CHAPTER – II

LITERATURE SURVEY

2.1 Introduction

ZnO is one of the most studied materials of the II-VI oxide materials that derive continuous attention of the researchers worldwide because of its possible applications in several novel devices. Several reviews and conference proceedings are published exclusively for ZnO to explore the feasibility of commercial application for future devices. Yet the ream of novel devices from this wonderful material is yet to be accomplished in full. To give a quantitative report on the state of art of ZnO is quite difficult as every day this evergreen valuable material receives many publications worldwide and attempt has been made to provide the literature review of this system that is relevant to the chemical growth only.

2.2 Survey on ZnO Material

Jian Weng et al [1] have studied on electrochemical deposition and characterization of wide bond semiconductor ZnO thin film. Film an aqueous solution of Zn (NO$_3$)$_2$ at 65°C on indium tin oxide (ITO) – covered glass substrates. X-ray diffraction, atomic force microscope and ultraviolet – visible spectrometer studies indicated that the obtained films were polycrystalline with hexagonal structure, different morphologies, grain size ranging approximately from 180 to 320 nm and their transmittance was close to 95% at the wavelength of 500 nm.

Mitra et al [2] have prepared Zinc Oxide thin films using chemical deposition technique. The structural, morphological properties of the prepared films are characterized using X-ray diffraction and scanning electron microscope. The electrical
studies show that the films have two activation barrier values of 0.3 eV and 0.8 eV in the low temperature (300k-420K) and high temperature (300-500K) ranges. Palladium sensitized ZnO films were exposed to hydrogen (H₂) with air as a carrier gas at different operating temperature.

Khashman et al. [3] have studied optical constants and band edge of amorphous zinc oxide thin films grown by radio frequency reactive magnetron sputtering. The amorphous nature of the ZnO films was verified by x-ray diffraction and the optical constants were obtained by ellipsometric spectra optical spectra indicated the band edge for ZnO thin film, which was about 3.35 eV.

Chapro et al [4] have proposed the spontaneous growth of ZnO thin films from aqueous solutions. An electroless – chemical process is proposed, consisting in the formation of the super oxide radical (O₂⁻) followed by chemical reaction of two O₂⁻ with Zn (NH₃)₄²⁺ cations.

Ramamoorthy et al [5] have grown highly textured Zinc oxide (ZnO) thin films with a preferred (101) orientation. They were prepared by chemical bath deposition using a sodium zinicate bath on glass substrates. The films were characterized by XRD, SEM, EDX, UV-Vis-NIR, FTIR and PL in order to justify the suitability for commercial device quality.

Natsume et al [6] have studied the d.c electrical conductivity and optical properties of zinc oxide film prepared by a sol-gel spin coating technique. The temperature dependence of the conductivity indicated that electron transport in the
The conduction band was due to thermal execution of donor electrons for temperatures from 250 to 300 K. For temperatures below 250 K, nearest-neighbor-hopping conduction was dominant in the films. The adsorption edge analysis needed that the optical bond gap energy for the films was 3.20 – 3.21 eV.

Wellings et al. [7] have deposited ZnO thin films from aqueous zinc nitrate solution at 80°C onto fluorine doped tin oxide (FTO) coated glass substrates. Structural analysis, surface morphology, optical studies and electrical conductivity were studied and thickness of the ZnO films was found to be 0.40 μm.

Tingting Ren et al [8] have found electrodeposited ZnO thin films exhibiting shifts in their optical absorption edges with changes in thickness (0.2 – 2 μm). Diffuse reflectance spectroscopic data and Raman spectroscopic data show both potential and thickness dependent changes in defect levels and absorption edges.

Li et al [9] have analyzed ZnO thin films deposited on silicon, silicon dioxide, and glass substrates by radio frequency magnetron sputtering. Field emission scanning electron microscopy, x-ray photoelectron spectroscopy, transmission and photoluminescence measurements were employed to analyze surface morphology, structure and optical properties of ZnO thin films.

