CHAPTER II

REVIEW ON ZnO THIN FILMS

2.1. Introduction

Semiconductor nanoparticles have attracted much attention in recent years due to novel optical, electrical and mechanical properties, which results from quantum confinement effects compared with their bulk counterparts. Among various semiconductor nanoparticles, nano-sized zinc oxide (ZnO) particles are the most frequently studied because of their interest in fundamental study and also their applied aspects such as in dye sensitized solar cell (Qifeng Zhang *et al*., 2009), gas sensors (Liwei Wang *et al*., 2012), microwave absorber (Ahsanulhaq Qurashi *et al*., 2009), optical switches (Hannes Kind *et al*., 2002) and light emitting diodes (Jae-Hong Lim *et al*., 2006). ZnO is one of the most important nanomaterials for integration in microsystems and biotechnology. It is a semiconductor with a wide band gap of 3.37 eV, high melting point 2248 K and large exciton binding energy of 60 meV. This makes it useful in a number of photonic applications. Due to its non-centrosymmetric characteristics, it is piezoelectric and is used in electromechanical coupled sensors and transducers (William *et al*., 2005).

ZnO crystals are composed of alternate layers of zinc and oxygen atoms disposed in a wurtzite hexagonal close packed structure with a longitudinal axis (c-axis) as shown in Figure 2.1. The oxygen atoms (ions) are arranged in close hexogonal packing, with zinc ions occupying half the tetrahedral interstitial positions with the same relative arrangement as the oxygen ions. In this crystal structure, both zinc and oxygen ions are coordinated with four ions of the opposite charge, and the binding is strong ionic type. Owing to the marked difference in size, these ions fill only about 44% of the volume in a ZnO crystal leaving some relatively large open spaces (0.095 nm). Typical properties of ZnO are listed in Table 2.1 (Brown *et al*., 1976, Brook *et al*., 1991.)

Table 2.1: Basic properties of ZnO

Crystal structure	Hexagonal, wurtzite
Molecular weight	Zn:65.38, O:16 and ZnO:81.38
Lattice constant	a = 3.246 Å, c = 5.207 Å
Density	5.67 g/cm^3 or 4.21 x 10^{19} ZnO molecules/mm^3
Cohesive energy	E_{coh} = 1.89 eV
Melting point	T_m = 2250 °K under pressure
Heat of fusion	4. 470 cal/mole
Thermal conductivity	25 W/mK at 20 °C
Thermal expansion coefficient	4.3 x 10^{-6} / °K at 20 °C 7.7 x 10^{-6} / °K at 600 °C
Band gap at RT	3.37 eV
Refractive index	2.008
Electron and hole effective mass	m_e^* = 0.28, m_h^* = 0.59
Debye temperature	370 °K
Lattice energy	964 kcal/mole
Dielectric constant	ε_0 = 8.75, ε_∞ = 3.75
Exciton binding energy	E_b = 60 meV
Pyroelectric constant	6.8 Amp./sec/cm^2/°K x 10^{10}
Piezoelectric coefficient	D_{33} = 12 pC/N

Figure 2.1(a) shows the structure of ZnO unit cell, including the tetrahedral-coordination between Zn and its neighboring O. (b) ZnO has a noncentrosymmetric crystal structure that is made up of alternate layers of positive and negative ions, leading to spontaneous polarization $\vec{P}$. The pseudo ferroelectric switching involves the reversal of these dipole moments. (c) A low-energy twin boundary that was used to model the grain boundary. (d) A 3D representation of the domain wall in the $\left(1\ \bar{1}\ 0\right)$ plane, separating two oppositely-polarized ZnO domains. (e) The corresponding 2D representation of Figure (d).

