2.1 Zinc Oxide Background Information

2.1.1 Introduction

Zinc oxide has attracted significant attention as a material for ultraviolet (UV) light-emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers and gas sensors and also as a window material for displays and solar cells. As a wide band gap semiconductor ($E_g = 3.37$ eV), zinc oxide is a candidate host for solid state blue to UV optoelectronics, including lasers. The applications include high density data storage systems, solid state lighting, secure communications and biodetection.

2.1.2 Natural sources and production

The most important zinc ore is zinc sulfide, found as the mineral sphalerite. The majority of zinc oxide is produced by the so called “French Process”, which has been utilized since 1844. For this metallic zinc is melted at 419.5°C in a graphite crucible and vapourized above 907°C. The zinc vapour then reacts with oxygen in the air to form zinc oxide, which normally consists of agglomerated zinc oxide particles with sizes ranging from 0.1μm to a few microns, and a purity of up to 99%. A modification of French process, known as the catalyst free combust-oxidized mesh (CFCOM) process, yields acicular ZnO nanostructures (rods, wires, tripods, tetrapods, plates) [Ralf Riedel et al., 2010]

2.1.3 Physical Parameters

Few important physical parameters [Han et al., 2002, Ralf Riedel et al., 2010, Claus F Klingshim et al., 2010, Klaus Ellmer et al., 2010] are given in the Table 2.1.
Table 2.1 Physical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable Phase at 300K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>‘a’ = 3.2495 Å</td>
</tr>
<tr>
<td></td>
<td>‘c’ = 5.2069 Å</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>For wurtzite – 2.049</td>
</tr>
<tr>
<td></td>
<td>For zinc blende – 2.008</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>Exciton Binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
</tbody>
</table>

2.1.4 Crystal Structure and Chemical Binding

Zinc oxide is a semiconducting compound of the group-II element $^{30}\text{Zn}$ and the group VI element $^{16}\text{O}$. Zinc has five stable isotopes, the prevalent ones are $^{64}\text{Zn}$ (48.89%), $^{66}\text{Zn}$ (27.81%), and $^{68}\text{Zn}$ (18.57%), while oxygen almost purely consists of the isotope $^{16}\text{O}$ (99.76%). Zinc has the electron configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2$: the oxygen configuration is $(1s)^2(2s)^2(2p)^4$.

The ZnO binding in its crystal lattice involves a sp$^3$ hybridization of the electron states, leading to four equivalent orbitals, directed in tetrahedral geometry. In the resulting semiconducting crystal, the bonding sp$^3$ state constitutes the valance band, while the conduction band originates from its antibonding counterpart. The resulting energy gap is 3.4 eV, i.e. in the UV spectral range, which has triggered interest in ZnO as
a material for transparent electronics. The cohesive energy per bond is as high as 7.52 eV, which also leads to a very high thermal stability: The melting temperature, $T_m = 2,242 \text{K}$. For comparison, the melting temperature of ZnSe is considerably lower: $T_m = 1,799 \text{K}$ \[Claus F Klingshim et al., 2010]\.

Zinc oxide normally has the hexagonal wurtzite (Fig 2.1 b) crystal structure. Additional to the wurtzite phase, ZnO is also known to crystallize in zinc blende (Fig 2.1 a) and cubic crystal structure. Fig 2.2 shows the XRD diffraction pattern of ZnO \[Yoshitake Masuda, 2010\]. For example nanoparticles formed by the oxidation of zinc vapor have the zinc blende structure when smaller than 20 nm, and form tetapod like crystals on further growth \[Shiojiri M et al., 1981\]. ZnO prepared via the flash evaporation method have a cubical crystal structure \[Tanigakita et al., 2002\].

![Fig 2.1](image)

**Fig 2.1** (a) zinc blende structure  
(b) Wurtzite structure.

The ZnO bond has a considerable degree of polarity. The bond polarity is caused by the very strong electronegativity of the oxygen, Which is as high as 3.5 on the Pauling scale. This is the second highest value of all chemical elements, it comes after the fluorine value of 4.0. Together with the quite low zinc electronegativity value of 0.91, this leads to an ionicity of 0.616 on the Phillips scale. Therefore zinc and oxygen in ZnO may well be considered as ionized Zn$^{2+}$ and O$^{2-}$. According to Pauling scale, the ionic bond radii of Zn$^{2+}$ and O$^{2-}$ amount to 0.074 and 0.140 nm \[Claus F Klingshim et al., 2010\].
Fig 2.2 XRD diffraction pattern of ZnO particulate films constructed from ZnO multi needle particles and thin sheets.

**JCPDS-ICDD**

<table>
<thead>
<tr>
<th>a</th>
<th>3.249</th>
<th>c</th>
<th>5.206</th>
</tr>
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SS/FOF: F27=131(0071, 29)

<table>
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<td>1</td>
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</tbody>
</table>

ZnO
Zinc Oxide
2.1.5 Mechanical properties

The mechanical properties of polycrystalline ZnO are of special importance for their applications as varistors. When a varistor experiences a high-current pulse, the electrical energy is quickly converted to heat. The inertia of the material, which resists its thermal expansion, and the resonances of the resultant elastic waves in the block, may lead to microcracks and finally to mechanical failure [Vojta A et al., 1997]. Characteristic values of mechanical properties of ZnO ceramics are 1.2-1.4 MPa for fracture toughness, and 100-125 Mpa for flexural strength [Ralf Riedel et al., 2010].

