Zinc Oxide

Zinc oxide (molecular formula : ZnO) is a multifunctional material, with its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, high photo stability and broad range of radiation absorption[1,2]. It is recognised as a potential II–VI photonic semiconductor materials due to its wide band gap (~3.3 eV) and high exciton binding energy (~60 meV)[3]. It possesses considerable potential for applications in optoelectronic devices such as UV lasers, LEDs, as electrode in solar cells, gas and bio sensors etc. The last few years have witnessed tremendous efforts on understanding the physical and optical properties of ZnO with particular attention on fabrication and device applications[4]. Many synthesis routes like sol-gel, hydrothermal, co-precipitation, wet chemical method etc has been used to obtain high quality nano/microstructure ZnO material[5]. It is also well established that ZnO optoelectronic properties strongly vary depending on its defect structure based on synthesis techniques.

1.1 Crystal Structure:

ZnO generally crystalizes in two forms: Hexagonal Wurtzite and cubic zinc blende. According to the first principle periodic Hartree-Fock linear combination of atomic orbitals theory, the hexagonal Zinc wurtzite is found to be the most thermodynamically stable form[6]. It belongs to the space group of $P6_3mc$ [6,7] which has two lattice parameters; a= 3.25 Å, c= 5.20 Å and is characterized by two interconnecting sub lattices of Zn^{2+} and O^{2-} where each anion is surrounded by four cations at the corners of a tetrahedron with a typical *sp3* covalent bonding. The number of alternating planes of tetrahedrally coordinated O^{2-} and Zn^{2+} ions which are pilled alternately along c-axis (Figure 1.1) describe the structure of ZnO. The zinc and oxide center in the wurtzite ZnO is tetrahedral and this tetrahedral symmetry plays an important role for polarity of ZnO. Piezoelectricity and pyroelectricity are the direct consequences of polar symmetry of ZnO along hexagonal axis. ZnO is generally found to be n-type structure. This n-type is due to the structural point defect (vacancies and interstitials) and extended defects (threading/planar dislocations). The presence of oxygen vacancies in ZnO lattice gives it n-type conductivity.

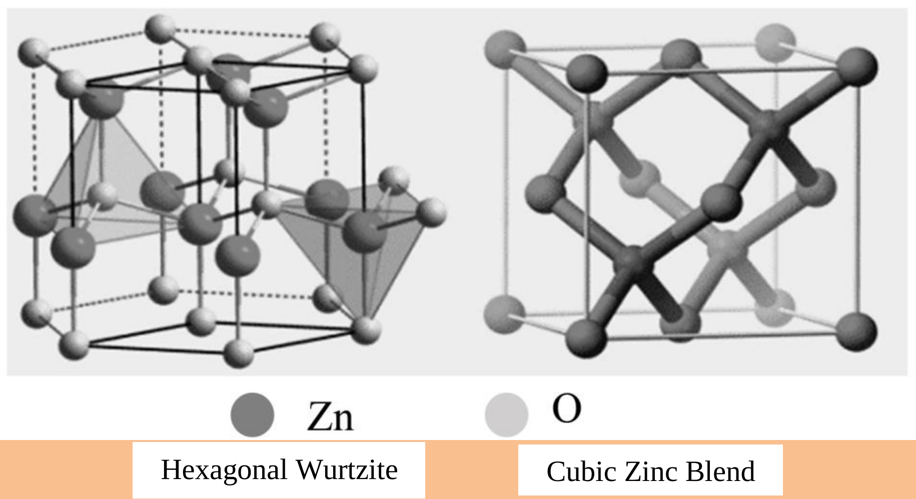

Figure 1.1: Hexagonal Wurtzite and Cubic Zinc blend structure of ZnO; Zn atoms are shown as dark grey spheres and O atoms as light grey spheres

1.1.1 Physical property:

Pure ZnO is white in colour and turns yellow on heating. Its molecular weight is 81.37. ZnO has relative density of 5.607. Under high pressure, the melting point of ZnO is 1900ºC and its heat capacity is 9.62cal/deg/mole at 25ºC. It is insoluble in water but soluble in acid.

1.1.2 Opto-electronic property:

ZnO has a large exciton binding energy around 60 meV at room temperature due to excitonic recombination[8]. This large exciton binding energy makes efficient excitonic emission in ZnO which suggests ZnO a promising material for optical devices at room temperature and higher. The process of optical absorption and emission are very much influenced transition related to dopants or defects which are usually responsible for creating mid gap discrete electronic state[8]. Many reports show that the photoluminescence of ZnO shows green emission and the intensity of green emission increases with decrease particle size and reduced nanowire diameter which gives quantum size effect. The reduction in particle size increases the binding energy and which in turn enhances the opto-electronic property of ZnO nanomaterial.

1.1.3 Optical properties:

As reported in different literature, the optical band gap of ZnO is 3.44eV at low temperature and 3.3eV at room temperature[9] which corresponds to energy of 375.75Å photons. So, zinc oxide is transparent to visible light but strongly absorbs ultra violet light below 375.75 Å. Due to this reason, ZnO is used in varieties of optoelectronic applications like Light Emitting Diode (LED's), Solar Cells, photo detectors etc. [6,10–12]. The band gap of ZnO depends upon the carrier concentration; Band gap tends to decrease as there is an increase in carrier concentration. Photoluminescence of ZnO represents a relatively sharp absorption peak at 380nm (due to band to band transitions) and a wider yellow-green emission band (due to presence of oxygen vacancies and other related defects).

1.1.4 Electrical Properties:

ZnO has a wide bandgap of 3.3 eV at room temperature. This wide band gap has many advantages like higher breakdown voltage, ability to sustain large electrical fields, lower electronic noise, high temperature and high-power operation. These properties make ZnO nanomaterial fit for wide varieties of electrical applications. Electron mobility of ZnO strongly dependent on temperature and possess a maximum of ~2000 $cm^2/(V\cdot s)$ at 80 K.

1.1.5 Mechanical Properties:

ZnO is a relatively soft material with approximate hardness ~ 5. Its elastic constants are smaller than other materials belonging to same group. The high heat conductivity, low thermal expansion and high melting temperature of ZnO are some of the basic characteristics of ZnO nanomaterial. High thermal conductivity makes it useful in rubber industry; ZnO is added in the rubber in order to increase the thermal conductivity of tyres. ZnO exhibits high radiation hardness property which makes it useful in space or at high altitude[13,14].

1.1.6 Magnetic property:

Various reports show that room temperature magnetism can be achieved by doping magnetic impurity in ZnO like Fe, Pb, Co etc. But preserving magnetism at room temperature in this material is still a challenge. Despite of many experimental results, the reason behind origin of magnetism in this material is not clear. In some cases, it is explained in terms of segregation of metallic clusters [15] while in other cases it is due to double exchange [16,17]. Double exchange occurs between ions of different oxidation state which predicts the way by which electrons are transferred between two species.

1.2 ZnO nanostructures:

Nanostructures possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region. Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure. The importance of these materials realized when researchers found that size can influence the physiochemical properties of a substance e.g. the optical properties. A 20-nm gold (Au), platinum (Pt), silver (Ag), and palladium (Pd) NPs have characteristic wine red color, yellowish gray, black and dark black colors, respectively. In fact, much of the interest in nanoscale materials arises from both an understanding of the novel physical, chemical, and size-dependent phenomena on the nanometer length scale and the development and beneficial uses of these materials in a wide-range of applications from environmental remediation and green chemistry to telecommunications and medicine.

The bandgap of the material is changed because of the discretization of the electron energy, which can be controlled by the nanometers size particles. Such quantum dots behave like atoms and become luminescent. Their emission can be continuously tuned through a large spectrum by changing their size. On decreasing the size, the electron gets confined to the particle (confinement effects) leading to increase in bandgap energy and band levels get quantized (discrete).