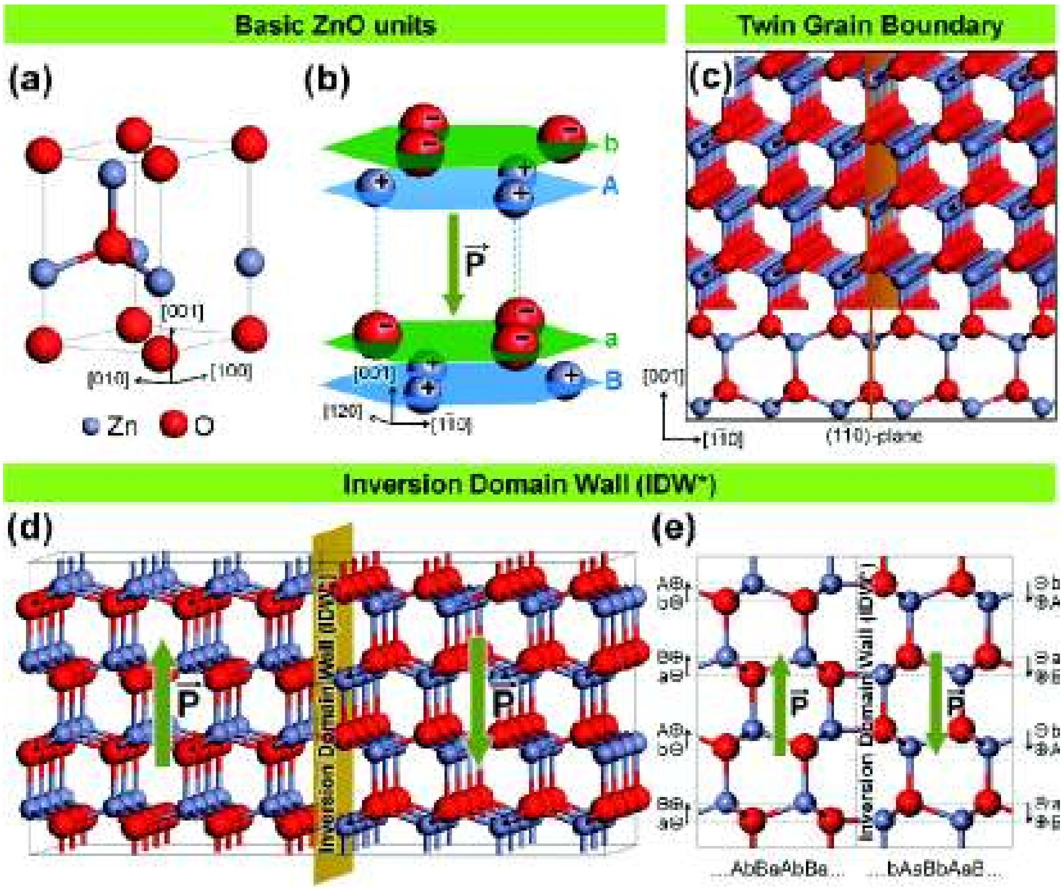

Figure 2.1: The atomistic model of wurtzite ZnO, a twin grain boundary and an inversion domain wall.

Pure ZnO, carefully prepared in a laboratory, is a good insulator. However, its electrical conductivity can be increased by special heat treatments and by introducing specific impurities into the crystal lattice. ZnO can even be made to exhibit metallic conductivity as for transparent electrodes similar to ITO. In general, 0.5-1% addition of trivalent cations (e.g Al and Cr) decrease the resistivity of ZnO by about 10 orders of magnitude (Brook *et al*., 1991).

2.2. ZnO Thin Films

Thin films are layers of a material whose thickness ranges from fractions of a nanometer to several micrometers. They are deposited on the substrate to achieve better properties than that of bulk materials. Electronic semiconductor devices and optical coatings are the main applications benefiting from this technology. Thin films of ceramic materials like $BaTiO_3$, ZnO etc , has the huge applications in Piezoelectric sensors.

The nanostructured thin film enhances the efficiency of solar cells, memory storage capacity of computers, reduces the costs of devices as well as material losses. However, thin films had to be developed using new semiconductor materials, including amorphous silicon, copper indium desalinize, cadmium telluride, zinc supplied, Zinc oxide and film crystalline silicon.

The pivotal role of thin film technology in the development of such diverse and challenging frontiers as microelectronics, optical coatings and integrated optics, thin film superconductivity and quantum engineering, surface science, engineering and technology, micro-magnetism, metallurgical coatings and amorphous materials are now a part of literature (Tina *et al*., 2008, Chakra borty *et al*., 2004, Bernardino *et al*., 1997, Wu *et al*., 2001, Chen *et al*., 2003). Deposition of thin films increases the contact area of the cell components, resulting in a high fraction of reactants.

ZnO, transparent conducting films continue to receive considerable attention from both fundamental and application point of view primarily because of their useful properties (Fifing Zhang *et al*., 2009, Lwei Wang *et al*., 2012, Ahsanulhaq Qurashi *et al*., 2009, Hannes Kind *et al*., 2002, Jae-Hong Lim *et al*., 2006, William *et al*., 2005). The thin films of ZnO generated immense interest as a transparent semiconducting materials, because of coating of this material are relatively inexpensive and have sharp UV cut-off, that is why they are used as hetrojunction solar cells based on CdTe, $CuInSe_2$ (Romeo *et al*., 2004, Kazmerski *et al*., 1976) and CuInS (Allsop *et al*., 2009). ZnO is also used for piezoelectric devices such as surface acoustics wave (SAW) devices (Qi Jie Wang *et al*., 2008). Among the transparent conducting oxides, ZnO is probably the most commonly studied material as it has the following unique merits.

i) ZnO is a wide band gap semiconductor that has huge potential for electronic, opto-electronic and optical applications.

ii) It is unique in having semiconducting, piezoelectric, and pyro-electric properties, and is an ideal candidate for fabricating electromechanically coupled devices (Xudong Wang *et al*., 2006).

iii) ZnO is a biodegradable and possibly biocompatible material suitable for medical and biological applications (Yangyang Zhang *et al*., 2012).

