Literature Survey on Mn Doped ZnO thin films grown by SILAR Method

1.10 Introduction

ZnO is one of the most interesting materials of the II-VI semiconductor oxide materials that take incessant attention of the researchers worldwide because of its possible applications in various novel components. Several reviews and conference proceedings are published to explore the feasibility of commercial application for future devices. Yet the realm of new devices from this brilliant material is yet to be accomplished in full. To give a quantitative report on the state of art of ZnO is quite difficult but an attempt has been made to survey the chemical growth of this system that is relevant to this work. A review on growth of this valuable system is also added separately to stress the importance and versatility of the system.

1.11 Survey of Mn doped zinc oxide films by Chemical Methods

Yu-Jun Zhang et al [97] reported on the Mg/Cd doped Mn:ZnO thin films prepared by a sol-gel method. Our results indicate that Mg and Cd-doping can tune the bandgap of ZnO film (3.17-3.30 eV), and all of these thin films show room temperature ferromagnetic behaviors. As the bandgap of ZnO-based thin films changes, it effects the strength of the magnetic exchange interaction in the transition metal doped ZnO films, which results in the tunable ferromagnetism. This may be a practical way to achieve appropriate dilute magnetic semiconductor materials for future spintronic devices.
F.N. Jiménez-García et al [98] reported about ZnO and ZnMnO thin films obtained by the successive ionic layer adsorption and reaction (SILAR) method. All thin films were deposited on glass microscope slide. A precursor solution of 0.1M of ZnCl$_2$ complexed with ammonium hydroxide and water close to boiling point (92 °C) as a second solution was used for the ZnO films. An uncomplexed bath comprised of 0.1M ZnCl$_2$, 0.1M MnCl$_2$, and a second solution of 0.1ml of NH$_4$OH with water close to boiling point was used for the ZnMnO films. The film samples were deposited by the SILAR method and annealed at 200 °C for 15min. These samples were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS), and Atomic Force Microscope. Atomic absorption was used to determine quantitatively the amount of Mn incorporated into the films. According to the XRD patterns, these films were polycrystalline with wurtzite hexagonal structure. The morphology of the ZnO films were constituted by rice-like and flower-like structures that changed significantly to nanosheet structures with the Mn incorporation. The Mn inclusion in a ZnO structure was less than 4% according to the results from EDS, XRD, and atomic absorption.

S. Sun et al [99] reported a new type of large area metal organic chemical vapour deposition (MOCVD) system for the growth of high quality and large size ZnO materials is introduced. Materials properties of the un-doped, n- and p-doped ZnO films grown on sapphire substrates by this MOCVD system are studied by various techniques, including high resolution X-ray diffraction (XRD), UV–Visible optical transmission (OT), photoluminescence (PL) and photoluminescence excitation (PLE), synchrotron radiation
X-ray photoelectron spectroscopy (SR-XPS). The wurtzite (w) ZnO crystal structures grown with primary (0002) orientation were identified. Results have shown the high crystalline quality of MOCVD-grown ZnO films, indicated by the narrow XRD, PL and Raman line widths, strong PL signals, sharp OT edge and smooth surface. In particular, high p-type carrier concentration of \(> 10^{17} \text{ cm}^{-3}\) have been achieved besides the good n-type doping in ZnO.

J. Jin et al [100] reported element-specific electronic structure of (Zn,Mn) O thin films with various Mn concentrations has been investigated using X-ray absorption and emission spectroscopy. According to comparison between the experimental spectra and the density functional theory calculations (partial density of states and exchange interactions for various Mn defect configurations), the substitutional Mn impurities do not induce ferromagnetism in (Zn,Mn) O samples. The ferromagnetic properties can be obtained when defect configurations consisting of both substitutional and interstitial Mn atoms are present. The ferromagnetism in ZnO-based magnetic semiconductors is favored to be Ruderman–Kittel–Kasuya–Yoshida type and the established theoretical model is in a good agreement with the X-ray spectroscopic measurements.

B. Kharroubi et al [101] reported on the synthesis and characterization of Mn-doped ZnO thin films with different percentages of Mn content (0, 1, 3 and 5 at %) and substrate temperature of 350 °C, deposited by a simple ultrasonic spray pyrolysis method under atmospheric pressure. The chemical compositions and surface morphologies were examined by dispersive x-ray spectroscopy and scanning electron microscopy.
micrographs. They studied the structural and optical properties by using x-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy and ultra-violet visible near-infrared spectroscopy. The lattice parameters calculated for the Mn-doped ZnO from XRD pattern were found to be slightly larger than those of the undoped ZnO, which indicate substitution of Mn in the ZnO lattice. Compared with the Raman spectra for ZnO pure films, the Mn-doping effect on the spectra is revealed by the presence of an additional peak about 524 cm$^{-1}$ due to Mn incorporation. With increasing Mn doping the optical band gap increases indicating the Burstein–Moss effect.

