical coupling coefficients, ZnO has been widely used for different applications in force sensing, acoustic wave resonator, acousto-optic modulator, etc. [Catti *et al.* (2003); Corso *et al.* (1994); Gardeniers *et al.* (1998); Molarius *et al.* (2003); Wuethrich *et al.* (1998); Itoh *et al.* (1994); Paneva *et al.* (1997); Hutson *et al.* (1960)]. Being the surface acoustic wave (SAW) filter, the most common application of ZnO has been occupied by mass consumer items such as TV filters and wireless communication systems. ZnO-based SAW devices have been also used for UV photodetection [Emanetoglu *et al.* (2004)] and for gas [Ippolito *et al.* (2005)] and biochemical [Zhang *et al.* (2006)] sensing.

Table 1.1 Physical parameters of ZnO

Physical parameters	Values
Crystal structure (Space grup)	Wurtzite ($P6_3mc$)
Lattice constant at 300K (nm)	$a=0.32495$, $c=0.52069$ $c/a=1.602$, $u=0.3825$
Thermal expansion coefficient ($10^{-6}/K$)	6.5 (a -axis); 3.02 (c -axis)
Thermal conductivity (W/cm.K)	1.10 (O plane); 1.16 (Zn plane)
Density at 300K (g/cm^3)	5.606
Energy band gap (direct band gap at 300K,eV)	3.37
Band gap temperature coefficient (eV/K)	2.9×10^{-4}
Exiton binding energy (meV)	60
Intrinsic carrier concentration (cm^{-3})	$<10^6$
Carrier concentration for n-type doping (cm^{-3})	$\geq 10^{20}$ electrons $<10^{17}$ holes
Carrier concentration for p-type doping (cm^{-3})	
Mobility ($cm^2V^{-1}S^{-1}$) at 300 K	205 (Electron); 180 (Hole)
Conductivity ($\Omega.cm$)	10
Effective mass	0.24 (Electron); 0.59 (Hole)
Specific heat (cal/g. °C)	0.125
Saturation electron drift velocity ($10^7cm/S$)	3
Static dielectric constant	8.47
Index of refraction	2.09 (0.45 μ m)
Melting point (°C)	1975
Radiation resistance (Me V)	2
Hardness	4.5

1.2.2 Electrical Properties

ZnO is a wide bandgap material, due to which it is considered for variety of electronic and optoelectronic applications. The major advantages associated with a large bandgap involves high-temperature and high-power operation, low noise generation, high breakdown voltages, and capability to sustain large electric fields. The electron transport in ZnO semiconductors for sufficiently low electric fields, using Monte Carlo simulations Albrecht *et al.* (1999) have calculated the room-temperature electron mobility $\sim 300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Usually, as grown ZnO shows n-type semiconducting behaviour and the highest room-temperature electron mobility for a bulk ZnO single crystal grown by vapour-phase transport method is reported to be about $205 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a carrier concentration of $6.0 \times 10^{16} \text{ cm}^{-3}$ [Look *et al.* (1998)], which is very close to the calculated mobility value. Further for high electric fields, the steady-state velocity field characteristics have been resolved using the Monte Carlo method for electric field strengths upto 350 kVcm^{-1} in bulk wurtzite ZnO at lattice temperatures of 300, 450, and 600 K [Albrecht *et al.* (1999)]. The calculated electrons drift velocity versus electric field characteristics are plotted in Fig. 1.3 for wurtzite-phase of ZnO along with GaN for comparison.