Various techniques have been used for deposition of ZnO thin film namely, Pulsed laser Deposition (Christian C Weigand *et al*., 2011), Spray Pyrolysis (Nielsen *et al*., 1982), Metal Organic Chemical vapour Deposition (An-Jen Cheng *et al*.,), DC magnetron Sputtering (Arroyo-Hernández *et al*., 2011), photo Induced MOCVD (Feng Shi and Chengshan Xue 2012), Molecular beam epitaxy (Kwang Gug Yim *et al*., 2011). The ZnO deposited from the above techniques has both low resistivity and high transparency in the visible region. There is lot of variation in the results reported by different workers using different techniques. The variation is due to the difference in the deposition parameters, and purity of the elements. The ultraviolet luminescence from nanophase ZnO crystals in the form of thin film or particles has been widely studied in recent years (Kim *et al*., 2002, Liu *et al*., 2008, Liu *et al*., 2006, Rode *et al*., 2003, Fouchet *et al*., 2007, Chang *et al*., 2009, Colis *et al*., 2006, Damonte *et al*., 2007, Bouloudenine *et al*., 2006, Choi and Kim 2007, Belghazi *et al*., 2009, Belghazi *et al*., 2007, Ma *et al*., 2008, Belghazi *et al*., 2009, Petersen *et al*., 2008, Lee *et al*., 2002). By optimizing the process parameters in the thermal evaporation systems we can make ZnO nano-dots, nano-rods, nano-springs and nano-belts (Mandal *et al*., 2006, Deepa *et al*., 2009, Srivastava *et al*., 2007, Fukumura *et al*., 2004, Srivastava *et al*., 2005, Bahadur *et al*., 2007).

The preparation of ZnO thin films has been the subject of continuous research for a long time because the properties of ZnO films depend upon the method of preparation. Currently, there is a great interest in the methods of creating nanostructures on surfaces by various self-organizing techniques. These nanostructures form the basis of nanotechnology applications in sensors and molecular electronics for next generation high performance nano-devices. ZnO exist in a variety of nanostructures (Ahsanulhaq Qurashi *et al*., 2009, William *et al*., 2005, Xudong Wang *et al*., 2006) and is expected to be the next most important nanomaterial after the carbon nanotubes.

One of the most popular growth techniques for early ZnO investigations was sputtering (dc sputtering, RF magnetron sputtering and reactive sputtering). As compared to sol gel and chemical vapor deposition (Tiku *et al*., 1980, Kasuga and Mochizhuki 1981, Srikant *et al*., 1995), the magnetron sputtering was a preferred method because of its low cost, simplicity and low operating temperature (Hachigo *et al*., 1994). ZnO films grow at a certain substrate temperature by sputtering from a high purity ZnO target using an RF magnetron sputter system. For piezoelectric studies ZnO films have been deposited on diamond (Xue *et al*., 2002, Lu *et al*., 2001, Jeong *et al*., 2003), glass, GaAs and Si substrates (Chen *et al*., 2003, Water and Chu 2002, Li *et al*., 2003). Kim *et al*., (2000a) and Kim *et al*., (2000b) have been reported high quality single crystal ZnO films prepared on sapphire by RF magnetron sputtering. In the sputtering growth of oxide films, O^{2-} ions are mainly responsible for the resputtering phenomenon (Park and Le 1995, Tominaga *et al*., 1981). The stress in the sputtered ZnO was investigated as a function of the substrate temperature in the range of 250-450°C, the sputtering pressure and the type of substrates (Silicon, GaAs) (Maniv *et al*., 1982, Jou *et al*., 1992, Hinze and Ellmer 2000). Post deposition annealing also has been used to relieve the stress and improve the structure and optical properties of the sputtered ZnO films (Osaki and Gomi 2002, Ryu *et al*., (2002).

The main advantage of molecular beam epitaxy is its precise control over the deposition parameters and in situ diagnostic capabilities. For ZnO thin film deposition by MBE, Zn metal and O_2 are usually used as the source materials. High purity Zn metal is evaporated from an effusion cell, where the cell temperature can be varied to examine the effect of the Zn flux on the growth rate and material properties. Successful growth of ZnO films by using hydrogen peroxide vapor as a source of active oxygen has also been reported (Izyumskaya *et al*., 2004). RF radical sources are employed by most groups nowadays because of the high reactivity of oxygen radicals produced and reasonable oxygen pressures. The effect of substrate offset angle on MBE growth of ZnO on c-plane sapphire were investigated by Sakurai *et al*.,(2000). Nitridation of sapphire substrate was also used to improve the quality of ZnO films grown by plasma assisted MBE (Wang *et al*., (2003). The control over the ZnO surface polarity has also been achieved on GaN substrates by plasma assisted MBE (Hong *et al*., 2002). GaN is a closely lattice matched material to ZnO with a lattice mismatch of 1.8%. In this vein, Ko *et al*., (2000) studied the growth and characteristics of as grown and annealed ZnO thin films with buffer layers on GaN templates given by MOCVD on sapphire.