Usman Ilyas et al [102] reported on the un-doped and Mn doped ZnO thin films, with oxygen rich stoichiometry, deposited onto Si (1 0 0) substrate using spin coating technique. The structural analysis revealed the hexagonal wurtzite structure without any impurity phase formation. A consistent increase in cell volume with the increase in Mn doping concentration confirmed the successful incorporation of bigger sized tetrahedral Mn$^{2+}$ ions (0.83Å$^-$) in ZnO host matrix that was also endorsed by the presence of Mn 2p$^{3/2}$ core level XPS spectroscopic peak. Extended deep level emission (DLE) spectra centered at $\sim$627 nm and confirmed the presence of oxygen interstitials. Moreover, the magnetic measurements of field dependent M – H curves revealed the origin of ferromagnetic ordering from Mn-defect pair exchange coupling with oxygen interstitials in ZnO host matrix.
Q. Wang et al [103] reported First-principles calculations based on gradient corrected density functional theory performed on Mn-doped ZnO thin film. Magnetism and energetics were studied for two Mn concentrations and varying Mn configurations. It was found that in the dilute limit when Mn atoms were far apart, the ferro-magnetic and antiferromagnetic states are energetically nearly degenerate. The resulting fluctuation would, therefore, make the system paramagnetic as found in the experiment. But, as the concentration of Mn atoms increases, there is a tendency for Mn atoms to form nearest neighbors and cluster around oxygen. For such a configuration, the antiferromagnetic coupling between Mn atoms is energetically more favorable. The results are compared with a diverse range of experiments on Mn-doped ZnO thin film.

Shenghong Yang et al [104] reported about the undoped and Mn-doped ZnO thin films were prepared on quartz glass and Si (1 0 0) substrates by the sol–gel method at room temperature, and the effects of Mn content on the structural, optical, and magnetic properties of these films were investigated. X-ray diffraction patterns revealed that all the films were single phase and have wurtzite structure with (0 0 2) preferential orientation along c-axis, indicating there were not any secondary phases. X-ray photoelectron spectroscopy patterns suggested that Mn$^{2+}$ ions were successfully incorporated into the lattice position of Zn$^{2+}$ ions in ZnO host. Optical transmittances of the films were recorded in the wavelength range of 300–800 nm, and the band gaps of the films were determined. As the content of Mn increased, the crystallite size and the optical band gap of the films decreased while the crystalline quality deteriorated gradually. The intensity of photoluminescence spectra was suppressed with Mn doping. Magnetic
measurements indicated that undoped ZnO was diamagnetic in nature whereas Mn-doped ZnO samples exhibited ferromagnetic behavior at room temperature, which is possibly related to the substitution of Mn$^{2+}$ ions for Zn$^{2+}$ ions in the ZnO lattice. It was also found that the Mn doping content can affect the ferromagnetic behavior of the films effectively.

W. M. Hlaing Oo et al [105] reported that we studied the dopant concentration distribution and conductivity in ZnO:Mn films grown by metalorganic chemical vapor deposition. The ion beam, surface, and microstructural properties of undoped ZnO films were compared with Mn-doped ZnO films. Suppression of ZnO conductivity was observed for Mn doping up to 4.5 at. %. The presence of Mn$^{2+}$, confirmed by x-ray photoelectron spectroscopy, is correlated with the reduction in conductivity. Variable-temperature Hall effect measurements yield activation energy of 170 meV, consistent with deep donors in the bulk or at the interface. The results suggest that the incorporation of substitutional Mn suppresses the formation of native defects such as oxygen vacancies.

E.R. Shaaban et al [106] reported that Nanocrystalline Zn$_{1-x}$Mn$_x$O films ($x = 0, 0.05, 0.1, 0.15$, and $0.2$) were deposited onto corning glass substrates by a non-vacuum sol–gel spin coating method. All of the films were annealed at 450 °C for 2 h. The structural, optical and magneto-transport properties were investigated by X-ray diffraction, spectroscopic ellipsometry and a system for the measurement of the physical properties. X-ray diffraction analysis of the films revealed that the Mn-doped ZnO films crystallized in the form of a hexagonal wurtzite-type structure with a crystallite size decreased with an increase of the Mn concentration. It was also found that the microstrain
increases with the increase of the Mn content. Evidence of nanocrystalline nature of the films was observed from the investigation of surface morphology using transmission, scanning electron microscopy and atomic force microscopy. The optical constants and film thicknesses of nanocrystalline $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films were obtained by fitting the spectroscopic ellipsometric data ($\psi$ and $\Delta$) using a three-layer model system in the wavelength range from 300 to 1200 nm. The refractive index was observed to increase with increasing Mn concentration. This increase in the refractive index with increasing Mn content may be attributed to the increase in the polarizability due to the large ionic radius of $\text{Mn}^{2+}$ compared to the ionic radius of $\text{Zn}^{2+}$. The optical band gap of the nanocrystalline Mn–ZnO films was determined by an analysis of the absorption coefficient. The direct transition of the series of films was observed to have energies increasing linearly from 3.17 eV ($x = 0$) to 3.55 eV ($x = 0.2$). Magneto resistance (MR) was measured from 5 K to 300 K in a magnetic field of up to 6 T. Low-field positive MR and high-field negative MR were detected in Mn-doped ZnO at 5 K. Only negative MR was observed for temperatures above 200 K. The positive MR in Mn-doped ZnO films was observed to decrease drastically when the temperature increased from 5 K to 100 K. The isothermal MR of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films with different Mn concentrations at 5 K reveals that the increase of the Mn content induces a giant positive MR above $x = 0.05$ and reaches up to 55% at an applied field of 30 kOe for $x = 0.2$.