Kotlyarchuk et al [10] have prepared undoped and indium doped ZnO thin films by pulsed laser deposition. The influence of deposition parameters on the electrical and optical parameters of the indoped and the indium doped ZnO thin films are also analyzed.
Look et al [11] has been grown p type ZnO thin film by molecular beam epitaxy. Hall effect and conductivity measurements on the layer give resistivity $4 \times 10^1 \ \Omega \text{cm}$, hole mobility $2 \text{ cm}^2/\text{vs}$ and hole concentration $9 \times 10^{16} \ \text{cm}^{-3}$.

Sadrnezhaad et al [12] have studied the effect of addition of Tiron as a surfactant on the microstructure of chemically deposited zinc oxide. Addition of tiron charges the surface morphology and causes to form the fine – grained structure. The obtained results indicate that increasing the number of dipping carves to progress the deposition process.

Tang et al [13] have studied room – temperature ultraviolet (UV) laser emission of ZnO microcrystalline thin films. The optical gain for the room temperature UV stimulated emission is of an excitonic nature and has a peak value an order of magnitude larger than that of bulk ZnO crystal.

Chou et al [14] have synthesized integrated ZnO thin films using an RF magnetron sputter deposition. The resulting specimens are analysed using scanning electron microscopy (SEM) transmission electron microscopy (TEM) and x-ray diffraction (XRD).

Gorla et al [15] have prepared high quality epitaxial ZnO films which were grown on R – plane sapphire substrates by metalorganic chemical vapour deposition. The structural, piezoelectric and optical properties of the ZnO films on sapphire have been investigated.
Cracium et al [16] have deposited ZnO thin films on glass and silicon substrates by pulsed laser deposition. All the films grown over a rather wide range of deposition conditions were found to be optically transparent, electrically conductive and c-axis oriented.

Peiro et al [17] have reported microwave-activated chemical bath depositions of zinc oxide thin films. Scanning electron microscopic characterization suggested that both the shape of the crystals and the textures of the film were highly influenced by the chemical path composition. Composition of films grown on bone glass or fluorine – doped tin oxide (SnO$_2$: F) showed that heterogeneous deposition was favoured on conducting substrates due to the localized heating.

Cheng et al [18] have fabricated thin films transistors (TFTs) with active channel layers of zinc oxide using a low – temperature chemical bath deposition. Current voltage (I-V) properties measured through the gate reveal that the ZnO channel is n-type.

Lokhande et al [19] have prepared zinc oxide thin films on glass substrates by spray pyrolysis techniques. The obtained film with hexagonal Wurtzite crystal structure, have resistivity in the order of $10^{-1}$ Ω cm, and the band gap energy is around 3.27 eV and conductivity is n-type.

Srinivasan et al [20] have studied optical and structural characterization of ZnO oxide thin films. The photoluminescence spectra of the films show the band – edge and sub-band transitions. The structural property of the films has been evaluated
using x-ray diffraction. The AFM images show improvement in the surface of the annealed films as compound as – grown ZnO films coated on sapphire substrates.

Tahir Saeed et al. [21] have deposited thin films of mono phase crystalline hexagonal ZnO from solutions of zinc acetate in the presence of ethylenediamine and sodium hydroxide on to glass microscope studies. Two distinct morphologies of ZnO were observed by scanning electron microscopy. The deposited films were specular and adherent. The band gap of the films was estimated to be 3.15 eV by optical absorption.

Norton et al [22] have studied growth, doping and fabrication processes for ZnO deuces with possible applications to ultraviolet (UV) light emitters, spin functional devices, gas sensors, transparent electronics and surface acoustic wave devices.