With reducing size of the particle the density of states becomes more quantized and the bandgap shifts to higher energies (shorter wavelengths). By changing the size of the nanoparticles the frequency of emission can be tailored.

ZnO nanostructures are of intense interest since they can be prepared by a variety of methods and in a range of different morphologies like nanorods, nanobelts, nanoflowers, nanoneedles, nanorings etc. as shown in Figure 1.2. Vapour phase synthesis method is the most extensively and commonly used method by different research group for the synthesis of 1-D nanorods or nanowires. The typical vapour phase synthesis method includes vapour liquid solid (VLS) growth, chemical vapour deposition (CVD), metal organic chemical vapour deposition (MOCVD), physical vapour deposition (PVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and metal organic vapour phase epitaxy (MOVPE). Nano flower and nano belts are mainly synthesized by using hydrothermal, solid state process, pyrolysis, wet chemical method, precipitation process and many others methods. However, the primary motive of ZnO research is its great potential for a variety of practical applications, such as in optoelectronic devices, energy harvesting devices, electronic devices, sensors, catalysts, active compounds in sunscreens, etc.

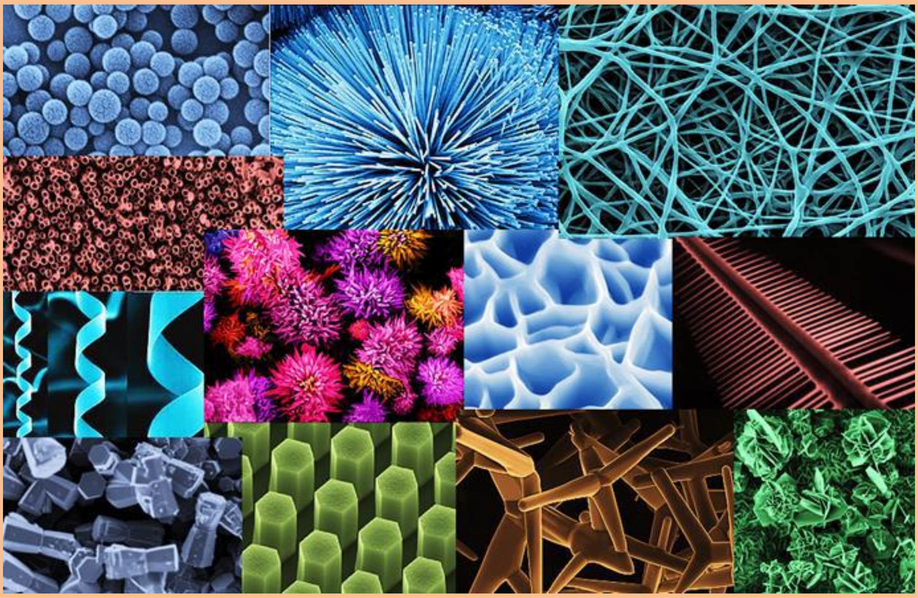

Figure 1.2: Various morphologies of ZnO Nanostructures

1.3 Synthesis Techniques:

Most of the present technological applications of ZnO, such as photodetectors, varistors, transparent conductive electrodes for solar cells, piezoelectric devices and gas sensors have made use of polycrystalline material that are synthesized by a variety of techniques like chemical vapour deposition[18–28], sol–gel synthesis[29–35], Hydrothermal[36–45], co-precipitation[46–50] , mechanochemical[51–56] etc. Although, range of solution based techniques have been emerged but among these sol-gel is the most versatile technique. This technique offers some advantage over other methods - It provides control over particle size and morphology, allows the use of low temperature during synthesis, reduces the cost and results in a homogenous and highly pure sample.

1.3.1 Sol-gel synthesis route:

Sol-gel process is a known process since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glass was produced without high temperature melting process [57].

Sol–gel chemistry is the preparation of inorganic polymers or ceramics from solution through a transformation from liquid precursors to a sol and finally to a network structure called a 'gel' (figure 1.3). A "sol" is a colloidal suspension of solid particles of ions in a solvent. A "gel" is a semi-rigid mass that forms when sol begins to transform into a more dense form in between solid and liquid by evaporation of the solvent. Particles or ions are left behind to join together in a continuous network.

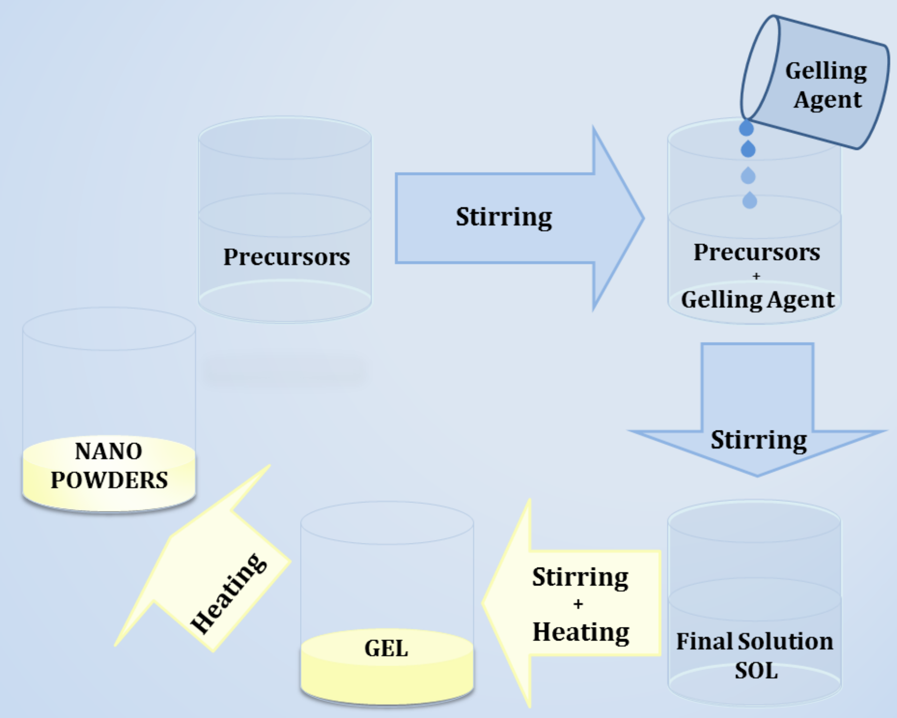

Figure 1.3: Schematic diagram of sol-gel synthesis route

Formation of metal oxides involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. After drying process, the liquid phase is removed from gel. In the sol–gel process, there are many different ways that a gel can be formed. Sometimes, the same precursors can result in very different structures with only small changes in conditions. Generally, gel state is simply defined as a non-fluid 3D network that extends through a fluid phase.

1.3.2 Citrate:

Citric acid is a small organic molecule which often used in sol–gel chemistry is citric acid. Being a weak triprotic acid with three carboxylic acid moieties which are able to dissociate. It is readily available and cheap making it an effective chelating agent. In a typical synthesis, aqueous metal salts (*e.g.* nitrates) are mixed with citric acid and the resulting solution heated to form a viscous solution or gel. Although there are several types of gel (Table 1.1) but citric acid sol–gel method is commonly used for the synthesis of metal oxide powders.