2.1.6 Thermodynamic properties

Intrinsic point defects are deviations from the ideal structure caused by displacement or removal of lattice atoms. Possible intrinsic defects are vacancies, interstitials, and antisites. In ZnO these are denoted as \( V_{\text{zn}} \) and \( V_{\text{o}} \), \( Zn_{\text{i}} \) and \( O_{\text{i}} \) and as \( Zn_{\text{o}} \) and \( O_{\text{zn}} \) respectively. There are also combinations of defects like neutral schotty (cation and anion vacancy) and Frenkel pairs (cation vacancy and interstitial), which are abundant in ionic compounds like alkali halides.
As a rule of thumb, the energy, to create a defect depends on the difference in charge between the defect and the lattice site occupied by the defect, e.g., in ZnO vacancy or an interstitial can carry a charge of ±2 while an antisite can have a charge of ±4. This makes vacancies and interstitials more likely in polar compounds and antisite defects less important. [Ralf Riedel et al., 2010].

2.1.7 Electronic band structure

The band structure of a given semiconductor is pivotal in determining its potential utility. Consequently, an accurate knowledge of the band structure is critical if a particular semiconductor material is considered for device applications. Several theoretical approaches of varying degrees of complexity have been employed to calculate the band structure of ZnO for its wurzite, zinc-blende, and rocksalt polytypes. Besides, a number of experimental data have been published regarding the band structure of the electronic states of wurtzite ZnO. X-ray- or UV reflection/absorption or emission techniques have conventionally been used to measure the electronic core levels in solids. These methods basically measure the energy difference by inducing transitions between electronic levels (for example, transitions from the upper valence-band states to the upper conduction-band states, and from the lower valence-band states) or by exciting collective modes (for example, the upper core states to the lower edge of the conduction band and to excitations of plasmons). Another important method for the investigation of the energy region is based on the photoelectric effect extended to the x-ray region, namely, photoelectron spectroscopy (PES). The peaks in emission spectrum correspond to electron emission from a core level without inelastic scattering, which is usually accompanied by a far-less-intense tail region in the spectrum. More recently, angle-resolved photoelectron spectroscopy (ARPES) technique has started to be used. This technique together with synchrotron radiation excitation has been recognized as a powerful tool that enables experimental bulk and surface electronic band structure determinations under the assumptions of k conservation and single nearly-free electron-like final band.
Since ZnO is a direct gap semiconductor with the global extrema of the uppermost valence and the lowest conduction bands (VB and CB, respectively) at the same point in the Brillouin zone, namely at $k = 0$, i.e. at the Γ-point, we are mainly interested in this region. The lowest CB is formed from the empty 4s states of Zn$^{2+}$ or the anti-bonding $sp^3$ hybrid states. A typical representation of the band structure looks as in Fig 2.3 [Fan et al., 2006].

![Band Diagram](image)

**Fig 2.3** Band Diagram.

### 2.1.8 Magnetic Materials and Nanomagnetism

A bulk ferromagnetic material displays a distinct nonlinear magnetic response to an applied magnetic field, referred to as a hysteresis loop or $M–H$ curve (Fig 2.4). Despite a ferromagnet’s characteristic spontaneous internal magnetic moment, without an applied field the magnetization is usually zero, that is, the $M–H$ curve starts at the origin. This is because in order to minimize the magnetostatic energy within a bulk ferromagnet, magnetic domains-small regions of magnetic alignment are formed. When a magnetic field is applied, the energy of the field can overcome the magnetostatic energy associated with the domain formation, and the magnetization of the material increases until all of the moments are aligned with the field.
Fig 2.4 Hysteresis loop or $M-H$ curve.

The magnetic alignment with the field occurs in two ways: (i) the walls that make up the domains can shift resulting in the “growth” of domains already aligned with the field at the expense of those not aligned, and (ii) the rotation of the magnetization vector away from one crystallographic axis and toward the field. The final magnetization associated with the complete alignment of the electronic spins is referred to as the saturation magnetization, or $M_s$. Once the magnetization is saturated, if the field is decreased back to zero, the magnetization will not return to zero. The material will maintain some net magnetization, called the remnant magnetization, $M_r$. In order for the magnetization to return to zero, a field must be applied in the opposite direction. The field at which the moments of the domains are again in different directions and the magnetostatic energy is minimized is called the coercivity, $H_c$. The full cycle of the magnetic field can be achieved by saturating the magnetization in the opposite direction, $-M_s$, going through the zero field resulting in a remnant magnetization in the opposite direction, $-M_r$, and increasing the field until $M = 0$, corresponding to $-H_c$. When the magnetization is once again saturated in the initial direction the hysteresis loop is complete [Cullity, 1972]. Materials used in magnetic information storage are chosen based on their values of the parameters described above. The magnetic components of a disk drive are the read head, the write head, and the media.
2.1.9 Physical References

Physical references for the main precursor material and the dopants used in this work are given in Table 2.2 [C Kittel, 2007].

Table 2.2: Physical references

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Atomic number</th>
<th>Electron Configuration</th>
<th>Lattice Parameter ‘a’ Å</th>
<th>Lattice Parameter ‘c’ Å</th>
<th>Melting point in K</th>
<th>Ionic Radii Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc (Zn)</td>
<td>hcp</td>
<td>30 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3d)^10 (4s)^2</td>
<td>2.66</td>
<td>4.95</td>
<td>692.7</td>
<td>0.74</td>
<td></td>
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<tr>
<td>Oxygen (O)</td>
<td>complex</td>
<td>8 - (1s)^2(2s)^2(2p)^2</td>
<td>-</td>
<td>-</td>
<td>54.36</td>
<td>1.4</td>
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<tr>
<td>Aluminium (Al)</td>
<td>fcc</td>
<td>13 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^1</td>
<td>4.05</td>
<td>-</td>
<td>933.5</td>
<td>0.50</td>
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<tr>
<td>Cadmium (Cd)</td>
<td>hcp</td>
<td>48 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3d)^10 (4s)^2(4p)^6(4d)^10(5s)^2</td>
<td>2.98</td>
<td>5.62</td>
<td>594.3</td>
<td>0.97</td>
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<tr>
<td>Manganese (Mn)</td>
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<td>25 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3d)^5</td>
<td>complex</td>
<td>-</td>
<td>1520</td>
<td></td>
<td></td>
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<tr>
<td>Cobalt (Co)</td>
<td>hcp</td>
<td>27 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3s)^2(3d)^7</td>
<td>2.51</td>
<td>4.07</td>
<td>1770</td>
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<tr>
<td>Nickel (Ni)</td>
<td>fcc</td>
<td>28 – (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3s)^2(3d)^8</td>
<td>3.52</td>
<td>-</td>
<td>1728</td>
<td>0.55</td>
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<tr>
<td>Cerium (Ce)</td>
<td>fcc</td>
<td>58 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3d)^10 (4s)^2(4p)^6(4d)^10(4f)^2 (5s)^2(5p)^6(5d)^2</td>
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<td>1072</td>
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<tr>
<td>Erbium (Er)</td>
<td>hcp</td>
<td>68 - (1s)^2(2s)^2(2p)^6 (3s)^2(3p)^6(3d)^10 (4s)^2(4p)^6(4d)^10(4f)^12 (5s)^2(5p)^6(5d)^2</td>
<td>3.56</td>
<td>5.59</td>
<td>1797</td>
<td>0.88</td>
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</tbody>
</table>
2.2 Literature Review- Introduction