M. Yuonesi et al [107] reported that there are many techniques used to deposit high-quality ZnO thin films. One of these based on chemical method for the production of ZnO thin films is the sol-gel. ZnO:Mn nano films doped with manganese on different
concentrations were deposited on glass substrates by the spin-coating method. The precursors for the synthesis ZnO:Mn are: Zinc acetate dehydrate, manganese acetate dehydrate, 2-mithoxyethanol and mono ethanolamine as zinc and manganese source, solvent and stabilizer respectively. Seven samples of diluted magnetic semiconductors ZnO:Mn were prepared with different atomic ratio Mn/Zn. Characterization techniques of XRD, EDX and UV-visible spectra measurements were done to investigate the effects of Mn doping concentration on the optical and structural properties of ZnO:Mn nano films. The XRD patterns of all nano films show the crystallization behavior and are hexagonal wurtzite structure for different x, without existing other phases. Their results reveal that with high percent manganese not only the degree of crystalline decreases but also peak broadening occurs. The compositional analysis was carried out by energy dispersive x-ray (EDX) measurement. Compositional analysis shows 0.00, 0.01, 0.018, 0.029, 0.041, 0.05 and 0.059 Mn/Zn ratios in samples. The optical studies show that the band gap of ZnO:Mn decreases for smaller x than 0.03 from 3.3 to 3.26 because there are a strong interaction between localized moments of the d electrons of Mn atom and band carriers of host material, and increases for higher x than 0.03 because of the structural changes.

B. Kharroubi et al [108] reported on Mn-doped ZnO thin films with different percentages of Mn content (0, 1, 3 and 5 at%) and substrate temperature of 350 °C, were deposited by a simple ultrasonic spray pyrolysis method under atmospheric pressure. The chemical compositions and surface morphologies were examined by dispersive x-ray spectroscopy and scanning electron microscopy micrographs. They have studied the
structural and optical properties by using x-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy and ultra-violet visible near-infrared spectroscopy. The lattice parameters calculated for the Mn-doped ZnO from XRD pattern were found to be slightly larger than those of the undoped ZnO, which indicate substitution of Mn in the ZnO lattice. Compared with the Raman spectra for ZnO pure films, the Mn-doping effect on the spectra is revealed by the presence of an additional peak about 524 cm\(^{-1}\) due to Mn incorporation. With increasing Mn doping the optical band gap increases indicating the Burstein–Moss effect.

G. Srinivasan et al [109] reported on Mn-doped and undoped ZnO nanocrystalline thin films were synthesized 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 623 K and then annealed at 873 K 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.

Yan Wensheng et al [110] reported about the thin films with wurtzite structure were grown by inductively coupled plasma enhanced CVD method. Although both
samples exhibit ferromagnetism at room temperature, the saturation magnetic moment (1.4\(\mu_B\)/Mn) of the Mn- and N-codoped sample is much larger than that (0.3\(\mu_B\)/Mn) of the N-free one. The x-ray absorption near edge structure analysis reveals that the codoped Mn and N impurities can be substitutionally incorporated into the ZnO host in the \(\text{Zn}_{0.96}\text{Mn}_{0.04}\text{O}:\text{N}\) thin film. The first-principles calculations suggest that the N substitution for the O site in Mn-doped ZnO can change the interaction of neighboring Mn–Mn pairs from antiferromagnetic to ferromagnetic, and accordingly the effective magnetic moment per Mn is greatly enhanced.

Wen Chen et al [111] reported about thin films of Mn-doped ZnO with different doping concentration (0.8, 1, 3, 5 at %) were prepared on Pt/Ti/SiO\(_2\)/Si substrates by using sol–gel method. The effects of the doping concentration on the structural properties, electrical characteristics and element binding energy in films were investigated. X-ray diffraction (XRD) results showed that the c-axis orientation of ZnO films was affected by Mn\(^{2+}\) content. Current–voltage (\(I–V\)) measurements indicated that resistivities of ZnO films were observably enhanced by dopant of Mn\(^{2+}\) and the resistivities value increased with a doping level up to 5 at% Mn. X-ray photoelectron spectroscopy (XPS) patterns suggested that the binding energies of O 1s and ZnL\(_3\)M\(_{4.5}\)M\(_{4.5}\) were affected by the content of Mn\(^{2+}\).
Jing Wang et al [112] reported on the Mn-doped ZnO piezoelectric films prepared by sol–gel method. The ZnO films with perfect c-axis orientation were obtained in the annealing temperature range of 470–700 °C when 1% Mn ion (molar percent) was doped into precursor sol. The resistivity of the ZnO films annealed at 600 °C increased from 800 Ω cm (undoped) to $2 \times 10^7$ Ω cm (1% Mn-doped). The XPS spectra of Mn-doped ZnO films were analysed.