Table 1.1: Different types of gels used for sol–gel synthesis

Type of gel	**Bonding**	**Source**
Colloidal[58]	Particles connected by Vander Waals or hydrogen bonding	Metal oxide or hydroxide sols
Metal-oxane polymer[59]	Inorganic polymers interconnected via covalent or intermolecular bonding	Hydrolysis and condensation of metal alkoxides
Metal complex[60]	Weakly interconnected metal complexes	Concentrated metal complex solution
Polymer complex I insitu polymerizable complex (Pechini method)[61]	Organic polymer interconnected by covalent and co-ordinate bonding	Polyesterification between polyhydroxy alcohol and carboxylic acid with metal complex
Polymer complex II Co-ordinating and crosslinking polymers[62]	Organic polymer interconnected by co-ordinate and intermolecular bonding	Co-ordinating polymer and metal salt solution

Conversion of ‘gel’ to a metal oxide is simply achieved by pyrolysis in air, with temperature depending on specific properties of the samples. Using this method, binary, ternary and quaternary metal oxides in both crystalline aw well as amorphous forms can be synthesized. The key advantage of this method is the homogeneity of the starting material. As the metal–citrate 'gels' are heated, the organic component undergoes combustion at ~300–400 °C, depending on metal counterion and presence of additives. The organic matrix during the first stages of synthesis can signify when nucleation occurs, the sites are evenly dispersed, ensuring a small crystallite size. The matrix is can also the different metals remain mixed on an atomic scale in the case of ternary or quaternary systems. In this work, sol-gel technique has been used for synthesis of Zinc oxide where citric acid is used as a chelating agent.

1.4. Defect Physics and Chemistry in ZnO:

Control of defects and its engineering are most important factor for potential application of Zno in various field. However, despite of many reports published on ZnO, the relationship between defect chemistry, processing, and properties has not received much attention [63]. Defect studies in ZnO have been done from last four decades of years, but now there is need to revisit again in the context of its novel applications. A delicate balance of various defects in ZnO, gives rise to fundamentally new and newer material characteristics[64–66]. Understand of defects in doped ZnO with aliovalent ions is critically important to achieve certain functionality. The concentration of defects in a lattice depends on its formation energy. If there are N atoms, the equilibrium defect concentration n is given by[67]:

$$\frac{n}{N-n} = \exp\left(-\frac{E^f}{K_B T}\right)$$

Where E_f is the formation energy, K_B the Boltzmann constant and T being the temperature. This equation can be derived by considering free energy model of the system without taking into account defect-defect interaction.

In the limit n << N, the above equation reduces to a simple form

$$n \cong Nexp\left(-\frac{E^f}{K_B\, T}\right)$$

This equation indicates two important facts:

- The equilibrium vacancy concentration decreases with increase of temperature.

- Defects having high formation energies will occur in low concentrations.

Defects introduce levels in the band gap of semiconductors and transition from bands to these levels is responsible for green, blue, violet, yellow and orange-red emissions, but the chemical natures of the defects responsible for these emissions have not been conclusively established shown in figure 1.4. The basic native defects which are present in the ZnO are oxygen vacancies (V_0), Zinc Vacancies (V_{Zn}), Zinc interstitials (Zn_i), Oxygen interstitials (O_i), Oxygen antisite (O_{zn}) and Zinc antisite (Zn_O).

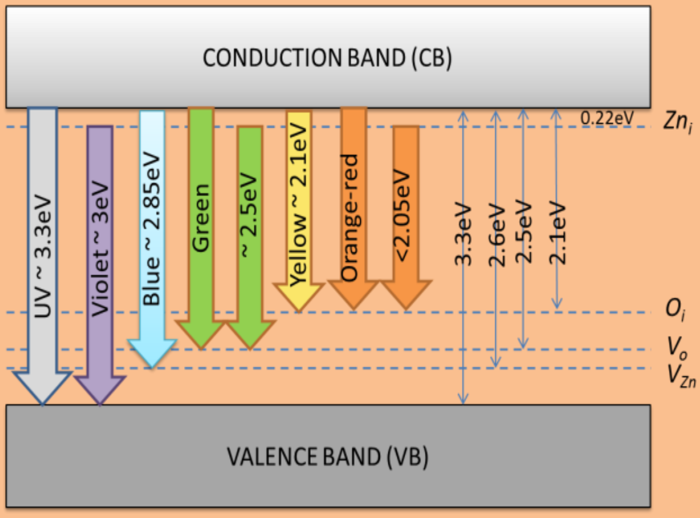

Figure 1.4: Defect structure and its related color emission

1.4.1 Oxygen Vacancies (V_0):

In determining the physical and chemical properties of ZnO, oxygen vacancies play crucial roles which are a common native point defect. The oxygen vacancy is the source of unintentional n-type conductivity[68]. Although there are many controversial reports on this fact as few reports suggested that oxygen vacancy (V_o) in ZnO are +2 charged near the conduction band minimum which establish the fact that oxygen vacancies are dominant donor type defect and responsible for n-type conductivity in ZnO. Other reports suggested that V_o is a deep rather than shallow donor and therefore cannot contribute to the n-type conductivity. An oxygen vacancy possesses three possible charge states: the neutral oxygen vacancy (V_o), the singly ionized oxygen vacancy ($V_o^{\bullet}$), and the doubly ionized oxygen vacancy ($V_o^{\bullet\bullet}$) (figure 1.5).

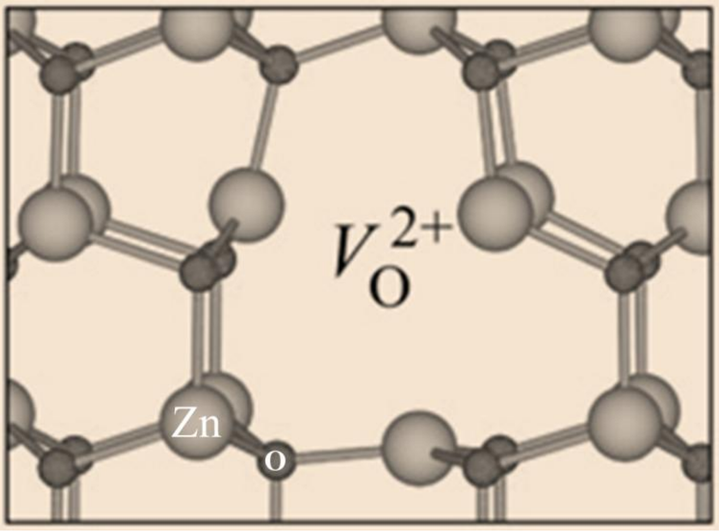

Figure 1.5: Geometry of Oxygen vacancy in 2+ charge state (V_o^{2+})

First principle calculations predict that the oxygen vacancies are negative-U centers[69]. As a result, the singly ionized state is thermodynamically unstable, and therefore oxygen vacancies will be either in neutral or doubly charged state, depending on the Fermi level position. The neutral oxygen vacancies have the lowest formation energy, and thus will dominate. The green luminescence band centred around 2.4 eV (510 nm) has been attributed to O vacancies due to an excited-to-ground state transition.

In case of oxygen vacancy in ZnO, formation energy is given by[67]:

$$E^f\left(V_0^q\right) = E_{tot}\left(V_0^q\right) - E_{tot}(ZnO) + \mu_0 + q(E_F + E_{VBM})$$

where $E_{\text{tot}}(V_0^q)$ is the total energy of a supercell containing the oxygen vacancy in the charge state q, E_{tot}(ZnO) is the total energy of a ZnO perfect crystal in the same supercell and μ_0 is the oxygen chemical potential. Expressions similar to equation (2) apply to all native point defects. The chemical potential varies with the experimental conditions, which can be either Zn-rich, O-rich or in between, and is, therefore, explicitly regarded as a variable in the formalism.

Oxygen vacancies defects plays vital role in determining functionality of synthesized ZnO material.

1.4.2: Zinc Vacancies (V_{Zn}):

Electronic structure of Zinc vacancies (V_{Zn}) can be understood by removal of a Zn atom from the ZnO lattice which results in four oxygen dangling bonds and a total of six electrons[67] (figure 1.6). These four oxygen dangling bonds combine into a doubly occupied symmetric state located deep in the valence band and three almost degenerate states in the band gap, close to the valence band maxima (VBM). Only four electrons are present in these three states which therefore can accept up to two additional electrons showing acceptor behaviour of V_{Zn} in ZnO.