Nanomaterials are extremely useful in both present and future work in various fields. Among them, semiconductor industry plays vital role in science and engineering. Nano-sized zinc oxide prepared through different methods has been studied. Also the preparation of zinc oxide and their change in properties by different doping elements are reviewed.

2.2.1 Chemical vapour deposition (CVD)

Groenen et al., (2001) have reported expanding thermal plasma created by a cascaded arc is used to deposit surface textured ZnO films. Films have been deposited at 150-350°C at a rate of typically 0.70 nm/s. They exhibit low resistivity (<10^{-3} Ωcm), high transmittance in the visible wavelength region (>80%) and a rough surface texture. The crystallite size and surface roughness increase with increasing deposition temperature and flow of argon ions.

Doyoung Kim et al., (2010) have investigated the low pressure chemical vapor deposition (LP-CVD) of Al doped ZnO thin film for transparent electrode of thin film solar cell. For LP-CVD, diethyl-zinc and trimethyl-aluminum were used as Zn and Al precursors, respectively, while pure water was used as a reactant. Self-textured surface was obtained, resulting in the increase of haze factor reaching up to 35%. Based on the characterization of LP-CVD ZnO thin films, fabricated the optimized superstrate p-i-n a-Si:H solar cell on glass substrate.

Liping Dai et al., (2008) have prepared a-b axis orientation ZnO film on silicon (100) substrate by a single source chemical vapor deposition technique. X-ray photoelectron spectroscopy results revealed that the film was very close to stoichiometry but with a small amount of zinc deficiency. Temperature dependent (10–300 K) ultraviolet photoluminescence of the film was presented. Comparing the photon energy
separation of the several groups in the near band edge ultraviolet luminescence bands, as well as the variation of the relative intensities and the shift of the luminescence lines at different temperatures, free-, bound-exciton and its assisted phonon emission were observed, which corresponded to the mechanism of the ultraviolet emission properties. A strong ultraviolet emission resulting from the recombination of free-exciton was observed at 300K photoluminescence spectrum examined in atmosphere environment. Contrasted to the relatively weak ultraviolet emission of the film in vacuum, atmosphere environment was found to be an important contribution to the strong ultraviolet emission of the film.

2.2.2 Sputtering

Jeong et al., (2008) have reported zinc oxide (ZnO) is an excellent piezoelectric material with simple composition. ZnO film is applied to the piezoelectric devices because it has high resistivity and highly oriented direction at c-axis. Structural and electrical properties in ZnO films are influenced by deposition conditions. Lithium-doped ZnO (LZO) films were deposited by RF magnetron sputtering method using Li-doped ZnO ceramic target with various ratios (0 to 10 wt.% LiCl dopant). LZO films revealed high resistivity of above 107 Ω cm with smooth surface when they were deposited with 4% LiCl-doped ZnO target under room temperature. However, their c-axis orientation was worse than the c-axis orientation of pure ZnO films.

2.2.3 Pulsed laser deposition (PLD)

Sandana et al., (2009) compared the forms and properties of ZnO nanostructures grown on Si (111) and c-plane sapphire (c-Al2O3) substrates using three different growth processes: metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), and physical vapor transport (PVT). A very wide range of ZnO nanostructures was observed, including nanorods, nanoneedles, nanocombs (Fig 2.5 (a,b)), and some novel structures resembling “bevelled” nanowires. PVT gave the widest family of
nanostructures. PLD gave dense regular arrays of nanorods with a preferred orientation perpendicular to the substrate plane on both Si and c-Al2O3 substrates, without the use of a catalyst.

![SEM images of ZnO nanostructures grown by PLD on Si (111) and Si(111) nanostructures grown by PVT](image)

**Fig 2.5** (Color online) SEM images of ZnO (a) nanostructures grown by PLD on Si (111) (b) on Si(111) nanostructures grown by PVT

Yaodong Liu *et al.*, (2007) deposited transparent aluminum-doped zinc oxide (AZO) thin films on quartz glass substrates by pulsed laser deposition (PLD) from ablating Zn–Al metallic targets. The structural, electrical and optical properties of these films were characterized as a function of Al concentration (0–8 wt.%) in the target. Films were deposited at a low substrate temperature of 150°C under 11 Pa of oxygen pressure. It was observed that 2wt % of Al in the target (or 1.37 wt.% of Al doped in the AZO film) is the optimum concentration to achieve the minimum film resistivity and strong ultraviolet emission. The presence of Al in the ZnO film changes the carrier concentration and the intrinsic defects.
Karamat et al., (2010) have focused on the detailed characterization of (ZnO)_{1-x}(CuO)_x(Al_2O_3)_{0.002} bulk samples and their thin films. XRD of bulk samples showed ZnO peaks without impurity phase which indicates maximum substitution of copper inside the ZnO lattice. Raman spectra showed a random shift of modes which might be due to point defects created by copper and aluminium substitution in ZnO. VSM showed weak ferromagnetic behavior in samples indicating Cu ion substitution in ZnO. XPS further confirmed the presence of Cu^{+2} states in the bulk samples. After detailed characterization of bulk samples, these samples were utilized as targets for deposition of thin films using PLD technique. Highly crystalline films of doped ZnO with (002) orientation were grown on (100) Si substrates. Compositional analysis of thin films done by XPS showed the presence of Cu^{+2} ions which is the source of ferromagnetism in the thin film samples. M-H curves showed the ferromagnetic behavior for the films. Thin films are magnetic and conductive at room temperature.
2.2.4 Chemical Bath Deposition (CBD)