In recent years, great progress in synthesising p-type ZnO has achieved made [Park *et al.* (2002); Zeng *et al.* (2006); Lin *et al.* (2008(a)); Lin *et al.* (2008(b))]. As believed, the p-type semiconductor characteristic in ZnO appears after doping it with a proper element by substituting Zn or O atoms. Known acceptors in ZnO are group *IA* elements (Li, Na, K) [Look *et al.* (2004)], group *IB* elements (Cu, Ag, Au) [Mollwo *et al.* (1973)] substituted at the Zn site and, group *VA* elements (N, P, As, Sb) [Look *et al.* (2004)] substituted at the O site. But there still exist the difficulties in fabricating sufficient high quality p-type ZnO because of the lack of low resistivity and high mobility. To circumvent this problem, the *p*-doping level must be increased ($> 10^{18} \text{ cm}^{-3}$). On the other hand, highly conductive *n*-type ZnO

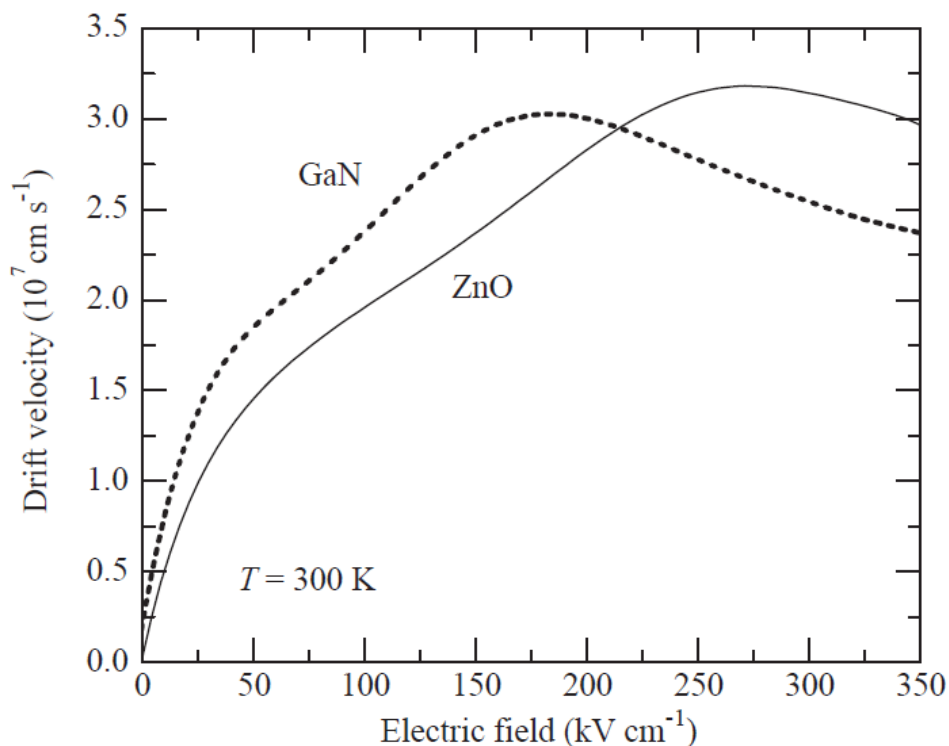


Figure 1.3: The Comparison of calculated electron drift velocity versus electric field for wurtzite structure ZnO (solid) and GaN (dashed) at 300 K [Albrecht *et al.* (1999)].

($n > 10^{20} \text{ cm}^{-3}$) can be produced by intentional doping of group III elements (Al, Ga, In) [Özgül *et al.* (2005)] at the Zn sites and group-VII elements (F, Cl, Br) [Klingshirn *et al.* (2007); Özgül *et al.* (2010); Fan *et al.* (1995)] at O-sites. The lack of growth of *p*-type ZnO semiconductors hinder the fabrication of ZnO *p*-*n* homojunction based LEDs. Provisionally, *p*-*n* heterojunctions based LEDs have been realised using *n*-type ZnO and different *p*-type materials such as Si [Xiong *et al.* (2002); Jeong *et al.* (2003); Nikitin *et al.* (2003)], GaN [Alivov *et al.* (2003); Yu *et al.* (2003)], AlGaIn [Alivov *et al.* (2003)], SrCu₂O₂ [Ohta *et al.* (2000); Kudo *et al.* (1999)], NiO [Ohta *et al.* (2003)], ZnTe [Tsurkan *et al.* (1975)], Cu₂O [Drapak *et al.* (1968); Ishizuka *et al.* (2004)], CdTe [Aranovich *et al.* (1980)], SiC [Alivov *et al.* (2005(a)); Alivov *et al.* (2005(b))], diamond [Wang *et al.* (2004)], ZnRh₂O₄ [Ohta *et al.* (2003)], and GaAs [Nikitin *et al.* (2004)]. The study of these *p*-*n* heterojunctions has been realized as great deals of activity in the area of electroluminescence (EL) under forward bias which can be used as ultraviolet photodetectors (PDs) [Coskun *et*