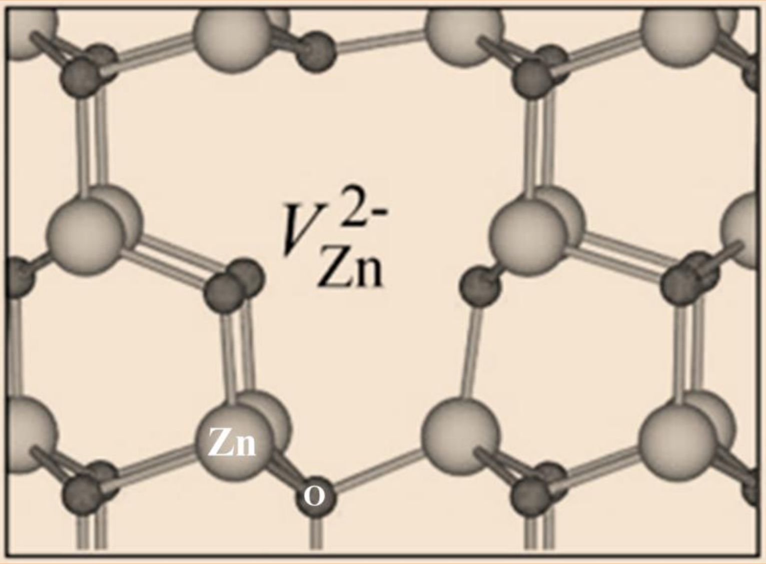

Figure 1.6: Geometry of Zinc vacancy in -2 charge state (V_{Zn}^{2-})

With increasing up Fermi level energy the formation energy of acceptor-type defects decreases thereby V_{Zn} can easily be formed in n-type materials. Whereas, in case of p-type ZnO, formation energy of V_{Zn} is very high. Concentration of V_{zn} should be negligible in p-type ZnO. First principle calculation revealed that V_{Zn} /V_{Zn}^{-1} and V_{Zn}^{-1}/V_{Zn}^{-2} acceptor levels lies 0.1eV-0.2eV and 0.9-1.2 eV above the valence band maxima respectively. According to full potential linear muffin tin orbital potential, transition from conduction band or Zinc interstitial to Zinc vacancy (V_{Zn}) leads to blue emission.

1.4.3 Zinc Interstitials (Zn_i):

Zinc interstitial might be the source of n-type conductivity of ZnO. There are two main sites for Zn_i in the wurtzite structure i.e., one at tetrahedral site and another at octahedral site[67]. At the tetrahedral site, Zni has one Zn and one O as nearest-neighbour atoms, at a distance of ∼0.833 d_0 (d_0 is the Zn–O bond length along the c axis). At the octahedral site, the Zn_i has three Zn and three O atoms as nearest neighbours at a distance of $\sim 1.07 d_0$.

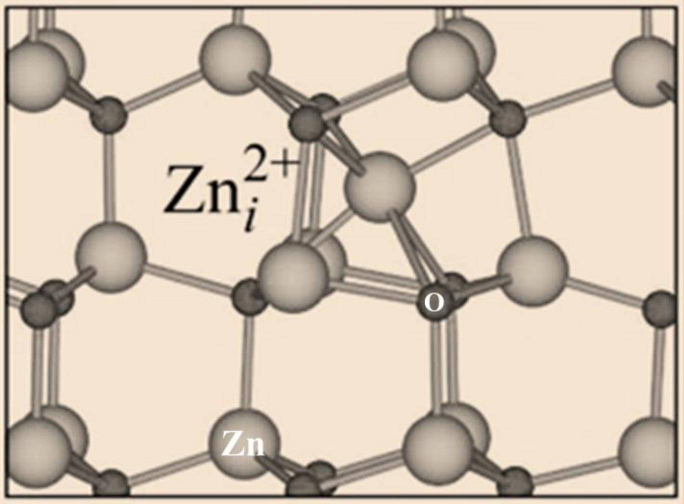

Figure 1.7: Geometry of Zinc interstitial in +2 charge state (Zn_i^{2+})

It has been reported that octahedral site is the most stable site for Zn_i, while Zn_i at the tetrahedral site is 0.9 eV higher in energy and highly unstable. Zn_i defects induces a state with two electrons above the CBM. These two electrons are transferred to conduction-band states, stabilizing the +2-charge state (Zn_i^{2+}) (figure 1.7). Hence, Zn_i donate electrons to the conduction band, thus acting as a shallow donor[68]. Formation energy of Zn_i in n-type ZnO, where fermi level lies near the conduction band minimum, is high. Therefore, concentration of Zn_i

defect in n-type ZnO is very low and unlikely to be responsible for n-type conductivity. While formation energy of Zn_i^{2+} decreases rapidly when the Fermi level lies near the the Valence band Minima, making Zn interstitials a potential source of compensation in p-type ZnO. According to full potential linear muffin tin orbital potential, Zn_i lies ~0.22 eV below conduction band and transition from Zinc interstitial (Zn_i) to valence band leads to Violet emission.

1.4.4 Oxygen Interstitials (O_i):

There are two non-bonded sites for oxygen interstitial (O_i) in the wurtzite ZnO i.e., tetrahedral site and octahedral site (figure 1.8). Density functional theory calculations revealed that O_i at tetrahedral site is unstable and relaxes into a split-interstitial configuration. The calculated O-O bond length in this case is 1.46 Å[68]. O_i at the octahedral site is stable and introduces states in the band-gap that could accept two electrons, so transition levels of O_i/ O_i^{-1}) and (O_i^{-1}/ O_i^{-2}) are located at 0.5 eV and 1.4 eV above the valance-band maximum, respectively. O_i do not contribute to n-type conductivity in ZnO. DFT calculation revealed the Zn-O_i distance is 2.19Å which is somewhat greater than the 1.98Å for the host Zn–O bond-length.

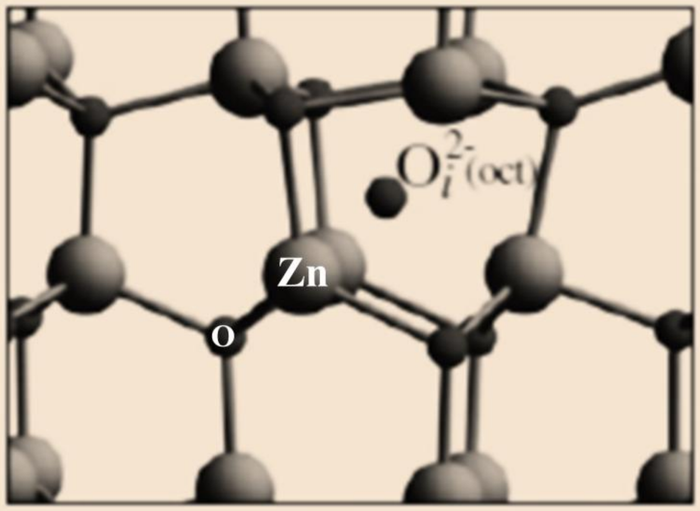

Figure 1.8: Geometry of Oxygen interstitial in -2 charge state (O_i^{2-})

First-principles studies suggest that the O interstitial are very high in formation energy and/or electrically inactive[70]. These defects are not expected to play important roles under thermal equilibrium. According to full potential linear muffin tin orbital potential, transition from conduction band to O_i and Zn_i to O_i leads to yellow and orange-red colour emission.