Park et al [23] have studied effects of substrate temperature on the properties of G-doped ZnO thin films by pulsed laser deposition. In x-ray diffraction, (002) and (004) peaks were detected, indicating that Ga doping did not cause structural degradation of Wurtzite ZnO. The GZO films formed at a substrate temperature of 300°C showed a low electrical resistivity of $8.12 \times 10^{-5} \ \Omega \text{cm}$, a carrier concentration of $1.46 \times 10^{22} \ \text{cm}^{-3}$ and a carrier mobility of $30.96 \ \text{cm}^2/\text{Vs}$ at an oxygen pressure of 0.76 pa.
Chris et al [24] have proposed, the first principle investigation, based on density functional theory, which produces strong evidence that hydrogen acts as a source of conductivity. It can be incorporated in high concentrations and behaves as a shallow donor.

Robbins et al [25] have synthesized nanocrystalline gallium doped zinc oxide thin films by plasma – enhanced chemical vapour deposition. X-ray diffraction showed that gallium doping had a profound impact on film orientation. Atomic force microscopy (AFM) revealed that the films were nanostructured, with an average grain size of 80 nm and a surface roughness of ~ 2 nm.

Goldsmith [26] has prepared undoped and doped ZnO thin films by filtered vacuum arc deposition. The electrical conductivity of as – deposited n-type thin ZnO film is in the range 0.2 – 6 x 10\(^{-5}\) Ω m, carrier electron density is 10\(^{23}\) – 2 x 10\(^{26}\) m\(^{-3}\) and electron mobility is in the range 10 – 40 cm\(^2\)/Vs.

Rajesh Kumar et al [27] have studied temperature dependence of conduction mechanism of ZnO and co-doped ZnO thin films. All the films were highly c-axis oriented and contained no impurity phase. The hopping conduction mechanism in the lower temperature in the film was Mott’s variable range hopping and not the nearest neighbor hopping.
Vijayan et al [28] have reported the various stages of growth of ZnO films by SILAR method. The resulting specimens are analysed using scanning electron microscopy (SEM) transmission electron microscopy (TEM) and x-ray diffraction (XRD).

Negar Naghavi et al [29] have studied structural and physical properties of transparent conducting pulsed laser deposited In$_2$O$_3$ – ZnO thin films. As the Zn/(Zn+In) atomic ratio increased, the film structure evolved from cubic In$_2$O$_3$ to hexagonal ZnO via a hexagonal layered Zn$_k$In$_2$ O$_{k+3}$ structure. An average transmittance of 85 – 90% in the visible region was obtained for all films independently of the composition.

Chandramohan et al [30] have given an overview of growing undoped and doped of ZnO films by SILAR method. The resulting specimens are analysed using scanning electron microscopy (SEM) transmission electron microscopy (TEM) and X-ray diffraction (XRD).

2.3 Survey on Ni- Doped ZnO (NZO) Thin Films

Elilarassi et al [31] have successfully synthesized nanocrystalline Ni-doped ZnO by sol-gel auto-combustion method. XRD analysis reveals the formation of hexagonal wurtzite structure for all the nickel doped ZnO samples annealed at 800°C. With increasing Ni content, phase segregation has occurred in the samples.
Ruby Chauhan, et al [33] have studied Nanocrystals of undoped and nickel doped ZnO using a chemical coprecipitation method. The crystalline structure, optical properties and band gap were determined by XRD and UV-visible spectra. XRD analysis shows that the prepared samples are in hexagonal wurtzite phase. The particle size can be adjusted by controlling the reaction temperature. The average size of nanoparticle increases as the heating temperature is increased and decreases as the doping percentage of nickel metal is increased. The strongest absorption peak appears at around 260 nm, which is blue shifted from the absorption edge of bulk ZnO (365 nm). The band gap value of prepared undoped and nickel doped ZnO nanoparticles decreases as annealing temperature increased from 300 to 800°C. Optical absorption measurements indicate red shift in the absorption band edge upon Ni doping.