In the pulsed laser deposition method, high power laser pulses are used to evaporate a material from a target surface such that the stoichiometry of the material is preserved in the interaction. Single crystal ZnO has been used to grow high quality ZnO thin film very recently. A pure Zn metal is used only in rare cases (Fouchet *et al*., 2004, Prellier *et al*., 2003). The properties of the ZnO films depend mainly on the substrate temperature ambient oxygen pressure and laser intensity. Sankur and Cheung (1983) and Nakayama (1983) have reported on high quality ZnO growth by PLD. However the influence of the growth conditions on the ZnO properties was studied much later (Choopun *et al*., 1999, Singh *et al*., 2001, Matsubara *et al*., 2002, Craciun *et al*., 1994).

Among other growth methods, CVD technology is particularly interesting not only because it gives rise to high quality films but also because it is applicable to larger scale production. When metal organic precursors are used, the technique is MOCVD, metal organic vapor phase epitaxy or organometallic vapor phase epitaxy (OMVPE). In the case of hydride or halide precursors, the technique is named hydride or halide CVD or VPE (Kasuga and Ogawa 1983, Takahashi *et al*., 1999). In the CVD method ZnO deposition occurs as a result of chemical reactions of vapor phase precursors on the substrate, which are delivered into the growth zone by the carrier gas. The reaction takes place in a reactor where a necessary temperature profile is created in the gas flow direction. For hydride VPE growth of ZnO, hydrogen was employed as a carrier gas (Abduev *et al*., 1987, Rabadanov *et al*. 1979, Ataev *et al*., 1999). The ZnO films grown by this method shows quite high crystal, electrical and luminescence properties (Chukichev *et al*., 2002, Ataev *et al*., 1999). For ZnO growth, MOCVD/MOVPE technique typically involves the use of metal alkyls, usually dimethyl zinc (DMZn) or diethyl zinc (DEZn) in combination with a separate source of O_2 and argon or nitrogen as a carrier gas. In earlier investigations O_2 or H_2O were used as oxygen precursors (Lau *et al*., 1980, Smith 1983). However, DEZn and DMZn, are highly reactive with O_2 and water vapor so that severe premature reaction in the gas phase occurs in the cold zone of the reactor, resulting in the formation of white powder, that degrades the film quality. Nevertheless, great progress has been made in ZnO growth by MOCVD recently. For group VI precursor a variety of oxygen compounds were employed; isopropanol (i-PrOH) (Gruber *et al*., 2002), tertiary butanol (t-BuOH) (Kaufmann *et al*., 1988, Hahn *et al* 1998, Sallet *et al*., 2002, Kirchner *et al*., 2003), acetone (Kern and Heim 1970), Na_2O, etc (Ogata *et al*., 2001, Ogata *et al*., 2002, Ogata *et al*., 2003). Kirchner *et al*., (2003) have reported direct comparison of MOVPE growth of ZnO layers on c-plane sapphire using i-PrOH and t-BuOH as oxygen precursors and DEZn as a Zinc source. Great potential of nitrous oxide for MOVPE of ZnO was demonstrated by Ogata *et al*., (2001). Low reactivity allows one to grow ZnO films at a high substrate temperature that results in high crystal perfection and good optical quality of the material. High quality homoepitaxial ZnO layers were grown on bulk ZnO substrates by using Na_2O and DEZn (Ogata *et al*., 2002). The improvement of MOCVD technology also gave rise to great progress in the quality of ZnO layers grown with the use of DEZn and O_2. With the use of different precursor systems, the MOCVD/MOVPE method was successfully applied to the catalyst free growth of ZnO nanowires on various substrates such as Si, GaN/sapphire (Muthukumar *et al*., 2003, Zhong *et al*., 2004), c-plane sapphire (Park *et al*., 2002, Jeong *et al*., 2004) and GaAs (Lee *et al*., 2004).

Controlled growth of different dimensional nanostructures such as 1D nanowires, nanotubes or 2D nanosheets and nanodiscs and 3D nanocrystals or nanoparticles are of great importance in studying the physical properties of nanomaterials or constructing nanodevices (Hu *et al*., 1999). Bing Guo *et al*., (2003) studied the time resolved PL study of ZnO thin film grown on a Si substrate. Using zinc chloride as source material, Xu *et al*., (2004) fabricated ZnO nanowires and nanorods by vapor phase transport. ZnO based varistor materials have been synthesized using colloidal suspension and centrifugal separation method (Koch *et al*., 1985, Viswanath *et al*., 2001). Rao *et al*., (2005) prepared oxide nanomaterials using microwave assisted solvothermal method Electrical properties of thin films and optical properties of nanostructures were studied by Grundmann *et al*., (2005). MBE technique was used by Iwata *et al*., (2005) to grow ZnO layers and to study the bandgap energy. ZnO thin films were deposited on Si substrate by radio frequency (RF) magnetron sputtering from metallic zinc target by Ondo-Ndong *et al*., (2003). Undoped and Bi-doped nanocrystalline ZnO was prepared by the inert gas condensation method by Ce-Wen Nan *et al*., (1999). The electrical properties were discussed using impedance spectroscopy. Lee *et al*.,(2004) prepared ZnO thin films by DC or rf magnetron sputtering on glass substrates to study the structural, electrical and optical properties. Thin films of ZnO were deposited onto soda lime glass substrates by Martin *et al*., (2005) using the spray pyrolysis method. Lavrov (2003) analyzed the IR absorption spectroscopy of hydrogen related defects in ZnO crystals.