1.4.5 Zinc antisites (Zn_O):

Zinc antisites (Zn_o) defect originates when zinc atom substitutes at oxygen atom site (figure 1.9). Zn_O is a double donor in n-type ZnO, but its high formation energy indicates that it is an unlikely source of unintentional n-type conductivity[67]. Electronic structure of Zn_O involves both deep and shallow donour levels[70]. It has shallow level of ($Zn_O^{+2}/Zn_O^{+1}/Zn_O$) near the conduction band maxima and deep level of (Zn_O^{+4} /Zn_O^{+3}) and (Zn_O^{+3}/ Zn_O^{+2}) levels located below the middle of the band gap.

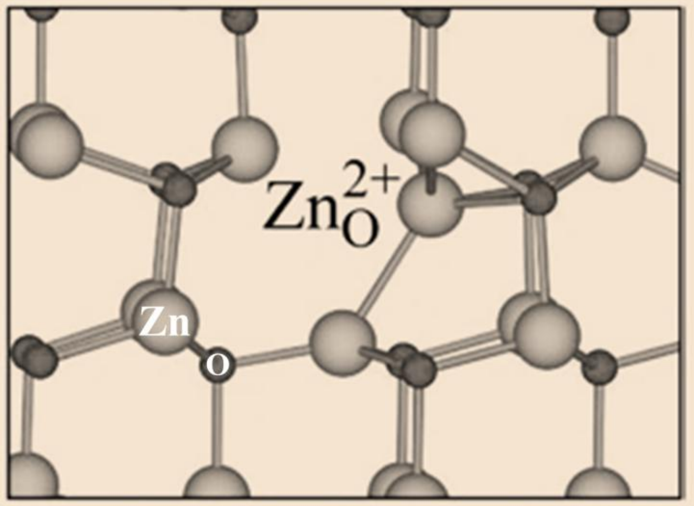

Figure 1.9: Geometry of Zinc antisites in +2 charge state (Zn_o^{2+})

Formation energy of Zn_O is even higher than that of Zn_i under n-type condition. While formation energy of Zn_O is lower in case of p-type ZnO because of the preference of the highly positive charge states, as is seen in the case of O vacancy and Zn interstitial. Hence, Zn_O is unlikely to form at a substantial concentration in *n*-type ZnO.

1.4.6 Oxygen antisites (O_{Zn}):

Oxygen antisites (O_{Zn}) defect originates when oxygen atom substitutes at zinc atom site (figure 1.10). The oxygen antisite (O_{Zn}) is an acceptor-type defect having very high formation energy and electrically inactive, even under the most favourable O-rich conditions. Therefore, concentration of O_{Zn} defects are very low in ZnO at equilibrium.

However, O_{Zn} could potentially be formed under non-equilibrium conditions such as under irradiation or ion implantation. It was found that O on the ideal Zn site is unstable and spontaneously relaxes to an off-site configuration[68]. DFT calculation suggested that O–O bond length is 1.46Å in the −2 charge state and 1.42Å in the neutral charge state. The distances between O_{Zn} and other nearby oxygen atoms are ~2.0 Å, much larger than twice the oxygen covalent radius of 0.73 Å, thus indicating the absence of bonding. O_{Zn} are deep acceptors with transition levels O_{Zn}/O^{-1}_{Zn} and O^{-1}_{Zn}/O^{-2}_{Zn} at 1.52 and 1.77 eV above the VBM.

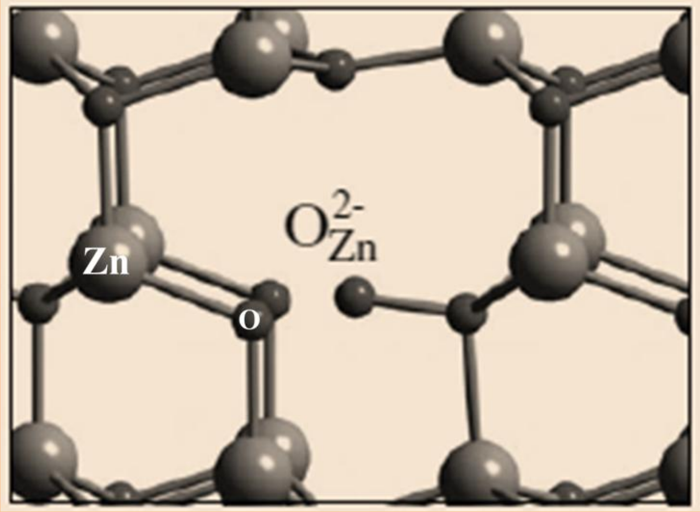

Figure 1.10: Geometry of Oxygen antisites in -2 charge state (O_{Zn}^{2-})

1.5 Photoluminescence:

In a semiconductor, photons with energy greater than that of the band gap excite electrons from the valence band into the conduction band. In the case of photoluminescence (PL) a laser is the primary means of achieving this. Electrons in an excited state always seek to return to their lowest energy state; in this case the ground state is at the top of the valence band. The question of what happens to the energy lost when transitioning between the conduction band and the valence band is answered in several parts. In semiconductors with a direct band gap and few mid gap energy states, a favourable outcome is the production of a photon, where the energy of the photon corresponds to the band gap of the semiconductor, however energy may also be lost through phonons (vibrations) in the lattice. In a perfect semiconductor, consisting of an infinitely homogenous and isotropic lattice, every emitted photon would exhibit the exact same characteristic energy and the PL. The schematic of the physics behind the PL phenomenon is shown in Fig. 1.11. PL of a semiconductor is largely dependent on the temperature due to the thermal expansion/contraction of the lattice and changes in the electron-phonon interaction[71,72].

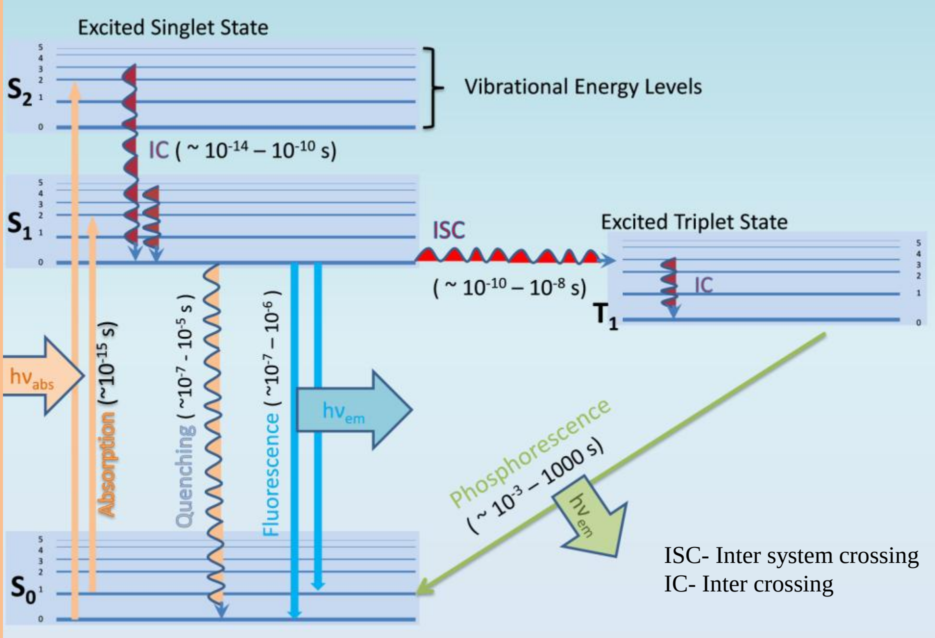

Figure 1.11: Schematic of Photoluminescence Spectroscopy

1.5.1: Photoluminescence of ZnO:

ZnO defect structure and its related colour emission (optical properties) can be studied using photoluminescence spectroscopy. The majority of reported luminescence spectra of ZnO nanostructures have been measured at room temperature. Room-temperature PL spectra of ZnO typically consist of a UV emission (near band edge) and possibly one or more visible bands due to defects and/or impurities also called deep level emission (DLE)[73]. The typical PL spectra of ZnO nanostructures grown using sol-gel technique is shown in Figure 1.12.