Hani Khallaf et al., (2009) investigated the Chemical bath deposition of ZnO thin films using six different complexing agents, namely ammonia, hydrazine, ethanolamine, methylamine, triethanolamine and dimethylamine. As-grown films were mainly ZnO\(_2\) with a band gap around 4.3 eV. Films annealed at 400ºC were identified as ZnO with a band gap around 3.3 eV. X-ray diffraction and micro-Raman spectroscopy revealed that as-grown films consist mainly of cubic zinc peroxide that was transformed into hexagonal ZnO after annealing. High-resolution transmission electron micrographs showed small variations of the order of 10 nm in film thickness which corresponds to the average grain size. A carrier density as high as 2.24×10\(^{19}\) cm\(^{-3}\) and a resistivity as low as 6.48 × 10\(^{-1}\) Ωcm were obtained for films annealed at 500ºC in argon ambient.

Dewei Chu et al., (2009) investigated the unique structure of ZnO films obtained from aqueous solution method. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) analyses indicate that unique morphology and structure of the region where precipitation on the substrate may occur in parallel with other regions. This is accompanied by a decrease of the electrical resistivity in the absorbed region. A possible mechanism for the resistivity transformation was discussed.

2.2.5 Atomic Layer Deposition (ALD)

Alexandre Pourret et al., (2008) have reported ZnO is a good option for improving electron transfer between quantum dots, since it is an n-type conductor. Its bulk conduction-band edge is below that of bulk CdSe, so electrons can easily tunnel between dots, and may even be extracted into the ZnO matrix. Furthermore, although ZnO has a strong tendency to trap holes, its ability to conduct electrons is remarkably resilient to disorder and defects, and should not be affected by the residual hydroxyl groups typically observed in ALD films deposited at low temperatures.
Carcia et al., (2006) have fabricated high-performance ZnO thin-film transistors on gate dielectrics of HfO$_2$, HfSiO$_x$, and Al$_2$O$_3$, grown by atomic layer deposition (ALD). Devices on HfO$_2$ had a mobility of 12.2 cm$^2$/V s with a threshold voltage of 2.6 V and subthreshold slope of 0.5 V/ decade. Device characteristics for all ALD dielectrics exhibited negligibly small hysteresis, suggesting a low defect density at the interface of ZnO with the gate dielectric.

2.2.6 Metal Organic Vapour Phase Epitaxy (MOVPE)

Ogata et al., (2002) have homoepitaxially grown zinc oxide (ZnO) layers by metalorganic vapor phase epitaxy (MOVPE) on ZnO layers on sapphire as well as on Si. MOVPE-ZnO on ZnO/sapphire pretreated at 1000ºC exhibited in photoluminescence at 15K a narrowing of line width of the emission from donor-bound-excitons (D$_0^X$) to 3meV with an appearance of free excitons emission. MOVPE-ZnO on ZnO/Si indicated a c-axis orientation, and a strong band-edge emission with a lesser deep level, when ZnO/Si was pretreated at 800ºC. These results have demonstrated the high potentials of MOVPE growth technology for the growth of ZnO on sapphire or on Si by appropriate surface treatments towards optical and electrical applications.

2.2.7 Spray pyrolysis

Fawzy A.Mahmoud et al., (2009) have deposited thin films of zinc oxide (ZnO) onto glass substrates using a simple and inexpensive ultrasonically spray pyrolysis technique. Aqueous methanolic solution of zinc acetate was used as a spraying solution. The concentration of the solution was 0.1 M. The films prepared at different substrate temperature were uniform and well adherent to the substrates. X-ray diffraction (XRD) studies showed that all the films were polycrystalline in nanosize scale. The SEM photographs reveal the nano-size of the constituents. The electrical resistivity of the films was found to be dependent on the deposition temperature. The room temperature electrical
resistivity was found to be varying in the range $10^{-5}$ to $10^{-6}$ $\Omega \text{ cm}^{-2}$. The sample resistance is measured with the presence of CH$_4$ in Ar carrier gas.

Preetam Singh et al., (2007) have reported the preparation and characterization of both the ZnO nanocrystalline thin films and nanopowder by ultrasonic spray pyrolysis technique. ZnO films were grown on polished Si (100) and amorphous glass substrates at different deposition temperature range varying from 200 to 500ºC. Both orientation and the size of the crystallites were found to depend on the substrate and substrate temperature. XRD patterns of the films deposited on glass show strong c-axis oriented crystal structure with preferred (002) orientation, while those deposited on Si show predominant (100) orientation. Field emission scanning electron microscopy (FESEM) further confirms the a- and b-axis orientation in ZnO films on Si substrate with hexagonal columnar like grains and c-axis orientation in case of glass substrate with grains perpendicular to the substrate. The morphology and crystallite size of the ZnO nanopowder characterized by FESEM and TEM revealed that the powder consisted of the mixture of nanoparticles with particle size of 50–100 nm. The XRD results indicated that the synthesized ZnO powder had the pure wurtzite structure with lattice parameters $a$ and $c$ of 3.244 and 5.297 nm, respectively. High-temperature XRD studies of ZnO nanopowder showed that the crystallite size increased with increasing temperature with a systematic shift in peak positions towards lower 2$\theta$ values due to change in lattice parameters. Temperature dependence of the lattice constants shows linear increase in their values. Diffraction patterns of ZnO nanopowder obtained from TEM were also in agreement with the XRD results. The synthesized powder exhibited the estimated direct band gap ($E_g$) of 3.43 eV.

