Thin film physics and technology is a keystone in modern applied physics. It is relatively young and ever growing field in physical, chemical, material, applied and nanosciences. It is the prime need of this informative, global society, to develop technology at nanoscale level which is also a fascinating research. It has taken a prominent part in revolutionary development of the various fields of science and technology, including diverse fields of electronics, optics, space science, aircraft science, defense and other industries. Applications of thin films range from micrometer dots in microelectronics to the coatings of several square meters on window glasses. This motivates researchers to develop different thin film deposition systems. In view of this an innovative attempt was made to deposit thin films by a novel, newly fabricated, homemade spray CVD technique. To fully exploit this, one requires knowledge of structure evolution of polycrystalline thin films by a pathway as nucleation, crystal growth and finally grain growth. Hence systematic studies on Zinc oxide were carried out to gain the necessary information of the system. In general thin film transparent to visible light and conducting electricity is called a transparent conductor. During last few decades' thin films of transparent conducting oxides (TCOs) with high optical transparency and electrical conductivity have been extensively studied for various applications. There is growing interest in the development of transparent conducting oxides. TCOs mainly include semiconducting oxides such as SnO₂, CdO, In₂O₃, tin-doped indium oxide (ITO) and Zinc Oxide. Among these materials Zinc Oxide is technologically important. The properties of Zinc Oxide material can be tuned to suit particular application by controlling different growth parameters of physical and chemical methods. In chemical spray pyrolysis technique parameters like film thickness, solution concentration, flow rate, substrate and core temperature etc are more important and necessarily required to optimize to tune the properties of zinc oxide for the particular application. The main aim of the present research work is to introduce an attempt for synthesizing undoped and doped ZnO polycrystalline thin films at low
substrate temperature by using spray CVD technique. The role of ZnO as transparent conductor and gas sensing element has been investigated.

It is well known that the structural, optical and other important properties of pure ZnO thin films are mainly determined by the crystals size, shape and morphology. The introduction of specific dopant in general modifies the properties of such ZnO nanocrystals in well-controlled ways. During the course of the present work it is observed that altering the atomic composition of the nanocrystals by introducing the specific dopants also lead to dramatic changes in morphology. Depending on the atomic composition of B, F, and Al dopants in ZnO thin films, changes morphology of nanostructures from well developed triangular pyramidal shaped to spherical morphology due to Boron doping, cauliflower shaped morphology due to Fluorine doping and finally into well developed disc shaped hexagonal crystal structure offered by Aluminium doping. These morphology exhibits tunable optoelectronic properties which are obtained for the first time. It is demonstrated that by using novel spray CVD technique; it is possible to synthesis pure and doped ZnO thin films. It is also observed that these surface morphology play major role in gas sensing mechanism as it depends on surface adsorption sites.

Hence as per the work discussed in this thesis, a newly fabricated, homemade spray CVD technique is a novel thin film technique for the fabrication of transparent conductive oxide layers as well as for the fabrication of chemically sensitive layers. In our recent investigations it is observed that, the preparative parameters of spray CVD technique such as core (reaction chamber) temperature, substrate temperature, spray rate, concentration of the initial ingredients etc. influence the structural, morphological, electrical and optical properties of pure and doped Zinc oxide thin film. The different phases of the work carried out during the course of the research work are mentioned in this chapter VIII.

Chapter-I commences general introduction to undoped and doped ZnO thin films with potential application towards Transparent Conducting Oxides as well as in the fields of harmful gas sensing properties. The nature of undoped and doped transparent conducting oxide materials with respect to structural and other intrinsic properties have been presented. An extensive survey of literature has been made on pure and doped ZnO thin films. The purpose of thesis is stated at the end of chapter.
Chapter Eight  Summary & Conclusion

The chapter II deals with the theoretical background. Chapter III explains in detail the homemade spray CVD set up. The details of structural, electrical, optical characterization techniques; such as X-Ray diffraction ((XRD), Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscopy (AFM), Hall Effect in Van Der Pauw configuration, optical absorption/ transmission also explained therein. The experimental setup used for the gas sensing was developed in the laboratory and explain in this chapter.