**1.12 Survey of Mn doped zinc oxide films by Physical Methods**

X. M. Chenga et al [113] reported that Epitaxial ZnO thin films doped with 7% Mn was prepared by reactive rf magnetron sputtering onto (1 1 2 0) sapphire substrates at 400 °C. X-ray diffraction measurements reveal that the Zn$_{0.93}$Mn$_{0.07}$O film has a ~0001 wurtzite single-crystal structure with a rocking curve width of 0.98 A°. UV–VIS absorption spectra show a band gap of 3.25 eV for pure ZnO films and 3.31 eV for the Zn$_{0.93}$Mn$_{0.07}$O film with states extending into the gap. The Auger electron spectroscopy shows homogeneous distribution of Mn in the film. The magnetic properties of the Zn$_{0.93}$Mn$_{0.07}$O film have been measured by a superconducting quantum interference device magnetometer at various temperatures with fields up to 5 T. No ferromagnetic ordering has been observed at temperature at 5 K. Instead, paramagnetic characteristics with a Curie–Weiss behavior have been observed.

Ueda Kenji et al [114] studied 3d-transition-metal-doped ZnO films (n-type Zn$_{1-x}$M$_x$O (x=0.05–0.25): M=Co, Mn, Cr, Ni) formed on sapphire substrates using a pulsed laser deposition technique, and their magnetic and electric properties are
examined. The Co-doped ZnO films showed the maximum solubility limit. Some of the Co-doped ZnO films exhibit ferromagnetic behaviors with the Curie temperature higher than room temperature. The magnetic properties of Co-doped ZnO films depend on the concentration of Co ions and carriers.

Zhengwu Jin et al [115] reported about the combinatorial laser molecular-beam epitaxy method was employed to fabricate epitaxial ZnO thin films doped with all the 3d transition metal (TM) ions in a high throughput fashion. The solubility behavior of TM ions was discussed from the viewpoints of the ionic radius and valence state. The magneto-optical responses coincident with absorption spectra were observed for Mn- and Co-doped samples. Cathode luminescence spectra were studied for Cr, Mn, Fe, and Co-doped samples, among which Cr-doped ZnO showed two sharp peaks at 2.97 eV and 3.71 eV, respectively, at the expense of the exciton emission peak of pure ZnO at 3.25 eV. Different magnetoresistance behavior was observed for the samples codoped with n-type carriers. Ferromagnetism was not observed for Cr- to Cu-doped samples down to 3 K.

C. Liu et al [116] made a study on the structural analysis of ferromagnetic Mn-doped ZnO thin films deposited by radio frequency magnetron sputtering, using transmission electron microscopy (TEM), high-resolution x-ray diffraction, and Rutherford backscattering spectroscopy (RBS) measurements. A TEM analysis revealed that the Mn-doped ZnO included a high density of round-shaped cubic and elongated hexagonal MnZn oxide precipitates. The incorporation of Mn caused a large amount of
structural disorder in the crystalline columnar ZnO lattice, although the wurtzite crystal structure was maintained. The observed ferromagnetism is discussed based on the structural characteristics indicated by TEM and the behavior of Mn when it is substituted into a ZnO lattice derived from RBS measurements.

Mariana Diaconu et al [117] reported that the incorporation of 3d transition metals into ZnO can produce ferromagnetism above room temperature. For Mn-doped ZnO films grown at low temperatures around 500 °C by PLD, the ferromagnetic behavior is correlated to their textured structure. For optimized films showing homogeneous magnetic domain formation in magnetic force microscope, the saturation magnetization and coercive field strength amount to 0.013 emu/g and 234 Oe at 300 K, respectively. Compared to undoped ZnO films, the luminescence of Mn-doped ZnO films is strongly quenched. However, luminescence can be observed around antiferromagnetic MnO or MnO₂ clusters that crystallize during the growth process on the film surface.

Harish Kumar Yadav et al [118] reported about the influence of postgrowth annealing on the structural and optical properties of rf cosputtered Mn doped ZnO thin films deposited on glass substrate at room temperature has been investigated. All as deposited Zn₁₋ₓMnₓO films are highly textured, with the c axis of the wurtzite structure along the growth direction. The as grown films are in a state of compressive stress and a reduction in stress with post growth annealing treatment are observed. The band gap of Mn doped ZnO films (3.34eV) is slightly larger than the pure ZnO film (3.30eV) and is found to decrease with an increase in annealing temperature for all the samples. The
optical dispersion of refractive index with photon energy in Zn$_{1-x}$Mn$_x$O films with varying $x$ and different annealing temperature is studied in the light of single oscillator and Pikhtin-Yas’kov [Sov. Phys. Semicond.15, 81 (1981)] model, respectively.