al. (2004)]. The EL characteristics of ZnO have also been used for the fabrication of metal-insulator-semiconductor (MIS) which do not require p-type ZnO [Hwang *et al.* (2007)]. In addition, the deep study of the electrical properties of ZnO nanostructures is essential for developing their future applications in nanoelectronics. Some electrical transport measurements have already been performed on individual ZnO nanowires and nanorods [Chang *et al.* (2004); Chik *et al.* (2004); Liu *et al.* (2003); Li *et al.* (2004); Heo *et al.* (2004); Arnold *et al.* (2003); Park *et al.* (2004)].

1.2.3 Optical Properties

ZnO is a wide direct band gap (3.3 eV) semiconductor and shows high exciton energy (60 meV) due to which it is considered as a potentially attractive material for light-emitting devices emitting in the ultraviolet (UV) region at room temperature [McCluskey *et al.* (2009); Kikkawa *et al.* (1999); Zutic *et al.* (2001); Didosyan *et al.* (2004)]. ZnO is a solar blind material, therefore it may be used as transparent front electrodes or transparent contact layer (transparent window) in solar cells. Due to its high conductivity and transparency in addition to its low cost (needs to be lowered further), nontoxicity, and relatively low deposition temperature; ZnO has a significant advantage over the ITO. The transparency of ITO at 450 nm is about 80% [Hadis Morkoc and Umit Ozgur (2009)], while the transparency of ZnO at same wavelength is found to be more than that of ITO (~90%) [Dehuff *et al.* (2005); Song *et al.* (2007); Ozgur *et al.* (2010)]. Moreover, the intrinsic optical properties of ZnO nanostructures are being rigorously studied for execution in photonic devices. For example, ZnO nanostructures like nanowire/nanorod shows near-cylindrical geometry and large refractive index (~2.0) which is important for making optical resonant cavities to facilitate highly directional lasing at room temperature [Yang *et al.* (2002), Johnson *et al.* (2003)]. Recently, ZnO nanowires are reported as sub-wavelength optical waveguide [Law *et al.* (2004)]. These findings show that ZnO nanostructures can be potential building blocks for integrated optoelectronic devices.

1.2.4 Magnetic Properties

ZnO is diamagnetic in nature. However, it has been widely used as a host material for the development of transition metal doped diluted magnetic semiconductor for the purpose of spintronic devices [Hadis Morkoc and Umit Ozgur (2009)]. Spintronic materials exhibit the combination of ferromagnetic, semi-conducting as well as magneto-optical properties and can be much more efficient than the current electronic and opto-electronics devices. Due to wide band gap, the ferromagnetic ZnO is regarded as an excellent material for short wavelength magneto-optical devices [Ando *et al.* (2001)]. Magnetic dopants, such as Mn, Fe, Ni, Co, etc., have been extensively studied to enhance the ferromagnetism in ZnO semiconductor at room temperature. In addition, the ability to grow magnetic ZnO nanostructures enables the use of nanoscale spin-based devices [Ronning *et al.* (2004)].