In room-temperature PL spectra, there is a variation in peak position for different nanostructures. Peak positions (387 nm for tetrapod, 381 nm for needles, 397 nm for nanorods, 377 nm for shells, 379 nm for faceted rods, and 385.5 nm for ribbons/combs) can be observed[73].

Since the defect density on the surface is higher than in the bulk, spectral shifts due to different defect concentrations are expected to occur in nanostructures with different sizes due to different surface-to-volume ratios. The defects could affect the position of the band-edge emission as well as the shape of the luminescence spectrum. Therefore, clarifying the origins of different defect emissions is an important issue. However, it should be noted that the ratio of the intensity of Near Band Edge (NBE) (I_{NBE}) and Deep Level Emission (DLE) (I_{DLE}) is dependent on the excitation density as well as the excitation area[74].

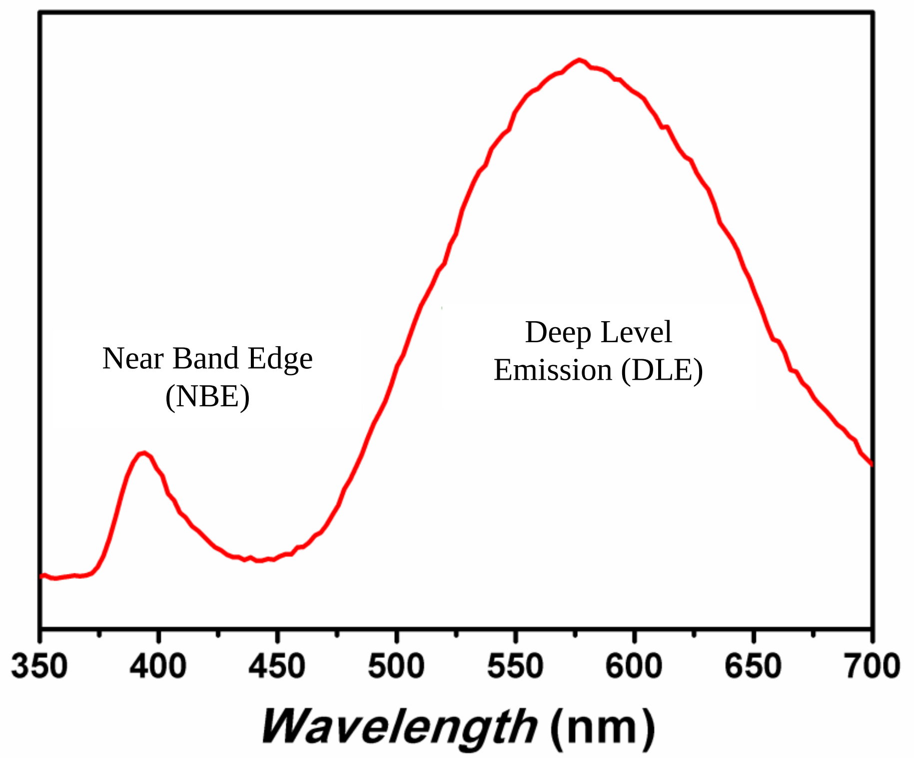

Figure 1.12: Typical PL spectra of ZnO nanostructures

The ratio of NBE and DLE is useful in comparing the quality of different samples when the measurements are performed under identical excitation conditions. Keeping this into account, ratios of areas of NBE (P_{NBE}) and DLE (P_{DLE}) has also been estimated in this work for more accurate analysis. Yellow-Green emission is the most commonly observed defect emission in ZnO nanostructures similar to other forms of ZnO. Several different hypotheses have been proposed for the explanation of the origin of various deep level emissions: Green emission is often attributed to singly ionized oxygen vacancies although this assignment is highly controversial. Various transitions related to intrinsic defects, such as donor–acceptor transitions, recombination at Vo++ centres (where these centres are generated by surface trapping of photo generated holes, followed by recombination with electron in an oxygen vacancy Vo+), zinc vacancy, and surface defects. The origin of the green emission is still an open and controversial question and the identification of the exact origin of this emission requires further study. Although, green emission has not yet been conclusively identified, there is convincing evidence that it is located at the surface. It was shown that coating ZnO nanostructures with a surfactant suppressed green emission. Polarized luminescence experiments from aligned ZnO nanorods also indicated that green emission originated from the surface of the nanorods. Also, the possible presence of $Zn(OH)_2$ and OH^- at the surface, especially for nanostructures prepared by solution methods, could affect the emission spectra from ZnO nanostructures. Yellow emission (defect related) is very commonly reported in ZnO nanostructures represents a common feature in samples prepared from aqueous solutions of zinc nitrate hydrate and hexamethylenetetramine. This emission is typically attributed to oxygen interstitial, although a Li impurity represents another possible candidate[73]. The deep levels responsible for green and yellow emissions were found to be different; unlike the defect responsible for the green emission, the defect responsible for the yellow emission is not located at the surface[73,75]. In addition to green and yellow emissions, orange-red emissions are also observed.

Orange-red emission can be attributed to oxygen interstitials. The orange-red and the yellow emissions exhibit different decay kinetics. Both the emissions involved a similar final state related to excess oxygen but with different initial states (conduction band and donor centres). It should be noted that although the majority of studies attribute red-NIR emission to excess oxygen, zinc interstitials were also proposed to explain the origin of a red emission in ZnO particles. Thus, although this emission is less controversial than the green one, further studies are needed to clarify its origin.

1.6 Doping in ZnO:

Wide bandgap semiconductors such as GaN, ZnSe, CdTe and metal oxides (like ZnO) show a pronounced doping asymmetry. The materials occur naturally as n-type or p-type and it is quite difficult to achieve stable opposite conductivity by conventional extrinsic doping methods. Impurities and deliberate doping with aliovalent (differently charged) ions have remarkable effects on the defect equilibria. Further Carriers in ZnO are introduced depending on whether the ions have a lower valence (e.g. Li^{1+} introduces holes) or higher valence (e.g. Al^{3+} introduces electrons) than the Zn. Element doping offers a method to tailor electrical, optical, and magnetic properties of ZnO. For achieving n-type conductivity in ZnO, group III elements (B, Al, Ga and In), group IV elements (Si, Ge, Sn) on Zn- site and group VII elements (F,Cl) on O-site has been reported[76–80]. Although achieving p-type conductivity in ZnO is difficult but doping group I elements (Li, Na, K, Cu, Ag) on Zn-site & Zn vacancies and group V elements (N, Sb and As) on O-site has been reported to produce p-type conductivity in ZnO[81–85]. Effect of doping on ZnO is determined by three factors i.e., dopant formation energy, dopant ionization energy and dopant solubility.

Doping affects luminescence of ZnO either by modifying native defects of ZnO or by introducing new defect state in ZnO, e.g. red emission in Co doped ZnO[86], yellow-orange-red emission in Mn doped ZnO[87], blue emission in Cu doped ZnO[88], green emission in Tb doped ZnO[89], red emission in [90,91], blue emission in Ce doped ZnO[92] etc. Bandgap also gets modified by doping different materials like Cr, Ni, Cd doping decreases the band gap, whereas Mg, Co and Mn doping increases the band gap[93].

Doping in ZnO modifies carrier concentration, luminescence, electronic structure (bandgap and defects structure) and structural parameters (lattice parameter, strain, c/a etc.) and therefore determines the functionality of the modified ZnO.