V.R. Shinde et al [119] studied about undoped and manganese doped Zinc oxide (ZnO) thin films were prepared 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 350–850 nm was found to be decreased 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 $10^6$ Ω cm.

Jin et al [120] reported on the Combinatorial laser molecular-beam epitaxy method was employed to fabricate epitaxial Zn$_{1-x}$Mn$_x$O thin films in a high throughput fashion. Local structures around Mn were investigated for these $c$-axis-oriented epitaxial films by fluorescence x-ray absorption fine structure measurements. It was shown that Mn substitutionally replaces Zn in Zn$_{1-x}$Mn$_x$O ($x$≤0.22) films. Well-structured blue and ultraviolet cathode luminescence peaks corresponding to the intra-d-shell transitions
of Mn$^{2+}$ were observed, especially for smaller x. The luminescence is quenched rapidly as x is increased. By comparing the relative absorption strength per mole Mn$^{2+}$ with the statistical probability of isolated Mn$^{2+}$, it was concluded that the quick decrement of isolated Mn$^{2+}$ with increasing x is responsible for the severe suppression of the blue and ultraviolet luminescence.

H. Y. Xu et al [121] studied and reported about the Zn$_{1-x}$Mn$_x$O (x=0, 0.16, and 0.25) thin films were grown on fused quartz substrates by reactive magnetron co-sputtering. X-ray-diffraction measurement revealed that all the films were single phase and had wurtzite structure with c-axis orientation. As Mn concentration increased in the Zn$_{1-x}$Mn$_x$O films, the c-axis lattice constant and band-gap energy increased gradually. In Raman-scattering studies, an additional Mn-related vibration mode appeared at 520 cm$^{-1}$. E$_2$H phonon line of Zn$_{1-x}$Mn$_x$O alloy was broadened asymmetrically and red shifted as a result of microscopic structural disorder induced by Mn$^{2+}$ random substitution. The Zn$_{0.84}$Mn$_{0.16}$O film exhibited a ferromagnetic characteristic with a Curie temperature of $\sim 62K$. However, with increasing Mn concentration to 25 at. %, ferromagnetism disappeared due to the enhanced anti ferromagnetic superexchange interactions between neighboring Mn$^{2+}$ ions.

Harish Kumar Yadav et al [122] reported on the the influence of Mn doping on the vibrational properties of rf sputtered ZnO thin films. Raman spectra of the Mn doped ZnO samples reveal two additional vibrational modes, in addition to the host phonon modes, at 252 and 524 cm$^{-1}$. The intensity of the additional modes increases continuously
with Mn concentration in ZnO and can be used as an indication of Mn incorporation in ZnO. The modes are assigned to the activation of ZnO silent modes due to relaxation of Raman selection rules produced by the breakdown of the translational symmetry of the crystal lattice with the incorporation of Mn at the Zn site. Furthermore, the $A_1$ (LO) mode is observed with very high intensity in the Raman spectra of undoped ZnO thin film and is attributed to the built-in electric field at the grain boundaries.

Jun Zhang et al [123] reported about the structure and magnetic properties of Zn$_{1-x}$Mn$_x$O thin films grown on Si (0 0 1) substrates by PLD. Structure and phase evolution with Mn doping was studied using x-ray diffraction, electron diffraction, and high-resolution electron microscopy. The undoped and 1% Mn-doped ZnO films were completely (0 0 1) oriented, and further Mn doping deteriorates the (001) orientation. For Mn concentrations below 3%, only the hexagonal ZnO phase existed in the films without secondary phases. As the Mn concentration reached 5%, secondary phase Mn$_2$O$_3$ was found aggregating at grain boundaries. All the Mn-doped films show ferromagnetic properties at room temperature, and the magnetic moment decreases as the Mn concentration increases. Their results suggest that the ferromagnetism observed in Zn$_{1-x}$Mn$_x$O thin films is intrinsic rather than associated with secondary phases.

J. Elanchezhiyan et al [124] reported about the investigation of the Zn$_{1-x}$Mn$_x$O ($x = 0.05$, 0.10 and 0.15) thin films grown by RF magnetron sputtering. The grown films on sapphire [Al$_2$O$_3$ (0 0 0 1)] substrates have been characterized using X-ray Diffraction (XRD), Photoluminescence (PL) and Vibrating Sample Magnetometer
(VSM) in order to investigate the structural, optical and magnetic properties of the films respectively. It is observed from XRD that all the films are single crystalline with (002) preferential orientation along c-axis. PL spectra reveal that the addition of Mn marginally shifts the Near Band Edge (NBE) position towards the higher energy side. The magnetic measurements of the films using VSM clearly indicate the ferromagnetic nature.