1.2.5 Sensing Properties

Among the different metal oxides (e.g. SnO₂, ZnO, CuO, WO₃), ZnO is found highly sensitive to distinguish different gas molecules and biomolecules [Wollenstein *et al.* 2003]. Generally, in gas sensors, detection of gas molecules is achieved by measuring the resistivity change in the material [Hadis Morkoc and Umit Ozgur (2009)]. It is found that the surfaces of metal-oxide are rich in native defects like vacancies. For example, presence of V_O and V_{Zn} are reported in ZnO [McCluskey *et al.* (2009)]. These vacancy sites are electrically and chemically active and often, significantly change the conductivity of oxide in the presence of different gas environments [Hadis Morkoc and Umit Ozgur (2009)]. For example, upon adsorption of charge accepting molecules at the vacancy sites, such as NO₂ and O₂, electrons are effectively depleted from the conduction band, leading to a reduced conductivity. On the other hand, molecules, such as CO and H₂, would react with surface adsorbed oxygen and consequently remove it, leading to an increase of conductivity [Fan *et al.* (2005)]. ZnO bulk and thin films, working as a solid state gas sensors already have been utilised for CO [Ryu *et al.* (2003)], NH₃ [Sberveglieri *et al.* (1995)],

alcohol [Trivikrama *et al.* (1999)] and H₂ [Cheng *et al.* (2004)] sensing under elevated temperature (~400 °C). From the aspect of sensing performance, one dimensional ZnO, such as nanowires and nanorods, is expected to be superior to its two dimensional thin film counterpart [Kolmakov *et al.* (2004)]. On the other hand, the key factor for biosensors is the sensitivity of material with respect to the small change in the *pH* of concentration created by the release of H⁺ ions during biochemical reactions. The basic principle for the *pH* detection is the polarization-induced bound surface charge by interaction with the polar molecules in the liquids. One dimensional ZnO biosensors, due to stability in air, non-toxicity, chemical stability, electrochemical activity, ease of synthesis, and bio-safe characteristics, have been found to be advantageous. However, only limited successes have been achieved in developing the ZnO based biosensors [Kim *et al.* (2006); Batista *et al.* (2005); Kang *et al.* (2005); Dulub *et al.* (2005); Al-Hillia *et al.* (2007); Al-Hilli *et al.* (2006)]. The sensitivity (change in surface potential) of ZnO is observed as high as ~59 mV per decade change in the *pH* value at room temperature and application of ZnO nanorods as *pH* sensors for intracellular chemical sensing is under progress [Al-Hilli *et al.* (2006)].

1.2.6 Other Applications

Apart from the applications mentioned above, zinc oxide can also be used in other branches of industry, for example, rubber industry, textile industry, photocatalysis, pharmaceutical, cosmetic industries and many more. In rubber industry, ZnO is used as an additive to increase the thermal conductivity of typical pure silicone rubber [Das *et al.* (2011)]. ZnO shows better photocatalytic activity under the UV light [Kuo *et al.* (2007), Darzi *et al.* (2009)]. In the presence of a photocatalyst, an organic pollutant can be oxidised directly by means of a photogenerated hole. ZnO provides similar or superior activity to that of TiO₂, but is less stable and less sensitive to photocorrosion [Hariharan *et al.* (2006)]. In textile industry, ZnO nanostructures have become very attractive as UV-protective textile coatings for water repellent and self-cleaning [Uddin *et al.* (2008); Gao *et al.* (2009); Atienzar *et al.* (2010); Lim *et*

al. (2010); Gomez *et al.* (2013); Tanasa *et al.* (2012); Vigneshwaran *et al.* (2006)]. For an example of self-cleaning activity, when ZnO nanowire is coated over cotton fabric, it shows considerable degradation of methylene blue under UV irradiation [Ates *et al.* (2012)]. Due to its antibacterial, disinfecting and drying properties, zinc oxide is widely used in the production of various kinds of medicines [Liu *et al.* (2013)]. ZnO possesses the characteristics to absorb UV radiation and is further used in sunscreen creams [Piroot *et al.* (1996); Lansdown *et al.* (1997)]. These creams protect the skin from UV rays of sun light without creating any aggravation to the skin.

Therefore, looking at the varieties of application of ZnO in the field of electronic, photonic, and spin-based devices, it is proved itself as a multifunctional material. Despite this, progress, there are still few areas on ZnO that need further investigation so that it can replace the highly successful GaN that competes for similar applications. ZnO can also be obtained in different nanostructures such as nanowires, nanorods, etc which may open up the path to create a new age of devices, but a deliberate effort has to be expanded for ZnO nanostructures to be taken seriously for large-scale device applications.