Al doped ZnO nanomaterials were grown by various techniques (Shou-Yi Kuo *et al*., Xiao-Tao Hao *et al*., 2006, Parmod Sagar *et al*., 2005, Jung *et al*., 2005, Noriaki *et al*., 2005, Cao *et al*., 2004, Hong *et al*., 2004, Su-Shia Lin*et al*., 2004, Shan and Yu, 2004, Lee *et al*., 2004). Co, Cr, Mn, Ni doped (Samanta *et al*., 2005, Kenji Ueda *et al*., 2001) ZnO nanomaterials were prepared and characterized. Ni doped ZnO powders were synthesized by Guangqing *et al*., and Zhingang Yin *et al*.,(2005) Various groups

(Li *et al.*,2006, Wang *et al.*, 2005, Shinde *et al.*, 2005, Mariana Diaconu *et al.*, 2005, Nagata *et al.*, 2004, Jiaping Han *et al.*, 2002, Tal Meron and Gil Markovich 2005, Ranjani Viswanatha *et al.*, 2004, Hua-Wei Zhang *et al.*, 2006, Alaria *et al.*, 2005, Nicola A. Spaldin 2004, Parmanand Sharma *et al.*, 2004, Roy *et al.*, 2004, Ip *et al.*, 2003, Paul Joseph *et al.*, 2005, Masahiro Kunisu *et al.*, 2005) worked for the magnetic behaviour of Mn doped ZnO nanocrystals and thin films. Using MBE method Mn doped ZnO were grown by Jung *et al.*, (2002), Kwang Joo Kim and Young Ran Park (2003). Naoyuki Ueda *et al.*, (1998), Look (1969) prepared cdo thin films on silica glass substrates by rf sputtering.

In order to realize the bandgap engineering to create the barrier layers and quantum wells in optoelectronic devices, the modulation of the bandgap is an important requirement. The bandgap can be increased by incorporating Mg (Ohtomo *et al.*, 1999, Choopun *et al.*, 2002, Gruber *et al.*, 2004) and decreased by Cd (Makino *et al.*, 2000, Ma *et al.*, 2004). One of the reports on the synthesis of $Mg_xZn_{1-x}O$ with a Mg content of up to 33% was by Ohtomo *et al.*, (1998) by PLD. It was found that MgO segregates in the wurtzite MgZnO lattice above 33% of Mg content, limiting the maximum bandgap to 3.9eV. XRD studies show that the a-axis length gradually increases and the c-axis length gradually decreases with increasing Mg content, and therefore the cell volume is hardly changed. Increasing the Mg composition further resulted in $Mg_xZn_{1-x}O$ films in metastable cubic phase with bandgaps above 5.0eV. The Mg content strongly depends on the growth temperature and consequently showing strong dependence of bandgap energy on the growth temperature ranging from room temperature to 750°C. For narrower band gaps, which are desirable for wavelength tunability and attaining bandgaps corresponding to the visible spectrum, the $Cd_xZn_{1-x}O$ alloy would be a good candidate because of the small direct bandgap of CdO (2.3eV). A decrease in the band gap down to 2.99eV could be achieved by incorporating Cd^{2+} with y=0.07. Ma *et al.*, (2004) succeeded in depositing good quality $Cd_xZn_{1-x}O$ thin films on glass and sapphire substrates using the DC reactive magnetron sputtering method. The samples exhibited good transmittance (over 85%) in the visible spectral range and a red-shift was observed in the PL with increasing Cd composition. The films with x less than or equal to 0.53 have single phase structures of pure $Cd_x Zn_{1-x}O$ with the c-axis perpendicular to the substrate surface , while the film with x=0.77 were mixtures of a hexagonal ZnO phase and a cubic CdO phase. The bandgap of the $Zn_{1-x}Cd_xO$ alloy films ($0<x < 0.53$) could be nonlinearly tuned from 3.28- 2.65eV with the Cd contents from x=0.0 to x=0.53. $Zn_xCd_{1-x}O$ nanostructured thin films were synthesized using spray pyrolysis method by Vigil *et al.*,(2000). Using the same method Tabet *et al.*, (2002) studied the structural and electrical characterizations of the $Zn_xCd_{1-x}O$ thin films. Nanocantilever arrays of Cd doped ZnO were fabricated in large scale by Shao-Min Zhou *et al.*, (2005). PLD method (Sang Yeol Lee *et al.*, 2004, Hong Seong Kang *et al.*, 2006, Makino *et al.*, 2001) was used to prepare alloyed ZnCdO films. Wurtzite heterostructures were successfully grown by remote plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD) by Atsushi Nakamura *et al* (Atsushi Nakamura *et al.*, 2000). Blue luminescence from textured ZnCdO films grown by Molecular Beam Epitaxy was observed by Keiichiro Sakurai *et al.*, (2000) MBE method was adopted by some other workers (Makino *et al.*, 2005, Jau-Jiun Chen *et al.*, 2005, Jau-Jiun Chen *et al.*, 2006, Keiichiro Sakurai *et al.*, 2002, Wang *et al.*, 2005). Using MOVPE method (Zuniga-Perez *et al.*, 2006, Gruber *et al.*, 2003) ZnCdO thin films were grown. ZnCdO was also grown using PVD (Fazhan Wang *et al.*, 2005), DC reactive magnetron sputtering (Ma *et al.*, 2004, Zhizhen Ye *et al.*, 2003), spray pyrolysis (Osvaldo Vigil *et al.*, 2000) and MOCVD (Beertram *et al.*, 2006).