Bin Zhang, et al [32] have fabricated Ni-doped ZnO NCs have been by using a simple chemical vapor-deposition method, in which the process is friendly environment. Such one-dimensional nanoscale nanocomb arrays may indicate a new way to assemble uniform semiconductor nanowires into highly ordered. Microstructure analyses and RTPL measures have been performed, which indicate Ni²⁺ substitute into ZnO lattice at Zn²⁺ site and show doping influences the light emission behavior result in a slightly blueshift emission. The simple friendly environment doping technique can be applied to fabricate other semiconductors nanocombs or nanocantilevers and may be viable for large-scale applications of nanotechnologies.
Zhigang Yin et al [34] have studied in the solubility of Ni in ZnO lattice could reach a rather high value (less than 20%), as demonstrated by both XRD and Ni 2p PES measurements. No ferromagnetic signals were found down to 5 K for Zn0.86 Ni0.14O. Valence-band PES measurements reveal that Ni 3d states locate w2 eV below the Fermi energy. This does not agree with the former theory predictions.

Lei Li et al [35] have studied p-type conducting NiO:AZO films on glass substrates has been demonstrated using a sol–gel solution method. These results suggest that the p-type conductivity could be achieved by annealing the NiO:AZO films in N2/H2 forming gas at 550°C. The NiO:AZO films with 1.5–2 mol% NiO showed p-type conductivity with a hole concentration, hole mobility and resistivity of 3.15×10^{18}–2.18×10^{20} \text{ cm}^{-3}, 2.33–12.76 \text{ cm}^{2}/\text{Vs} and 2.39×10^{-1}–1.24×10^{-2} \text{ Ω cm}, respectively. The ITO/NiO:AZO (2.0 mol% NiO) junction displayed apparent electrical rectification in the I–V measurement, confirming the formation of a typical p–n junction. The feasibility of obtaining p-type conduction in AZO films by doping with NiO is important to the development of potential AZO-based optoelectronic devices.

2.4 Survey on Mn - Doped ZnO (MZO) Thin Films

Nirmala et al [36] have studied transparent nanostructured undoped and Mn doped ZnO thin films on glass substrates were prepared by a sol-gel method using a dip-coating method. The films were found to be highly c-axis oriented and the transmittance was increased in the visible region with increase of manganese. The present work represents a better method for synthesizing ZnO nanosized crystals using stable solutions with few additives and then forming homogeneous layers on glass substrates. The thin films were characterized by XRD, SEM and ultraviolet-
visible spectrophotometry, which indicate that solgel ZnO films have potential applications such as catalyst and transparent electrodes in optoelectronic devices. The EDX analysis showed that the amount of an Mn element in the sample increased depending on increased Mn incorporation in the solution. As a result, the Mn incorporation has a strong effect on the optical, structural and morphological properties of ZnO.

Su-Young Cha et al [37] have studied We fabricated p-type ZMO semiconductors at room temperature by using Mn as a single dopant. The Ar working pressure was adjusted in the range of 2 to 50 mTorr. The 50-mTorr sample showed p-type properties with a hole carrier density of $1.7 \times 10^{17} \text{ cm}^{-3}$, a mobility of $0.85 \text{ cm}^2/\text{V} \cdot \text{s}$, and a resistivity of $29.7 \cdot \text{cm}$. The p-type property was attributed to a transition from Mn$^{3+}$ to Mn$^{2+}$ plus a hole with increasing Ar working pressure. The p-type property was confirmed by device fabrication using an n-type Si substrate. Additionally, the contact property was improved using isostatic pressure treatment, and the driving voltage of the device decreased with increasing mobility.

Rusu et al [38] have studied the Mn-doped ZnO thin films by thermal oxidation of evaporated multilayered Zn/Mn thin films. The XRD analysis revealed that as prepared Mn-doped ZnO thin films have a polycrystalline wurtzite structure with (002) plane of crystallites parallel to the substrate surface. The optical band gap was found to be of 3.17 eV and 3.22 eV for un-doped and doped samples, respectively. The temperature dependence of electrical conductivity of heat treated Mn doped samples present a semiconducting characteristics, with activation energy of
electrical conduction, in the higher temperature range of about 1.10 eV. At room temperature, the studied samples have no magnetic properties.