1.7 Different functionalities of modified ZnO:

Depending upon structural, opto-electronics, electrical and optical properties, functionalities of ZnO can be determined. Especially, modification of native defect of ZnO on doping or new defects introduced by dopants determine its application. Mechanism behind few applications (like Transparent Conductive oxides, Humidity sensing, Light sensing etc) which has been explored in this thesis is explained here:

1.7.1 Transparent conductive oxide:

Transparent conductive oxides (TCOs) are those material which are highly transparent to visible light and electrically conductive. TCOs are used as transparent electrodes in Dye sensitized solar cells (DSSC) and flat panel displays such as liquid crystal displays (LCDs), plasma display panels, electronic paper displays, light-emitting-diodes (LEDs)[94], and touch panels[95,96]. A carrier concentration on the order of 10^{20} cm^{-3} or higher and a band-gap energy above 3 eV are usually required for high conductivity and transmittance[97]. Various TCOs material like impurity-doped SnO_2 (SnO_2: Sb and SnO_2: F), In_2O_3 (In_2O_3: Sn, or ITO), and ZnO (ZnO:Al and ZnO:Ga) have been researched so far in this field [5, 6]. Among them, tin-doped indium-oxide (ITO) is the one in practical use[98,99]. But due to its high cost, scarcity of Indium, toxicity and thermal instability, alternative material is required[94].

Fortunately, ZnO may be a promising alternative to the commonly used ITO, because of being low cost, nontoxic, thermally stable, highly durable in comparison to ITO[100]. Besides, it has a more proper work function for the transparent contact cathode electrodes of transparent OLEDs[101]. Pure ZnO is resistive and absorbs visible light due to presence of defects in the lattice. Doping of appropriate material in appropriate concentration in ZnO can make it a promising candidate for TCOs. Several reports are available on doped ZnO TCOs.

Several reported elements such as B, Al, Ga, In, F etc are doped in ZnO. Among them Al-doped ZnO and Ga-doped ZnO are most studied for TCOs applications due to its high transparency, high conductivity and thermal stability. Although, Al-doped ZnO and Ga-doped ZnO have capacity to become TCOs material but they cannot withstand high humid condition. At high humid condition, they start degrading their electrical properties as suggested by few reports[102–105]. In this thesis, Silicon doped ZnO is proposed to be a strong candidate for TCOs application which can withstand high humid condition (explained in further chapters).

1.7.2 ZnO as electron transport layer in Organic photovoltaics/Dye sensitized solar cells:

Organic photovoltaics (OPVs) is nowadays a promising energy technology in the field of renewable sources due to its low cost, light weight, flexibility and easy manufacturing.

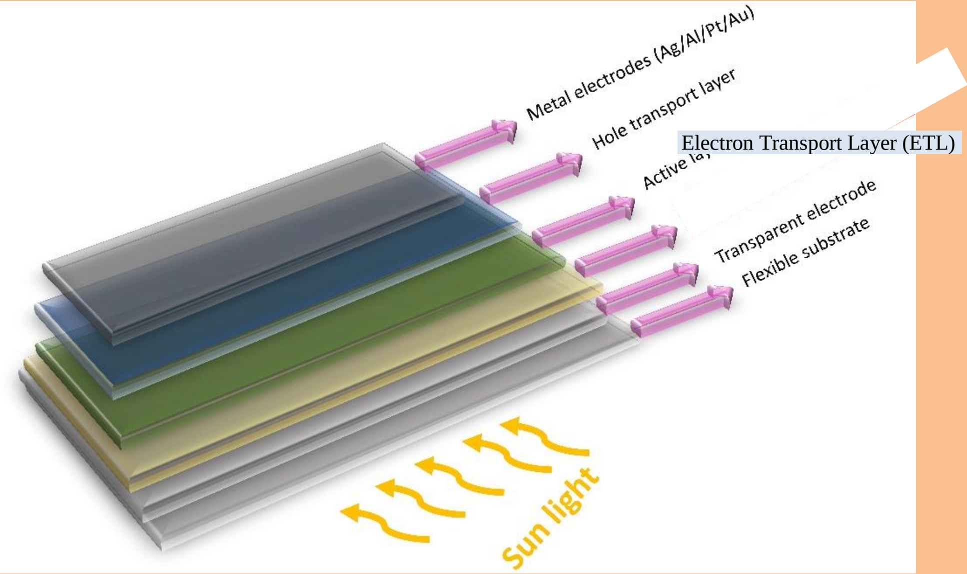

Figure 1.13: Schematic of OPVs using ZnO as Electron Transport Layer (ETL)

In this device configuration as shown in figure, the bottom transparent electrodes (TCOs) are modified by interlayers with low work function, which is known as electron transporting interlayers (ETLs). Photo stability of organic photovoltaic devices is a key requirement for commercialization of this technology which is major challenge nowadays due to surface defects of ETL material. A variety of solution based methods used to synthesize ETL materials have been demonstrated. Metal oxides such as zinc oxide (ZnO), titanium oxide (TiO_2) and aluminum oxide (Al_2O_3) have been widely investigated as electron extraction layers (ETL) in inverted organic solar cell devices[106]. In particular ZnO has drawn special interest due to its appealing properties, such as excellent visible transparency, high electron mobility, environment-friendly nature, and ease of fabrication. In addition, ZnO can be synthesized in the form of nanoparticles (ZnO NPs) which can be deposited from solution generating thin films with high conductivity without the need of strong thermal treatments. The major problem with the ZnO used as an ETL in solar cells: Under dark condition, O_2 molecules captures electrons from the conduction band of ZnO and gets chemisorbed which reduces the conductivity of the material. This chemisorption actually occurs on the surface defects (oxygen vacancies) created during synthesis process. Under UV irradiation, oxygen molecules can be released from the ZnO layer leading to an improvement of the ZnO conductivity. Although light irradiation could restore the conductivity of ZnO but prolonged illumination could induce irreversible degradation. Moreover, these intra-gap states which is produced due to surface defects act as recombination centres for photo generated charge carriers, causing significant photo current loss[107]. Hence, there is a need of alternative materials for ETL which shows low surface defects and low trap states and therefore do not get affected by oxygen and water molecules. Doping other element in ZnO structure, surface passivation, synthesizing under special environment etc are few reported ways to reduce/remove the surface defects.

1.7.3 Humidity sensing:

Humidity sensors are very important device which are used in monitoring the environmental moisture for human comfort. Humidity sensors can also be used in automotive, medical, construction, semiconductor, meteorological and food processing industries[108,109]. Several sensing principles can be used for these purposes, but solid-state sensors are an attractive choice due to their low cost and functionality. In this field, several materials (ceramics, semiconductors and polymers) have been tested and have shown diverse results related to humidity sensing. Metal oxide semiconductors such as tin oxide (SnO2), zinc oxide (ZnO), tungsten oxide (WO3) and iron oxide (Fe2O3) are the most popular humidity sensing materials. ZnO is commonly used due to its high thermal stability, low cost, abundancy and non-toxicity. Development of an ideal humidity sensor depends on some key criteria, such as accuracy, power consumption, precision, repeatability, long-term stability, response time, size, packaging, and cost.