The undoped zinc oxide films were deposited by using the optimized preparative parameters of Lokhande et al in case deposition of zinc oxide thin films by conventional spray pyrolysis system. The behavior of the newly design technique was studied during these experimentation. The effect of core (reaction chamber) temperature and substrate temperature variation was studied to deposit ZnO thin films. This chapter also includes the optimization of preparative parameters of the spray CVD set up to achieve good quality films of ZnO. The quality of thin films depends on various preparative parameters and hence it is essential to optimize each process parameter in order to obtain good quality films with optimum transmittance, conductance to use as transparent conductor.

Chapter IV contains two different sections. The first section deals with synthesis of Boron doped ZnO thin films with varying doping concentration. The doping concentration was varied in the range of 0.2 atomic wt% to 1.0 atomic wt% in steps of 0.2. Section two of the chapter deals with the thickness variation of Boron doped ZnO thin films; which are deposited by spray CVD technique at low substrate temperature.

The effect of concentration variation of Fluorine doping on ZnO thin films was studied. The effect of doping concentration on the electrical and optical properties of the films was explained in detail in chapter five. The chapter six explains the effect of concentration variation of Aluminium doping in ZnO thin films on the physical and chemical properties of the films were explained in detail. All these films were tested for reducing gases such as H₂S and LPG and their response was recorded. The results were explained with reference to doping and variation in operating temperature. The variation in concentration of gas and response time also studied for all samples and results were explained in detail. Chapter Eight deals with the summary and conclusions.
**Effect of core temperature variation on the properties of ZnO thin films**

The intrinsic nanocrystalline ZnO thin films are synthesized with a newly designed, homemade spray CVD technique. The major benefits of the technique are precise stoichiometry and its ability to deposit vapors on a large surface area with a high uniformity of thickness. The commercialization potential is enhanced by the low deposition temperature.

During the synthesis of ZnO thin film the decomposition temperature of the initial ingredient (Zinc Acetate) was obtained by using TG-DTA analysis. The total weight loss with no phase of Zinc Acetate has been observed at 327°C. The pilot experiment shows that films prepared at 330°C with the spray rate 6ml/min are polycrystalline and without any traces of zinc acetate. During the synthesis of pure ZnO thin films in non aqueous medium (solution quantity- 200ml ) by spray CVD technique the substrate temperature was kept constant at 220°C and effect of core temperature variation was studied in the range 300°C to 360°C in steps of 30°C. 0.075M solution was used as initial ingredient and spray rate was kept constant at 6ml per minute. XRD analysis reveals that all films show preferential orientation along (002) plane. The crystallite size determined from XRD was 28 nm. Among all the three samples, films deposited at 330°C are highly textured. FESEM micrographs reveal the triangular pyramidal shaped microstructure. The 2D AFM micrograph exhibits similar triangular pyramidal shaped crystallites. Surface topography observed from three dimensional AFM shows increase in roughness. The electrical resistivity studies indicate shallow and deep donor levels in the band gap of zinc oxide semiconductor. The activation energy values at low and high temperatures are low for the sample prepared at 330°C core temperature. The optical transmittance curve exhibits the interference fringe pattern showing enhanced optical transmittance with core temperature. Absorption data is used to calculate band gap energy. The sample prepared at 330°C core temperature shows minimum band gap energy. This may be attributed to the better crystallinity of the films at that core temperature.