Sasanka Deka, et al [39] have studied the increasing content of Mn, lattice parameters of doped ZnO increase due to the larger ionic radius of Mn$^{2+}$. Optical absorption investigations reveal the presence of Mn$^{2+}$ in tetrahedral coordination, possibly due to the substitution of Mn for Zn in the ZnO lattice. All samples are paramagnetic at room temperature, and the susceptibility data give evidence for strong antiferromagnetic interactions. A large increase in the magnetization below 50 K and nonlinear M–H behavior at 12 K indicates that the samples are ferrimagnetic at low temperatures. However, the presence of small fractions of other ferrimagnetic impurities in the paramagnetic samples cannot be ruled out.

Shim et al [40] have investigated the effects of oxygen pressure and substrate temperature on the magnetic and magneto transport properties of the Mn-doped ZnO thin films grown by PLD. Found that ferromagnetic ordering in the Mn-doped ZnO films grown at 700°C and 800°C under 10$^{-1}$ torr persists up to 300 K, whereas that in the films grown under 10$^{-3}$ torr was found to disappear at 300 K. They also found the large positive MR at high fields and small negative MR at low fields, regardless of oxygen pressure. Although the observed MR behaviors cannot be direct evidence indicating the ferromagnetic ordering in the Mn-doped ZnO films, it reflects doping of Mn into ZnO. On the other hand, the observed AHE reveals intrinsic ferromagnetic ordering in the Mn-doped ZnO thin film grown at 700°C under 10$^{-1}$ torr in oxygen pressure. Our results support that charge carriers mediate the ferromagnetic exchange
coupling between the localized magnetic ions due to the presence of significant oxygen vacancies in the Mn-doped ZnO thin film.

Yan et al [41] have reported the properties of Co-doped ZnO and ~Mn, Co-doped ZnO thin films were strongly dependent on substrate temperature and ambient oxygen pressure, when deposited on Al2O3 ~0001 substrates using PLD method. Single phase doped/codoped ZnO thin films, with room-temperature ferromagnetism, could be only obtained at a substrate temperature of 400 °C and oxygen pressure of 531025 Pa. The surface of the doped ZnO is very smooth and the crystallites are very fine. No big particles can be found from the SEM image. the ~Mn, Co codoped ZnO thin film had semiconductor conductivity with high resistivity.

2.5 Survey on ZnO Gas Sensor

Suchea et al [42] have reported ZnO transparent thin films for gas sensor applications. XRD measurements have proved that the dc sputtered films are polycrystalline with the (002) as preferential crystallographic orientation. The gas sensing characteristics of such films are strongly influenced by surface morphology.

Nemeth et al [43] have reported single step deposition of different morphology ZnO gas sensing films. This method offers the controllable deposition of ZnO sensing layers for the simultaneous manufacturing of sensors with different properties.
Dikovska et al [44] have studied periodically structured ZnO thin films for optical gas sensor application. The periodic structure was used for easy coupling of the light into the films to ensure optical detection sensitivity of the ZnO sensors to 1000-ppm butane diluted in nitrogen was proven.

Nunes et al [45] have studied the sensitivity to methane gas of zinc oxide thin films deposited by spray pyrolysis. A linear dependence on the sensitivity between 100 and 2000 ppm of methane was also obtained.

Mitra et al [46] have investigated electrical and gas sensing properties of chemically deposited zinc oxide films. The adsorption of oxygen on ZnO leads to a stable and highly resistive surface suitable for sensor operation in the resistive – mode. For liquid petroleum gas (LPG), a high sensitivity (s = 50 – 70%) is observed in the 0.4 – 1.6 vol % concentration.

Bhattacharyya et al [47] have analysed methane sensor using nanocrystalline zinc oxide thin films. The resistance change was studied at different temperatures (50, 150, 200, 250, 300 and 350°C) with two different metallic contacts to ZnO.