Kyu-Seog Hwang et al., (2007) prepared highly c-axis-oriented ZnO thin films on soda–lime–silica glass substrates by chemical solution deposition process using zincnaphthenate precursor as a starting material. In order to investigate the effect of pyrolysis temperature on properties of the films such as crystallinity, surface morphology and transmittance in visible spectra region, the precursor films were pyrolyzed at 300ºC
or 500°C, followed by final heat treatment at 600°C. Highly transparent films in visible spectra region were obtained. The relationship between residual organics and properties of the annealed films were discussed.

2.2.8 Sol-gel method

Nitul Kakati et al., (2010) fabricated ZnO thin films by sol-gel method using Zn(CH$_3$COO)$_2$·2H$_2$O as starting material in order to prepare an acetone gas sensor. A homogeneous and stable solution was prepared by dissolving the zinc acetate in a solution of ethanol and monoethanolamine. The sol-gel solution is coated on alumina substrates with various thicknesses by spin coating technique and heat treated to grow crystalline ZnO thin films. The effect of thickness on physical and electrical properties of as deposited ZnO thin films has been studied. The as deposited ZnO thin films were characterized by X-ray diffraction spectroscopy, field emission scanning electron microscopy and atomic force microscopy. The root mean square surface roughness factors increase with thickness of the films. The activation energies of the films are calculated from the resistance temperature characteristics. The sensitivities of the ZnO films towards the acetone gas were determined at an operating temperature of 200°C. The sensitivity towards acetone vapour is strongly depending on surface morphology of the ZnO thin films.

Duy-Thach Phan et al., (2011) deposited zinc oxide (ZnO) thin films on a polycrystalline (polycrystalline (poly) 3C–SiC buffer layer using RF magnetron sputtering and a sol–gel method. The post-deposition annealing was performed on ZnO thin films prepared using both methods. The formation of ZnO piezoelectric thin films with less residual stress was due to a close lattice mismatch of the ZnO and SiC layers as obtained by the sputtering method. Nanocrystalline, porous ZnO film prepared using the sol–gel method showed strong ultraviolet UV emission at a wavelength of 380 nm. The 3C–SiC buffer layer improved the optical and piezoelectric properties of the ZnO film produced by the two deposition methods. Moreover, the different structures of the ZnO films on the 3C–SiC
intermediate layer caused by the different deposition techniques were also considered and discussed.

Vishwas et al., (2010) have deposited zinc oxide (ZnO) thin films on glass substrates via sol–gel technique using zinc acetate dihydrate as precursor by spin coating of the sol at 2000 rpm. Effects of annealing temperature on optical, structural and photo luminescence properties of the deposited ZnO films have been investigated. The phase transition from amorphous to polycrystalline hexagonal wurtzite structure was observed at an annealing temperature of 400°C. An average transmittance of 87% in the visible region has been obtained at room temperature. The optical transmittance has slightly increased with increase of annealing temperature. The band gap energy was estimated by Tauc’s method and found to be 3.22 eV at room temperature. The optical band gap energy has decreased with increasing annealing temperature. The photoluminescence (PL) intensity increased with annealing temperature up to 200°C and decreased at 300°C.

2.2.9 Hydrothermal method

Naoyuki Ueno et al., (2010) synthesized aligned ZnO nanorods by a simple hydrothermal method without calcination. A seed layer of zinc acetate (ZnAc2)/sodium dodecyle sulfate (SDS) nanocomposite was used for nucleation of ZnO nanorods. First, a ZnAc2/SDS composite was deposited on a Si substrate by spin-coating. And then, ZnO nanorods were grown under hydrothermal conditions at 90°C. ZnO crystals were grown in the direction of c-axis perpendicular to the surface of the Si substrate. However, nucleation did not occur on the substrate of a ZnAc2 seed layer without SDS, indicating that the presence of the ZnAc2/SDS seed enhanced the nucleation of ZnO crystals. These results show that high dispersion of ZnAc2 in the nanocomposite effectively assists a nucleation of ZnO crystals.

Mouhssine Benlarbi et al., (2010) have demonstrated the possibility of designing semiconducting thin films with controlled electrochemical properties. The thin films are
composed of (i) an insulating binder and (ii) a semiconductor nanopowder which enables the fine tuning of the semiconducting properties of the layers. Thus, p and n-type silicon particles (obtained from a top-down technique), or metal-oxide ZnO, SnO2 and NiO nanoparticles (synthesized using a bottom-up protocol) are successfully integrated into spin-coated or screen-printed thin films and used as semiconducting materials. The flat band potential (Vfb) of the films is then easily tuned from 0V to −1.138 V.

Kenanakis et al., (2007) have grown zinc oxide nanostructured films by the aqueous chemical growth technique using equimolar aqueous solutions of zinc nitrate and hexamethylenetetramine as precursors. Silicon (100) and glass substrates were placed in Pyrex glass bottles with polypropylene autoclavable screw caps containing the precursors described above, and heated at 95°C for several hours. X-ray diffraction 2θ/θ scans showed that the only crystallographic phase present was the hexagonal wurtzite structure. Scanning electron microscopy showed the formation of flowerlike ZnO nanostructures, consisting of hexagonal nanorods with a diameter of a few hundred nanometers. The ZnO nanostructures exhibit an ultraviolet emission band centered at ~3.192 eV in the vicinity of the band edge, which is attributed to the well-known excitonic transition in ZnO.