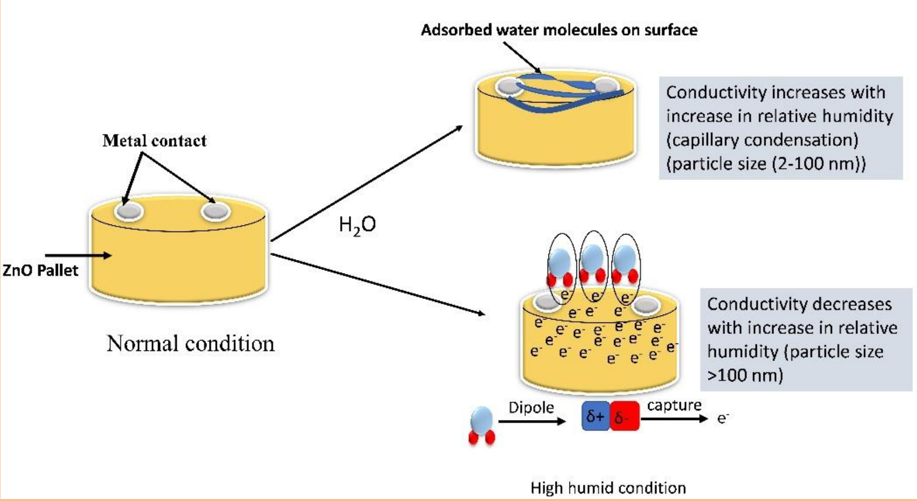

Figure 1.14: Humidity sensing mechanism in ZnO showing two different process depending upon particle size

There are two different humidity sensing mechanism depending upon the particle size and morphology shown in figure 1.14. For nanoparticle size between 2 nm to 100 nm, capillary condensation process occurs[110–113]. In this process, with increase in Relative Humidity (R_H), water molecule gets adsorbed on the surface and forms a path. Electrons, which were earlier flowing through ZnO surface, will now flow through the water channel due to high resistivity of the surface which increases the conductivity. In this mechanism, conductivity of the ZnO increases with increase in $R_{H.}$

While for particle size >100 nm (especially nanorods), inverse behavior takes place[114,115]. The hydrogen sites of water molecules are positively charged due to high electronegative nature of oxygen as compared to hydrogen. At high relative humidity, these charged hydrogen sites capture free electrons from the conduction band of ZnO and reduces the conductivity. In this mechanism, conductivity of the ZnO decreases with increase in R_H. In order to get high humidity sensitivity, different dopant has been introduced in ZnO to create more active adsorption sites for water molecules.

1.7.4: UV sensing in ZnO:

Ultraviolet detection is becoming important nowadays related to various important aspects of science/technology associated with health, environment and even space research[116,117]. Sensitive silicon based UV detectors are already available in market. But these detectors require costly visible light filters as they are sensitive to visible light. Faster, more sensitive, cost-effective UV detection is therefore an important research area. GaN, SiC and diamond are promising candidates[118–120]. But all of these are expensive materials. ZnO is an abundant, inexpensive, non-toxic and environmental friendly material with good thermal/chemical stability and high photoconductivity. UV sensing and response in ZnO, mainly depend on the surface reaction and therefore, surface defects, grain size and oxygen adsorption properties[121–123].

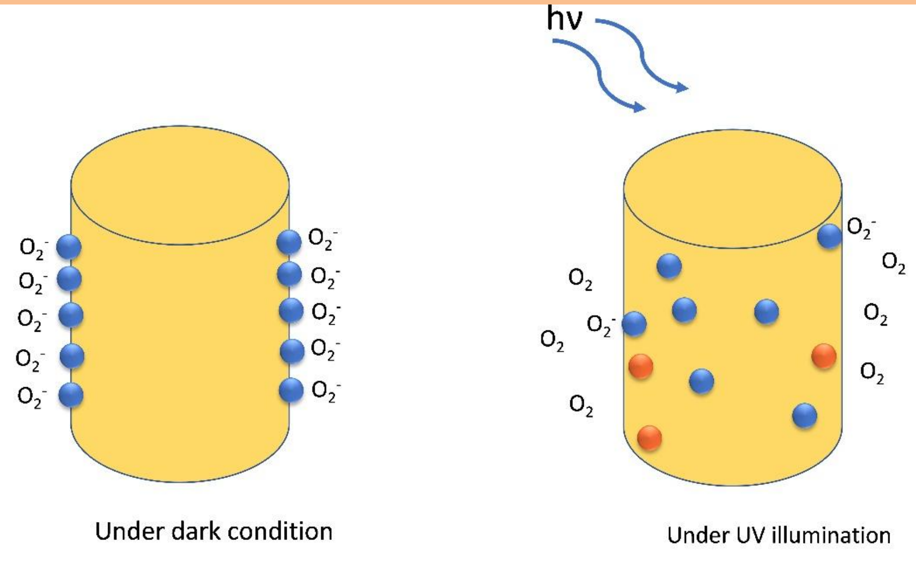

Figure 1.15: UV sensing mechanism in ZnO showing adsorption/ desorption under dark/ light condition

The mechanism of UV sensing is shown in figure 1.15. When the ZnO material is kept in the dark conditions, the oxygen molecules get absorbed on the surface of the ZnO by capturing free electrons from n-type ZnO

$$O_2(g) + e^- \rightarrow O_2^-(ad)$$

Which forms a high resistance region near the surface of ZnO. The electron–hole pairs are generated

$$h\nu \rightarrow e^- + h^+$$

when the ZnO surface is illuminated UV light. The photo generated holes oxidize the adsorbed oxygen molecules

$$O_2^- \text{(ad)} + h^+ \rightarrow O2\text{(g)}]$$

Oxygen molecules get desorbed from the surface of ZnO nanoparticles, increasing free carrier concentration and producing a large photocurrent.

However, pure ZnO materials typically exhibit a relatively poor UV sensing performance due to the large n-type carrier concentration as well as fast recombination rate of photoexcited electron–hole pairs. To resolve this fundamental issue, defect engineering and doping processes have been applied to tailor certain properties of ZnO.

The research work reported in present thesis has been accomplished systematically in following manner

(i) Synthesis of pure and doped ZnO samples

(ii) Analysis of structural properties of pure ZnO (strain. Lattice parameters etc) and its variation on doping.

(iii) Analysis of opto-electronics properties of ZnO and its variation on doping/co-doping other elements

(iv) Studying the co-relation between structural and opto-electronics properties.

(v) Investigation of functionalities of synthesized samples depending on its structural and opto-electronics properties

(vi) Understanding of mechanism behind proposed functionalities.

The remaining chapters of thesis are summarized as follows:

Chapter 2: Experimental Details:

This chapter covers - procedure used for the synthesis of pure and doped ZnO samples, basic description of characterization techniques and description of the inhouse fabricated set up used for testing functionalities of the material. Presently used techniques includes, Lab source x-ray diffraction (XRD), x-ray absorption near edge structure (XANES), UV-Vis spectroscopy, Raman spectroscopy, Photoluminescence etc. The basic working principle along with the schematic representation of used set-ups and attachments is discussed in detail.

Chapter 3: Structural properties of pure ZnO and its variation on doping other material;

This chapter presents an observation of effect in structural properties of ZnO on doping it with Silicon, Silicon/Sodium and Vanadium. Analysis of lattice parameters, particle size and strain has been done by Rietveld refinement using GASUS software. Oxidation state of vanadium doped in ZnO has been determined using Athena software from XANES. Deep analysis of structural properties of ZnO on doping has been done in this chapter.

Chapter 4: Opto-electronics properties of pure ZnO and its variation on doping other material:

This chapter provides an analysis of opto-electronic properties of ZnO and its variation on doping Silicon, Silicon/Sodium and Vanadium. Luminescence properties has been studied using Photoluminescence spectroscopy of all samples. Quantitative analysis of each defect state has been done. Co-relation between structural properties and opto-electronics properties has been analyzed and established in this chapter.

Chapter 5: Multi-functional application of synthesized material.

In this chapter, based on structural and opto-electronic properties, appropriate application of synthesized material has been determined. Functionalities like light sensing, UV sensing, humidity sensing has been carried out. Mechanism behind enhancement of functionalities on doping has been proposed.

Chapter-6: Conclusions and Future Research Scope;

This chapter summarizes the results of present research work with concluding remarks. The possible future scope of present study has also been discussed.