Choopun et al [48] have reported zinc oxide nanobelts were RF sputtered onto a copper tube for ethanol sensor. To characterize the sensor, experiments with ethanol at concentration levels of 50 – 2000 ppm and at operating temperatures ranging from 200 to 290°C were performed.
Camelia et al [49] have studied electrostatic spray deposited zinc oxide films for gas sensors. The microstructure studied with x-ray diffraction (XRD) and Raman spectroscopy indicated that the ZnO films are crystallized in a hexagonal Wurtzite phase. The films showed good sensitivity to 1-ppm nitrogen dioxide (NO₂) at 300°C while a much lower sensitivity to 12-ppm hydrogen sulphide (H₂S).

Shishiyanu et al [50] have reported NO₂ gas sensor was fabricated by successive ionic layer adsorption and reaction (SILAR) technique and rapid photo thermal processing of the Sn-doped ZnO film. The experimental results show that doping of zinc oxide thin films improves the sensor element sensitivity to 1.5-ppm NO₂ in air and down shifts the operating temperature.

Gruber et al [51] have reported a reactively sputtered ZnO thin film layer was employed as the gas – sensitive material in a novel gas sensor design. A CH₄ / H₂ / H₂O plasma etching process is established for the micro structuring of the ZnO to realize the novel sensor design. The sputter deposited ZnO thin films are characterized by scanning electron microscopy (SEM), surface profilanetry and x-ray diffractometry (XRD).

Jiaqiang et al [52] have studied sensing characteristics of double layer film of ZnO. It can be shown from experimental results that the gas sensitivity and selectivity of ZnO gas sensor can be improved by doping noble metal and using noble metal catalyst coating.
Sterveglier et al [53] have reported the preparation of ZnO – In thin films that are capable of detecting low ammonic concentrations in air. ZnO – In thin films can detect ammonia concentrations in the range 1 – 10 ppm by operating between 200 and 500°C.

Ferro et al [54] have identified peculiarities of nitrogen dioxide detection with sprayed undoped and indium doped zinc oxide thin films by adding 3 wt% of indium nitrate to the spraying solution it is possible to enhance the film gas response to 5 ppm of NO₂ at 275°C.

Chaabouni et al [55] have analysed metrological characteristics of ZnO oxygen sensor at room temperature. It was shown that the gas sensitive properties one strongly correlated with the fabricated microstructure, which depends on the deposition parameters and on the substrate nature.

2.6 Survey on SILAR

Raiduo et al [56] have reported the preparation and characterization of thin films by SILAR method. XRD measurements have proved that the hexagonal structure with c – axis is perpendicular to the surface. Such films are strongly influenced by surface morphology.

Sakthivelu et al [57] have successfully synthesized ZnO thin films by SILAR method. The structural, morphological and optical properties of the ZnO films were studied. Transmittance over the visible range exceeds 75% for all molarity of the films. For molarity increase, the transmittance of the film decreases. The band gap of the film is situated in the range 3.32 eV - 3.08 eV and decreases with the increase of the molarity.
Oleg Lupan et al [58] have investigated the structures on the nanostructured ZnO:Sn, ZnO:Ni films as a nitrogen dioxide and ammonia gas sensors obtained by SILAR. Undoped ZnO thin films have a very low sensing response towards NO2 and ammonia. The sensitivity is higher for sensor elements on the Ni–ZnO and Sn–ZnO rapid photothermal processed at 550 °C and 650 °C, 20 s, respectively.

Mondal et al [59] have reported Aluminium could be successfully incorporated in ZnO thin film by SILAR technique. The concentration of Al was intentionally chosen to be large (7 at.%) so that the effects of Al can be easily detected. It may be possible to try still lower concentrations. Experiments in these directions are in progress. Optimisation of Al incorporation can give ZnO thin films with improved properties.

2.7 Conclusion

The review clearly shows that several researchers are involved in this system worldwide because of its potential as sensor devices. The interest in the material is due to the significant improvements by altering synthesis method, depends etc. This study is aimed at using low cost combustion route to prepare high quality pristine and doped films.

2.8 References