Kathirvel *et al.*, reported that the ZnO thin film coated from Chemical bath technique act as an ammonia sensor at room temperature with quick recovery time of 45 seconds. Also deep level PL emission was absorbed at room temperature in addition to the band edge emission. It suggests that it can be used as an alternative for luminescent material.

ZnO thin films have been deposited onto the glass substrates by the sol-gel spin coating method at different chuck rotation rates. ZnO thin films deposited by spray pyrolysis (Nielsen 1982) and effect of indium on the properties of zinc oxide films were studied by Wang *et al.*, (2012) and Kim *et al.*, (2010). The XRD spectra indicate that the films are of polycrystalline structure. The grain size of crystallites was found to be in the range of 25-32 nm. The values of the optical band gap and Urbach energy change with chuck rotation rate. The shift of absorption edge is associated with Burstein-Moss effect. In the visible region, all the films are highly transparent more than 92 %. The I-V characteristics of the films in dark and under UV-illumination show that the sol gel spin coated ZnO thin films are sensitive to UV-light.

A series of ZnO films with various thicknesses was prepared on (001) sapphire substrate by pulsed laser deposition (PLD) using a Nd:YAG pulsed laser with a wavelength of 355 nm. The RT-PL measurements show that, for the films thinner than 4000 Ǻ, the position of the near band-edge emission exhibits large shift toward the lower-energy side while, for the films thicker than 4000 Å, it approaches to the value of bulk ZnO. These results are attributed to the fact that the films thinner than 4000 Å are under the severe tensile strain and it decreases with increasing the film thickness further. Therefore, it is believed that the films thicker than 4000 Ǻ are almost strain-free and exhibit the near-bulk ZnO properties. The near band-edge emission of bulk ZnO locates at 3.27 eV at room temperature. However, when the film is thin, the position of the near band-edge emission shifts toward the lower-energy side than that of bulk ZnO (Jae-Min Myoung *et al*., 2002).

The chemical bath deposition of ZnO thin films and the effect of annealing temperature have been studied. The crystallite size and band gap were found to change with the annealing temperature (Ta), the maximum grain size of the film is 60.993 nm at T_a=350ºC.

Polytypic ZnO thin films, with mixed evolution of hexagonal wurtzite and cubic zincblende structures, have been obtained by using sol gel spin coating. The films prepared at sintering temperature ~ 600 ºC yield maximum photocurrent and are more efficient for photosplitting of water. This can be attributed to the better optical absorption and decreased electrical resistivity of the samples. The effects of the thermal energy and the kinetic energy of the sputtered species on the growth of ZnO thin films were investigated by Kim *et al*.,(2000).

Pure ZnO and Al doped ZnO (1%) thin films were prepared by the sol-gel method associated with dip coating technique. The obtained samples were dried during 40 min at 200 ºC and then annealed at 500 ºC for one hour. The optical transmission spectra showed that the presence of Al in ZnO lattice improves the transmission in the visible and increases the optical gap. The introduction of aluminum atoms in the solution greatly enhances the UV emission with a shift to high energies of about 0.2 eV (Djouadi *et al*., 2012). Glassy thin films of undoped ZnO and Al^{3+} doped ZnO were synthesized at room temperature using chemical bath deposition and analyzed to determine their optical dispersions parameters namely: oscillator strength, oscillator energy, optical spectra moments, static refractive index and high frequency dielectric constants (Oriaku and Osuwa (2009).

The effect of preparative parameter, pH, of the sol on the properties of the sol-gel prepared ZnO films has been studied by Sivakumar *et al*., (2012). The increase in pH values of range 4, 6, 8 and 10 decreases the bandgap energy from 3·32 to 3·14 eV.

In general, zinc acetate is the precursor material for preparation of ZnO films using sol–gel process or spray pyrolysis techniques (Chander 2005, Nielsen 1982). However, zinc nitrate has also been used for preparation of nanosized zinc oxide powder. For example, Liu *et al*., (2006) have described the formation of ordered porous ZnO film using zinc nitrate by electrodeposition method using polystyrine array templates. Studenikin *et al*., (1998) describe the formation of undoped ZnO film by spray pyrolysis of zinc nitrate solution at high temperature. Zinc nitrate is also used for the synthesis of ZnO nanoparticles (Yoshida and Minoura 2000). Micropatterns of ZnO have been synthesized (Kim *et al*., 2005) on photocatalytically activated regions of TiO2 in an aqueous solution of zinc nitrate and dimethylamine- borane by an electroless deposition process. The as deposited ZnO micro patterns showed a polycrystalline quartzite structure. There are several reports (Liu *et al*., 2006, Studenikin *et al*., 1998, Yoshida and Minoura 2000) in which ZnO have been grown using zinc nitrate as the starting material.