2.3 Doped Zinc Oxide

2.3.1 Lithium doped ZnO

Antônio Claret Soares Sabioni et al., (2003) determined oxygen diffusion coefficients in pure and doped ZnO polycrystals by means of the gas-solid isotope exchange method using the isotope 18O as oxygen tracer. The diffusion experiments were performed from 900 to 1000°C, under an oxygen pressure of 10^5 Pa. After the diffusion annealings, the 18O diffusion profiles were determined by secondary ion mass spectrometry. The results of the experiments show that oxygen diffusion in Li-doped ZnO is similar to the oxygen diffusion in pure ZnO, while in Al-doped ZnO the oxygen diffusion is enhanced in relation to that observed in pure ZnO, in the same experimental conditions. Based on these results, they have proposed an interstitial mechanism for oxygen diffusion in ZnO.
2.3.2 Aluminium doped ZnO

Mondal et al., (2008) have deposited aluminum doped zinc oxide (AZO) thin film on microscopic glass substrate following a chemical technique called successive ion layer adsorption and reaction (SILAR). The technique involves multiple dipping of the substrate in an aqueous solution of sodium zincate kept at room temperature and deionized water kept near boiling point. Al doping was found to increase the film growth rate. It was approximately 0.20 μm/mole/dipping for ZnO film and 0.22μm/mole/dipping for AZO film. Structural characterization by X-ray diffraction (XRD) technique confirmed incorporation of aluminum in ZnO lattice. The c-axis orientation was significantly enhanced due to Al incorporation which was revealed from marked increase of (002) peak intensity compared to other peaks of hexagonal ZnO. The cross sectional view in SEM (Scanning electron micrograph) also reveals growth of large crystallites perpendicular to the substrate. 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.

Caglar et al., (2006), have deposited ZnO crystalline thin film onto glass substrates by the spray pyrolysis method. The crystallographic structure of the film and the size of the crystallites in the film were studied by X-ray diffraction. XRD measurement shows that the film is crystallized in the wurtzite phase and presents a preferential orientation along the c-axis. Only one peak, corresponding to the (002) phase (2θ=34.760º), appears on the diffractograms. Optical constants such as refractive index \( n \) and extinction coefficient \( k \), were determined from transmittance spectrum in the ultraviolet-visible-near infrared (UV-Vis-NIR) regions using envelope methods. Absorption coefficient \( \alpha \), and the thickness of the film \( t \) were calculated from interference of transmittance spectra. The energy band-gap, and the thickness of the films were evaluated as 3.283 eV and 635 nm, respectively.

Chen et al., (2008) prepared un-doped and doped ZnO powders by the sol–gel method. The nanoparticles were heated at 700–800 ºC for 1 h in air and then analyzed by
X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectra and photoluminescence (PL). The results of undoped (ZnO) and Al-doped ZnO (AZO) nanoparticles were also compared to investigate the structural characteristics and physical properties. XRD patterns of AZO powders were similar to those of ZnO powders, indicating that micro-Al ions were substituted for Zn atoms and there were no variations in the structure of the ZnO nanoparticles. From the XRD and SEM data, the grain size of the AZO nanoparticles increased from 34 to 40 nm when the annealing temperature was increased. The Raman intensity of the AZO nanoparticles (Al = 5 at %) increased when the annealing temperature was increased. Increasing the degree of crystalline not only reduced the residual stress, but also improved the physical properties of the nanoparticles.

Sahal et al., (2008) prepared thin films of intrinsic and Al-doped ZnO by the sol–gel technique associated with spin-coating onto glass substrates. Zinc acetate dehydrate, ethanol and monoethanolamine were used as a starting material, solvent and stabilizer, respectively. Structural, electrical and optical characterizations of the films have been carried out. All films are polycrystalline with a hexagonal wurtzite structure with a preferential orientation according to the direction (002). The four-point technique was used to characterize thin films electrically. All films exhibit a transmittance above 80–90% along the visible range upto 650 nm and a sharp absorption on set about 375 nm corresponding to the fundamental absorption edge 3.3eV. Intense UV photoluminescence is observed for undoped and 1% Al-doped ZnO films.

Serier et al., (2011) synthesized Al-doped ZnO powders by a Pechini process in order to obtain visible non-absorbent and near-Infrared absorbent particles. Firstly, it has been shown that synthesis under argon combined with the lowest synthesis temperatures (700ºC) allows getting the optimal properties for pure ZnO compounds due to creation of n-type defects segregated on oxide grain surface (Zn/O ratio superior to 1). Nevertheless, the near-Infrared absorption properties of the pure ZnO compounds remain low. The Al$^{3+}$ doping of ZnO compounds was then investigated. The Al solubility limit inside ZnO doped compounds decreases drastically with the grain size, i.e. with the synthesis
temperature. Then, the Al cations distribution varies inside ZnO grains, Al$^{3+}$ segregation at the grain surfaces taking place for high synthesis temperatures. The optimal optical properties (high near-Infrared absorption) are reached combining Al-doping and adequate synthesis conditions: annealing under argon at low temperatures. In these conditions, the highest extrinsic (via Al doping) and intrinsic n-types defects rates are reached.

### 2.3.3 Cadmium doped ZnO

Fahrettin Yakuphanoglu et al., (2010) have investigated the microstructure, and the electrical and optical properties of undoped zinc oxide (ZnO) and cadmium-doped ZnO (CZO) films deposited by a sol-gel method. The films have a polycrystalline structure with hexagonal wurtzite ZnO. Scanning electron microscopy (SEM) images indicated that the films have a wrinkle network with uniform size distributions. The elemental analyses of the CZO films were carried out by energy dispersive X-ray analysis. The fundamental absorption edge changed with doping. The optical band gap of the films decreased with Cd dopant. The optical constants of the films such as refractive index, extinction coefficient and dielectric constants changed with Cd dopant. A two-probe method was used to investigate the electrical properties, and the effect of Cd content on the electrical properties was investigated. The electrical conductivity of the films was improved by incorporation of Cd in the ZnO film.