E. de Posada et al [125] reported on the Pulsed laser deposition being used to prepare thin films of ZnO on (0 0 0 1) sapphire at 400 °C. The target-substrate distance and the background oxygen pressure were varied. A time-of-flight ion probe was used to investigate the interaction of the laser ablation plume with the background gas and measure the ion flux at the substrate. The film properties were measured using X-ray diffraction and photoluminescence spectroscopy. It has been shown that crystalline quality and the photoluminescence properties are better at higher oxygen pressures, which give a longer plasma residence time at the substrate.

Heo et al [126] reported that the ZnO films grown by PLD on c-plane Al₂O₃ substrates were annealed at temperatures up to 600 °C to produce n-type carrier concentrations in the range 7.5×10¹⁵ – 1.5×10²⁰ cm⁻³. After high-dose (3×10¹⁶ cm⁻²) Mn implantation and subsequent annealing at 600 °C, all the films show n-type carrier concentrations in the range 2 – 5×10²⁰ cm⁻³ and room temperature hysteresis in magnetization loops. The saturation magnetization and coercivity of the implanted single-phase films were both strong functions of the initial anneal temperature,
suggesting that carrier concentration alone cannot account for the magnetic properties of ZnO:Mn, and that factors such as crystalline quality and residual defects play a role.

Dhananjay et al [127] studied and reported about the Mn$_x$Zn$_{1-x}$O ($x = 0.20$) thin films deposited on Pt coated Si substrates using pulsed laser ablation technique. The structural characteristics of the films were investigated by X-ray diffraction (XRD), while the dielectric response of the films was studied as a function of frequency and ambient temperature by employing impedance spectroscopy. It was found that all the films deposited on Pt coated Si substrates had c-axis preferred orientation perpendicular to the substrate, with full width at half maximum (FWHM) of the (002) X-ray reflection line being less than 0.5°. The dc and ac electrical conductivity of Mn-doped ZnO films were investigated as a function of temperature. The ac conductivity, $\sigma_{ac}(\omega)$, varies as $\sigma_{ac}(\omega) = A\omega^s$ with $s$ in the range 0.4 – 0.9. The complex impedance plot showed data points lying on a single semicircle, implying the response originated from a single capacitive element corresponding to the bulk grains. The value of the activation energy computed from the Arrhenius plot of both dc and ac conductivities with $1000/T$ were 0.2 eV suggesting hopping conduction mechanism. The optical properties of Zn$_{0.8}$Mn$_{0.2}$O thin films were studied in the wavelength range 300–900 nm. The data were analyzed in the light of the existing theories and reflected a Burstein–Moss shift in these films. The films show magnetic properties, which are best described by a Curie–Weiss type behavior.
1.13 Survey of Other material doped on zinc oxide films by Chemical Methods

D. Djouadi et al [128] studied and reported about Al doped ZnO thin films were prepared by the Sol-gel method. The films were prepared by the method of dip-coating technique at room temperature on the glass substrates. Films were annealed at 500 °C for an hour. The X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmittance spectro photometry (TS) and luminescence spectroscopy (PL) were used for the sample characterization. The optical spectrum showed that the presence of A1 improves the transmittance in the visible range. The room temperature UV photoluminescence revealed that emission intensity was three times greater than that of pure ZnO. The Al doped ZnO thin films applied in the field of optics and optoelectronics.

Giwoong Nam et al [129] reported on the Al-doped ZnO thin films were grown by sol-gel dip coating method. The films have been investigated by characterization of the photoluminescence (PL) properties. It was observed that the nine different PL peaks were traced at different positions. The deep-level emissions (2.037, 2.592, 2.832, and 3.027 eV) were attributed to native defects. The near-band-edge (NBE) emission peaks at 3.354, 3.303, 3.260, 3.216, and 3.177 eV were attributed to the emission of the neutral-donor-bound excitons (D0X), two-electron satellite (TES), free-to-neutral-acceptors (e,A0), donor-acceptor pairs (DAP), and second-order longitudinal optical (2LO) phonon replicas of the TES (TES - 2LO), respectively. According to Haynes’ empirical rule, we calculated the energy of a free exciton (FX) to be 3.374 eV.
Hong-ming Zhou et al [130] reported that Aluminum doped zinc oxide (AZO) polycrystalline thin films were prepared by sol–gel dip-coating process on optical glass substrates. Crystalline ZnO thin films were obtained following an annealing process at temperatures between 300 °C and 500 °C for 1 h. The following characterizations were performed at room temperature. Those characterizations were X-ray diffraction (X-RD), UV – Visible spectrophotometry (UV-Vis), scanning electron microscopy(SEM), and electrical resistance measurement. The ZnO:Al thin films were transparent (90%) in near ultraviolet and visible regions. The grain size of the film increased, the transmittance also became higher and the electrical resistivity decreased.