Metal-doped ZnO films with various metal contents (Al, Ag and Li of 0–10 wt. %) were prepared by RF magnetron sputtering system with specially designed ZnO targets. The structural, optical and electrical properties of MZO films depended on the type and content of doping in target. Electrical resistivity of LZO thin films increased with increasing Li doping amounts between 0 and 4 wt. %, suggesting that an epitaxial LZO film has high resistivity (Sang-Hun Nam *et al*., 2010).

Among the various semiconducting oxide materials, ZnO has been chosen as the key gas sensing material since it has been widely studied and easily fabricated as high quality films by sputtering, compatible with Si-based IC process. In 1959, Heiland reported on the gas sensitive behaviour of ZnO's electrical conductivity (Heiland 1982). Recently ZnO has also attracted attention for it's possible application in short wavelength light emitting diodes (LEDs) and Laser diodes (LDs) because the optical properties of ZnO are similar to those of GaN (Komatsu *et al*., 2002, Ryu *et al*., 2000).

Lee *et al*., (1998) reported the dependence of the preferred orientation and grains size of sputtered ZnO films on film thickness. As the film thickness increased, the

(0 0 2) peak was reduced while other peaks such as (1 0 1), (1 1 0) and (1 1 2) appeared. For the thickness of 4.4 micrometer, the intensity of the peak (1 0 1) became as strong as that of (0 0 2) peak. Chou *et al*., (1994) investigated the effect of excess Zn on the structure of ZnO films deposited by DC reactive sputtering with a Zn metal target. When oxygen was gradually increased, the color of the films changed from dark brown to yellowish brown and finally transparent due to the increase of O content in the films. Also, the XRD patterns changed from weakly crystallized to a highly oriented (0 0 2) ZnO structure as the Zn content decreased.

Zhang *et al*., (2003) also showed a significant increase in the film crystalline with the increase of the O_2/Ar gas ratio during sputtering due to decrease in sputtering rate. The effect of sputtering pressure on the crystallinity was also investigated (Mainiv *et al*., 1982, Zhu *et al*., 2000). Zhu *et al.,* (2000) observed that the decrease of sputtering pressure improved the crystalline quality because depositing particles with high kinetic energy resulted in high surface mobility. (Bakers *et al*., 1997) deposited two ZnO films at room temperature with 90 and 180 w of sputtering power respectively. Although the ZnO (0 0 2) peaks are similar, the films at lower power gave noticeably better crystallinity and less stress. Thus, the ZnO films with higher substrate temperature show better crystalline quality (Zhu *et al*., 2000, Subramanyam *et al*., 1999, Yoshino *et al*., 2000) investigated the effect of substrate on sputtered ZnO films using Al, Au, Ni, Cu and glass substrates. ZnO films on glass, Au and Al showed good c-axis orientation, while the orientation of films on Ni and Cu was rather disordered.

Gupta and Mansingh (1996) studied the influence of post- deposition annealing on the structural and optical properties of ZnO films deposited at room temperature. The deposited ZnO films on quartz substrates exhibited compressive stress. The increase of post annealing temperature reduced this compressive stress and improved crystallinity. After annealing at 400 ºC for 1hour in air, the film became almost stress free, while annealing above 400 ºC induced tensile stress in the films as well as grain growth. The ZnO thick film sensor was investigated by Rao *et al*., (1999). The gas response of chemically deposited ZnO films were investigated by Mitra *et al*.,(1998).The ZnO sensors showed higher sensitivity to liquid petroleum gas (LPG) in the 0.4-1.6 vol % concentration in Air.

Dong *et al*., (1997) prepared nanometer ZnO by the arc plasma method and showed that nano-ZnO exhibit higher sensitivity compared to coarse-grained ZnO and lower operating temperatures (200-300 ºC). The effect of film thickness on sensor performance was investigated by Chang *et al*., (2002). Structural, morphological, and optical properties of undoped and Al-doped ZnO thin film spin-coated on glass substrates were investigated by Znaidi *et al*., (2010) .The prepared samples display a very strong (0 0 2) preferential orientation. The optical properties determined by m-lines spectroscopy are promising for further wave guiding application. All the films are displaying well guided modes meaning that the coupling and confinement of the light in the film is efficient. The optical loss was estimated to be around 1.6 dB/cm by using the moving fiber method.

Highly textured ZnO films exhibiting columnar structure have been grown successfully on amorphous glass substrates at various substrate temperatures by Saravanakumar *et al*., (2011). The results from XRD and AFM, showing the particle size decreasing with increases in substrate temperature. Dark-field cross-sectional TEM micrograph shows the growth pattern of the film is columnar. The change in the crystallite direction at grain boundaries was explained from the bright and dark columns.