Saliha Ilican et al., (2009) have deposited Cd$_x$Zn$_{1-x}$O films by sol–gel spin-coating method onto glass substrates. The Cd/Zn ratio in solution was changed from 0 to 1. Zinc acetate dehydrates, cadmium acetate dehydrates, 2-methoxyethanol and monoethanolamine were used as a starting material (zinc and cadmium), solvent and stabilizer, respectively. The crystal structure and orientation of the films were investigated by X-ray diffraction (XRD) patterns. XRD patterns show that the films are polycrystalline nature. As $x$ varies from 0 to 1, it was observed that the crystal structure changed from wurtzite (ZnO) to cubic (CdO) structure. The optical properties of these films have been investigated by means of the optical transmittance and reflectance.
spectra. A significant change in optical absorption edge, optical band-gap and optical constant with variation in composition was observed.

### 2.3.4 Manganese doped ZnO

_**Srinivasan et al., (2008)**_ synthesized Mn-doped and undoped ZnO nanocrystalline thin films by the sol–gel method using a spin-coating technique. The microstructure, morphology and optical properties of ZnO films were studied. The films that were dried at 623K and then annealed at 873K show hexagonal wurtzite structure, and presence of few manganese oxide peaks have also been observed from the XRD pattern. Two emission bands have been observed from CL spectrum. Mn-doped film showed shift in the near-band edge ultraviolet emission peak and also defect level emission peak in the visible range. Also SEM images of the films showed microstructure consisting of many spherical shaped nanoparticles and nanorods with wrinkle network. AFM image reflects the same structure observed in SEM and the surface roughness has been found for Mn-doped film.

_**Shinde et al., (2006)**_ prepared undoped and manganese doped zinc oxide (ZnO) thin films by pyrolytic decomposition of aqueous solution onto glass substrates. The structural properties studied using X-ray diffraction showed that the undoped ZnO films exhibit hexagonal wurtzite structure with strong c-axis orientation; however Mn doped ZnO films were polycrystalline. The surface morphological studies from SEM depicted the formation of clusters like structure of undoped ZnO while the Mn doped film showed the nanocrystalline grains on the surface. From the optical studies, the transmittance in the wavelength range 350–850 nm was found to decrease after doping of Mn. The optical band-gap was found to be 3.3 eV for undoped ZnO film and 3.10 eV for Mn doped films. From the electrical resistivity measurement, it is found that the Mn doping significantly caused to increase the room temperature resistivity from $10^4$ to $10^6$ $\Omega$cm.
Banu Bahsi et al., (2007) deposited both doped (Cu and Mn) and undoped zinc oxide thin films on glass substrates by a sol–gel technique. Zinc acetate, copper acetate and manganese nitrate were used as metal sources. A homogeneous and stable solution was prepared by dissolving Zinc acetate (ZnAc) in the solution of 2-propanol and ethanolamine (EA) followed by mixing with the doping solutions. ZnO:(Cu or Mn) thin films were obtained after preheating the spin coated films at 250°C for 1 min after each coating. A post-annealing at 550°C was applied to all films for 1 h after the deposition of the last layer. XRD analysis revealed that all films consist of single phase ZnO with zincite structure (Card no: 36-1451). While undoped films showed the strongest orientation, c-axis grain orientation was apparent in all films. TGA analysis of the undoped dried gel showed that weight loss continued until ~ 400°C. Compared to the undoped film, grain size of the films decreased by Mn doping and increased by Cu doping. All films had a very smooth surface with RMS surface roughness values between 0.23 and 1.15 nm and surface roughness increased by doping. Both Mn and Cu doping resulted in a slight decrease in the optical band gap of the films. The largest width of band tail was measured in Mn-doped film.

2.3.5 Cobalt doped ZnO

Patra et al., (2009) have grown large-area arrays of highly oriented Co-doped ZnO nano rods with pyramidal hexagonal structure on silica substrates by wet chemical decomposition of zinc–amino complex in an aqueous medium. In case of undoped ZnO with an equi-molar ratio of Zn²⁺ / hexamethylene tetramine (HMT), highly crystalline nano rods were obtained, where as for Co-doped ZnO, good quality nano rods were formed at a higher Zn²⁺ / HMT molar ratio of 4:1. Scanning electron microscope (SEM) studies show the growth of hexagonal-shaped nano rods in a direction nearly perpendicular to the substrate surface with a tip size of about 50nm. The XRD studies show the formation of hexagonal phase pure ZnO with c-axis preferred orientation. The optical studies also suggest Co ions to be present both in +2 and +3 oxidation states. From the photoluminescence studies, a defect-related emission is observed in an undoped sample of ZnO at 567nm. This emission is significantly quenched in Co-doped ZnO.
samples. Further, the Co-doped nanorods have been found to show ferromagnetic behavior at room temperature from vibrating sample magnetometer (VSM) studies.

**Elilarassi et al., (2011)** successfully prepared nanocrystalline 2% cobalt doped ZnO films using a simple chemical solution method on glass substrates and subsequently annealed in air at 300 and 500°C. Structural, morphology, chemical composition and photoluminescence properties of the films were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and Fourier transform infra-red spectroscopy (FTIR) and photoluminescence (PL) spectroscopy. X-ray diffraction studies of the annealed films reveal the formation of polycrystalline hexagonal wurtzite structure of ZnO crystals with out any co-related secondary phases. SEM micrographs of the films show the formation of spherical nanoparticles. Photoluminescence of the films showed a weak UV and defect related visible emissions like blue, blue–green, yellow and relatively intense orange–red emissions and their mechanism was discussed in detail.