H. Abdullah et al [131] reported about Sn doped zinc oxide polycrystalline thin films prepared by sol-gel process. The film was deposited on quartz substrate and annealed at various temperatures 400, 500 and 600 °C. The X-RD, SEM, photoluminescence (PL), and UV-Visible (UV-VIS-NIR) spectrometer characterization were performed. When the temperature is increased the particle size will also be increased. Size is directly proportional to the annealing temperatures. Due to the concentration of Sn the band gap is increased from 2.78 eV to 4.10 eV. Annealing temperature is also one of the important parameters for the formation of defects which is strongly to the non radiative recombination centers. The increment of the band gap is acceptable as a requirement for good anti-reflecting coating element. Therefore, these films can be applied on silicon solar cells.
Sergiu T. Shishiyanu et al [132] reported on NO\textsubscript{2} gas sensor fabricated by successive ionic layer adsorption and reaction (SILAR) technique and rapid photo thermal processing (RPP) of the Sn-doped ZnO film. The experimental results show that tin doping of zinc oxide thin films improve the sensor element sensitivity to 1.5 ppm NO\textsubscript{2} in air and down shift the operating temperature.

Shinobu Fujihara et al [133] reported about Li and Mg doped ZnO thin films prepared by sol-gel method. For studying the, doping effects the microstructure and electrical properties were characterized. The films were annealed at 500 °C for 30 min in flowing oxygen. When the crystalline size is increased by doping and the surface area of the film becomes rougher. The current density of the films is decreased by doping due to the creation of acceptor levels (Li-doping) and the reduction of oxygen defects (Mg-doping).

Shinobu Fujihara et al [134] reported on lithium-doped zinc oxide (ZnO:Li) thin films prepared on Pyrex borosilicate glass substrates by a sol–gel method. The prepared films were investigated by thermo gravimetry–differential thermal analysis (TG–DTA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), optical transmittance measurements, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). It was exposed that the films limited the organic compounds at temperatures up to 300 °C, which was the input to the conversion from the amorphous to the crystalline state. A Thermo dynamical reflection of nucleation and crystal growth was
made taking account of surface energies of the film and the glass substrate and an interfacial energy between them.

Qian Li et al [135] reported that these films were prepared by the method of dip-coating technique with various viscosity sols. For the different sols viscosity, the microstructure, optical and electrical properties of the Gallium doped zinc oxide films were investigated. When the roughness of the films also sols viscosity were directly proportional root mean square of the films. When the sols viscosity was obtained at 2.7cps, the film resistivity of $1.9 \times 10^{-2} \Omega \text{cm}$ and the hall mobility of $32 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were obtained. On the surface of the films several cracks and mountain like structure appeared on the surface of the film formed at 3.0 cps sol. For this sol transmittance of the Ga doped ZnO thin films is higher than 80% in visible range.

Haifan Liang et al [136] reported that the conducting ZnO:F were deposited as thin films on soda lime glass substrates by atmospheric pressure chemical vapor deposition (CVD) deposition at substrate temperatures of 480 – 500 °C. The electrical and optical characterization was performed for these films. Amorphous silicon solar cells were deposited using the textured ZnO: F films as the front electrode. The short circuit current was increased over similar cells made with fluorine doped tin oxide, but the voltages and fill factors were reduced. The voltage was restored by over coating the ZnO: F with a thin layer of SnO$_2$:F.
Sung-Kyu Kim et al [137] reported on K-doped ZnO films prepared on Al$_2$O$_3$ (0 0 0 1) substrates by solution deposition method. These prepared films were carried out by x-ray diffraction, transmittance spectroscopy, photoluminescence, Hall measurement and x-ray photoemission spectroscopy studies. From these studies we found that crystallinity, optical band gap, carrier concentrations and chemical binding states were changed at a K doping concentration and so on.

S. Mondal et al [138] studied about Cadmium-doped zinc oxide (Cd : ZnO) thin films prepared by SILAR method. From the structural characterization by X-Ray diffraction shows that the film exhibits the polycrystalline nature with increase cadmium incorporation. Particle size calculated from the line broadening with increasing cadmium incorporation. The presence of cadmium was confirmed by elemental analysis using EDX. The optical band gap of the films is decreased with increasing Cd dopant. The value of fundamental absorption edge is 3·18 eV for pure ZnO and it decreases to 3·11 eV for 10 % Cd:ZnO.

S. Ilican et al [139] reported on pure and indium doped Zinc oxide (IZO) thin films deposited onto glass substrates by the spray pyrolysis method. These films were incorporated by structural, electrical and optical properties with the indium incorporation. The structure and orientation were analyzed by XRD patterns. The morphological and elemental analyses were investigated by SEM and EDX analyses. The absorbance of the films was calculated by UV-Vis and the electrical resistivity was obtained by the Van der Pauw method in dark and under UV-illumination.
Q. G. Al-zaidi et al [140] reported about Palladium doped ZnO thin film deposited by chemical spray pyrolysis on a glass substrate to be a fast hydrogen gas sensor. The optical properties and surface morphology of the films were studied. The sensitivity and response time behaviors of the ZnO – based gas sensor to hydrogen gas were investigated.