Aluminum doped zinc oxide (AZO) thin film was deposited on microscopic glass substrate following a chemical technique called successive ion layer adsorption and reaction (SILAR). Al doping was found to increase the film growth rate. It was approximately 0.20 µm/mole/dipping for ZnO film and 0.22 µm/mole/dipping for AZO film. The resistance of the film decreased about one order in magnitude due to Al doping. The activation barrier value of 0.31 eV for ZnO film was however found to be unaffected due to aluminum incorporation.

Kathalingam reported the growth of ZnO thin films on Zn substrate by CBD (Kathalingam *et al*., 2010, Ku *et al*., (2007) used aqueous solution of zinc acetate dehydrate 9.05M) and hexamethylenetetramine for the depostion of ZnO films on ITO. Peng *et al*., (2006) used an equimolar (0.03M) aqueous solution of Zinc nitrate and hexamethylenetetramine to deposit ZnO thin film on ITO substrate. Drici *et al*., (2004) reported CBD growth of ZnO on bare soda glass and ITO coated glass using zinc acetate (0.0188 mol/dm^3) and ethylenediamine (0.03mol/dm^3). Similarly Saeed *et al*., (1995) have also used zinc acetate and ethelenediamine for the deposition of ZnO thin films on a glass slide.

ZnO thin films were grown on Si (1 0 0) substrates by pulsed laser deposition using a ZnO target. The substrate temperature was varied in the range of room temperature to 800 ± 5ºC, and the oxygen partial pressure of 0.1333 Pa (1 mTorr) to 1333 Pa (10 Torr).PL spectra of the ZnO thin films grown at different substrate temperatures from RT to 800 ± 5 ºC. At the temperatures of RT and 200±5 ºC, both UV and visible emission are very small. At 400 and 800 ± 5 ºC, the visible PL peak is dominant, while at 600 ± 5ºC an intense UV peak is observed with little visible luminescence. Based on the UV to visible emission ratio, as calculated by the integrated intensities of the two peaks, it is concluded that 600 ±5 ºC is the optimum substrate temperature (Xianqi Wei *et al*., 2013).

Nanosized ZnO films were prepared by sol-gel process on quartz substrates. The effects of sol concentration and annealing temperature on the surface morphology, microstructure and optical properties of the films were investigated. The optical band gaps in ZnO films by various annealing temperatures are from 3.265 eV to 3.293 eV (Xiao-Bo Lou *et al*., 2007). The violet emission located at 438 nm is probably due to the recombination transitions relating to the interface traps at the grain boundaries.

Zinc oxide (ZnO) thin films were grown on glass and copper substrates by the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The study of surface morphology reveals that deposited ZnO films take many shapes: nanorods, nanoprisms, flowerlike, needles, spindles and hexagonal structures. Obtained ZnO films exhibit a high transmittance of 90% in visible band, and optical band gap of 3.27 eV. Structured ZnO films have been fabricated on soda-lime glass slides at a low temperature (80–85°C) by a chemical bath deposition method in one step without seed layers. Mixed aqueous solutions of zinc sulfate, ammonia and thiourea were used at alkaline conditions. The influence of the ammonia concentration in the initial solution on the property of the deposited film was investigated systematically. Growth of ZnO thin film in an efficient way of CBD was reported by (Ortega-Lopez *et al*., 2003). ZnO precipitates and thin solid films were prepared, respectively, in the same solution via a modified chemical bath deposition method. When the citric acid as capping molecules was added into the solution, the precipitates were the pure microspheres and the ZnO hierarchical structure vanished completely. On the other hand, the thin solid films became more exiguous with the bigger surface areas in the solution with citric acid. ZnO thin films have been deposited by chemical bath deposition (CBD-ZnO). The deposition conditions, i.e. the pH and the temperature of the bath, have been adjusted to achieve the deposition of porous, but adherent, thin films. After annealing in air half an hour at 300 ºC ZnO films crystallized in the hexagonal structure are obtained. The films are porous and the grains are columnar, which allows achieving films with large surface area. The films are semi-conductor with a n-type conductivity. It is shown that the grain boundary influence on the conductivity is stronger in longitudinal than in transversal structures.

The influence of the choice of temperature, pH value, counter-ion, deposition time, and seed layer on the morphology as well as electrical properties of ZnO films grown from chemical bath deposition (CBD) are investigated by Chu *et al*., (2009)

. Chemical bath deposition of ZnO thin films using six different complexing agents, namely ammonia, hydrazine, ethanolamine, methylamine, triethanolamine and dimethylamine, is investigated. As-grown films were mainly ZnO_2 with a band gap around 4.3 eV. Films annealed at 400 ºC were identified as ZnO with a band gap around 3.3 eV.

The ZnO thin films were prepared by chemical bath deposition technique using glass substrates with bath temperature 80ºC and annealing temperatures 300 350 and 400 ºC. The optical absorbance of the deposited films was characterized by UV-VIS-NIR spectrometry and shows the presence of direct transition with band gap energy 3.32eV and after annealing, it decreases to 3.12 eV, 3.04 eV and 3.10 eV respectively.