### 2.3.6 Nickel doped ZnO

**Kyoung-Tae Kim et al., (2008)** have prepared transparent and conductive high preferential c-axis oriented Ni-doped ZnO (NZO) thin films as a function of Ni content by sol–gel method using zinc acetate and nickel acetate as starting material, anhydrous ethanol and 2-methoxyethanol as solvent. The NZO thin films with a dopant ratio (0.2, and 0.4 mol%) have a preferred orientation in the (002) direction. However, when the Ni doping ratio exceeds 0.6 mol%, films possessed a non-textured polycrystalline structure. The electric and optical properties of the Ni doped ZnO films were found to be strongly dependent on the Ni contents. The lowest resistivity value was 4.8×10⁻⁴ Ω cm, which was obtained in the 0.2 mol% Ni-doped ZnO thin film. The improvement of the electrical and optical properties of NZO films may be related to the both increase in the concentration of oxygen vacancies and free carries of Ni ions. The average optical transmittance values of the 0.2 mol% Ni doped NZO thin films were more than 91.2% in the visible range.
Farag et al., (2010) have successfully used the spin coating sol–gel technique to deposit highly uniform and good adhesion of nanostructure thin films of ZnO doped with different Ni concentrations. The morphological properties of ZnO: Ni films were studied by atomic force microscopy (AFM) technique. The surface morphology of the nanostructure films is found to depend on the concentration of Ni. The effects of Ni contents on the structural and photoluminescence (PL) properties of ZnO films were investigated. Optical constants (refractive index, n, and absorption index, k) of the undoped and Ni-doped ZnO of 0.2%, 0.4%, 0.6%, 0.8%, 1%, 3%, 5% and 7% concentrations have been obtained in the wavelength range 200–1000 nm by using spectrophotometric measurements. The dispersion parameters were determined and discussed based on the single oscillator model.

2.3.7 Cerium doped ZnO

DU Fangli et al., (2010) prepared Ce-doped ZnO films by the sol-gel method with spin coating onto glass substrates. Zinc acetate dihydrate, ethanol, diethanolamine and cerium nitrate hexahydrate were used as starting material, solvent, stabilizer and dopant source, respectively. Structure and microstructure of the films were characterized with X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM) and the energy dispersive X-ray spectrometry (EDS). The infrared properties were also investigated. It was found that Ce-doped ZnO films showed a hexagonal wurtzite structure and had a (101) preferred orientation. Metallic Ce existed in the form of CeO₂, and the addition of Ce had an effect on the infrared emissivity of the films. The infrared emissivity increased with the temperature rising when the ZnO films were doped with 3 at % and 7 at % of Ce concentration. However, the infrared emissivity decreased with the temperature increasing when the ZnO film was doped with 5 at.% of Ce. This suggests that the infrared emissivity of the films is remarkably changed by controlling the Ce doping concentration.
Sofiani et al., (2006) deposited zinc oxide (ZnO) and cerium-doped zinc oxide (ZnO:Ce) films by reactive chemical pulverization spray pyrolysis technique using zinc and cerium chlorides as precursors. The effects of Ce concentration on the structural and optical properties of ZnO thin films were investigated in detail. These films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurements. All deposited ZnO layers at the temperature 450°C are polycrystalline and indicate highly c-axis oriented structure. The dimension of crystallites depends on incorporation of Ce atoms into the ZnO films. The photoluminescence spectra of the films have been studied as a function of the deposition parameters such as doping concentrations and post growth annealing. Photoluminescence spectra were measured at the temperature range from 13 K to 320 K.

2.3.8 Erbium doped ZnO

Eugenio Hernan Otal et al., (2011) studied the introduction and stability of the heavy lanthanide Er, into ZnO by HRTEM, XRD and thermal treatments. The applied synthesis route allows introducing the Er atoms in the lattice in a metastable state. The stability depends on the Er concentration. ZnO with Er concentrations of less than 2% are stable up to 800°C, while higher concentrations result in a phase segregation at T > 700°C. Unit cell parameters obtained from the Rietveld refinement of XRD patterns provide a conclusive evidence of the incorporation of the Er ions in the host ZnO matrix.

Fanyong Ran et al., (2008) have fabricated using erbium acetate as an Er source, transparent ZnO films doped with Er by sol–gel method through spin-coating on quartz substrates. The as-prepared ZnO:Er films were annealed in air at 400°C for 6 h, at 600°C, 800°C and 1000°C for 2 h, respectively. The ZnO:Er films exhibit wurtzite structure with preferential orientation of the (002) plane. The film that annealed at 800°C shows the highest degree of preferential orientation. Coalescence of small grains result in very large and irregularly shaped grains for the film annealed at 1000°C. And the films annealed at other temperature all have rather uniform spherical grains with diameter ranging from 30
nm to 60 nm. The estimated optical band gap of Er-doped ZnO films annealed at different temperatures is 3.28 eV which is almost independent of annealing temperature and quite similar to that of undoped ZnO film. Due to the active oxygen movement during post-annealing process, the most active bonding state of Er–O is obtained for the films annealed at 800ºC, which is probably similar to a pseudo-octahedron with $C_{4v}$ point structure reported in literature.

Mi Ae Lim et al., (2006) prepared Er$^{3+}$ doped ZnO/zirconium-oxo-alkylsiloxane nanocomposites from anhydrous zinc acetate, dehydrated erbium (III) acetate, zirconium tetrapropoxide and methacryloxypropyl-trimethoxysilane in toluene solution. A crack-free nanocomposite films with uniform morphology of thickness about 6.0μm were fabricated by single step coating operation. The existence of in situ generated ZnO nanoparticles was characterized by photoluminescence measurement of the sample in the visible region. The near infrared photoluminescence study for the Er$^{3+}$ ZnO/zirconium-oxo-alkylsiloxane nanocomposites showed a broad and strong emission band at 1.55μm, which was attributed to the $^{4}I_{3/2} \rightarrow ^{4}I_{5/2}$ transition of Er$^{3+}$ ion. The emission intensity of Er$^{3+}$ was greatly enhanced by incorporating ZnO into zirconium-oxoalkylsiloxane system.
References