Fahrettin Yakuphanoglu et al [141] reported about pure and Cd doped ZnO thin films deposited by the sol – gel method. The films had 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.

A. Douayar et al [142] reported on Neodymium-doped zinc oxide (NZO) thin films deposited on glass substrates by spray pyrolysis technique. An x - ray diffraction pattern shows the undoped and doped films exhibit hexagonal wurtzite structure. The doping concentration has been firmd by Rutherford backscattering analysis tells the neodymium is not incorporated easily into the ZnO host matrix. The Roughness of the
films were increased with the increasing Nd atoms. Nd dopant of the films was highly transparent in the visible region. The lowest electrical resistivity value of about $4.0 \times 10^{-2}$ $\Omega$ cm was obtained for 1% Nd effective doping.

Kai Huang et al [143] reported that Undoped and Mg-doped ZnO thin films were deposited on Si (1 0 0) and quartz substrates by the sol–gel method. Microstructure, surface topography and optical properties of the thin films have been measured by X-ray diffraction (XRD), atomic force microscope (AFM), UV–vis spectrophotometer, and fluoro photometer (FL), respectively. AFM studies reveal that rms roughness of the thin film changes from 7.89 nm to 16.9 nm with increasing Mg concentrations. PL spectra show that the UV–violet emission band around 386–402 nm and the blue emission peak about 460 nm are observed. The optical band gap calculated from absorption spectra and the resistivity of the ZnO thin films increase with increasing Mg concentration. In addition, the effects of Mg concentrations of microstructure, surface topography, PL spectra and electrical properties are discussed.

1.14 Survey on Gas Sensor for Mn doped on zinc oxide films by Chemical Methods

Upadhye et al [144] studied and reported that the Mn doped nanostructure ZnO thin film prepared by soft chemically route method. ZnO thin films were deposited on glass substrate by successive ionic layer adsorption and reaction technique (SILAR). After deposit ZnO thin film dipped in MnSO$_4$ solution for 1 min. The optical properties as absorbance were determined using UV-Spectrophotometer and band gap was also calculated. The Structural properties were studied by XRD. The improvement in gas
sensing properties was found to enhance after doping of Mn on ZnO thin film. The Photo Sensor nature was calculated by I-V characteristics.

V. Sandip et al [145] reported on the Mn doped nanostructure ZnO thin film prepared by soft chemically route method. ZnO thin films were deposited on glass substrate by successive ionic layer adsorption and reaction technique (SILAR). After deposit ZnO thin film dipped in MnSO4 solution for 1 min. The optical properties as absorbance were determined using UV-Spectrophotometer and band gap was also calculated. The Structural properties were studied by XRD. The improvement in gas sensing properties was found to enhance after doping of Mn on ZnO thin film. The Photo Sensor nature was calculated by I-V characteristics.

Chatterjee et al [146] reported that during the past few decades, semiconductor metal oxide (SMO) gas sensors have become a prime technology in several domestic, commercial, and industrial gas sensing. The semiconductor properties of Zinc oxide along with its dopant remain to be trapped fully in its application as gas sensor. With the advent of nanotechnology, miniaturization and high sensitivity happens to be a key issue in sensor fabrication. Most of the SMO gas sensors fabricated by nanotechnology process operate at high temperature. This paper gives a new insight to hydrogen gas sensor characteristics, by reducing the operating temperature of hydrogen (H2) sensor, fabricated from the nano particle of manganese doped zinic oxide(ZnO), synthesized by chemical precipitation method.
Changsheng Xie et al [147] studied about the Nanostructured flat-type coplanar gas sensor arrays of ZnO with different MnO$_2$ additive concentration were fabricated by a combination of screen-printing technology and solution growth process. The morphologies and crystal structures were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). The results showed that ZnO nanostructures were induced on the surface of gas sensor arrays through the solution growth process. The nanostructures were composed of nanowalls and nanosheets with the thickness of about 50–200 nm and length of about 1–2 μm. The resistance–temperature characteristic and the response to formaldehyde revealed that the solution growth process could effectively control the morphologies, change the aspect ratio of ZnO nanostructures and significantly improve the response of gas sensor arrays. In addition, the response to formaldehyde of ZnO sensors with 0.5 wt % and 1.0 wt % MnO$_2$ additive was higher than that of pure ZnO sensor.
1.15 Conclusion

This literature for the Mn doped ZnO thin films prepared by chemical methods, physical methods and gas sensor was studied. This survey gives the information about properties of fabricated film like structural, optical, magnetic, electrical, spectroscopic, magnetic and sensor information. Based on this literature survey I carried my research work and completed successfully.
References


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