**Effect of substrate temperature variation on the properties of ZnO thin films**

The results of core (reaction chamber) temperature variation reveals that ZnO thin film prepared at 330°C core temperature through non aqueous route with 0.075M zinc acetate solution exhibits good structural, electrical and optical
properties. To optimize the substrate temperature all other parameters are kept constant and substrate temperature was varied from 190°C to 250°C in steps of 30°C. The structural analysis of as deposited samples was done by using X-ray diffraction technique. It is found that all samples are polycrystalline with wurtzite hexagonal crystal structure. It is also found that all films exhibits orientation along c-axis perpendicular to substrate. It is found that substrate temperature dominates reaction kinetics and results into very good films formation at 220°C substrate temperature. At high substrate temperature increase thermal moments of the particle may affect the growth along the (002) plane. The FESEM micrographs support the observations in X-ray diffraction studies. The dramatic change in surface morphology is also observed with variation of substrate temperature and very clear morphology is observed at 220°C. However, at 250°C substrate temperature reduction in size and shape of pyramidal morphology is observed. The 2D topography observed by AFM micrographs reveal the development of dense, triangular pyramidal shaped crystal structure which supports the results observed by FESEM micrographs. The 3D topography indicates that the triangular pyramidal shape at 220°C causes to increase the roughness (~380nm) as compared with other samples. The activation energy was compared and it is found to be minimum for the the sample prepared at 220°C substrate temperature. This decrease in activation energy may due to better crystallanity of the sample. The room temperature transmittance spectrum of ZnO thin films exhibits the interference phenomena indicating excellent homogeneity. From the optical study it is found that, transmittance increases with increase in substrate temperature. It may be attributed to the decrease in defect levels which may reduce the scattering of light. The other reason for improvement in transmission may be decrease in thickness with increase in substrate temperature. The photoluminescence measurements show that the near band edge UV emission is enhanced at substrate temperature 220°C and on the other hand for lower and upper substrate temperature it is suppressed. The narrower and higher energy near band edge emission UV peak indicate that the undoped ZnO thin films synthesized by spray CVD technique exhibits improved crystalline at substrate temperature 220°C. From these experiments it is observed that 330°C is the optimum core temperature and 220°C represents optimized substrate temperature to deposit undoped ZnO thin films by
spray CVD technique. For the further study these preparative parameters were used to deposit the doped ZnO thin film.

**Effect of Boron doping on the properties of the zinc oxide films**

The purpose of this study is to gain a better understanding of boron doped ZnO by spray CVD method. For synthesis of B: ZnO lattice matrix and characterized by XRD, FESEM, AFM and other techniques. In view of this, we have optimized the preparative conditions of ZnO thin film, to get good quality films using spray CVD technique. To prepare Boron doped thin films, the corresponding volume of 1M of Boric acid solution was added to the initial solution. In the first stage of this work, keeping all preparative parameters constant we have studied effects of Boron doping concentration variation. In the second stage we have investigated the effect of thickness variation of Boron doped ZnO thin film by varying corresponding volumes of spraying solutions (100ml to 500ml at a step of 100ml). To synthesize the optimum Boron doping concentration in ZnO lattice matrix, the range of 0.2 to 1 at% (in steps of 0.2) have been selected. Structural analysis indicates the key role played by different doping concentration of boron in the structural growth of ZnO thin films. It shows that (002) is the dominant diffraction peak along with (100) and (101) well defined peak. The dominant peak arises from diffraction of ZnO planes of grains oriented with c-axes perpendicular to the substrate. Among all doping range of Boron, 0.8 at% concentration exhibits maximum peak intensity. However, Boron doping shows deteriorated crystallinity as compared with undoped ZnO thin films.

In ZnO:B films, the boron atoms may goes to substitution or interstitial sites may promote meaningful changes in the films lattice parameters. The effect of crystallite size induced broadening and strain induced broadening in the full width at half maximum (FWHM) of XRD peak was studied using Williamson–Hall plot. It shows that the increase of the boron content deteriorates the pyramidal shapes of the grains resulting into the decrease in size of these grains. The lattice constant ‘c’ of ZnO films is shorter than the bulk ZnO; it indicates tensile stress in the films. The value of the bi-axial stress is positive indicating that the films are under tensile stress. Also, the value of the stress is found to increase with increase in B doping concentration. The morphologies of ZnO nanocrystals exhibited striking dependence on the concentration of dopant ions with transition of shapes from
triangular shaped pyramids to cluster of islands, followed by nanospheres, and finally into petal shaped morphology. However, among all doping range of Boron, the 0.8 at wt% doping shows uniform, homogeneous spherical grains indicating smooth bead like morphology. These results are inconsistent with AFM surface topography. The electrical resistivity study shows that the minimum activation energy observed for 0.8 at wt% doping in both lower and higher temperature zone. It may be due to occupation of Zn$^{+2}$ sites by B$^{+3}$ ions in ZnO lattice causing to increase electron density. At optimum doping concentration, the maximum electron density causes the reduction in the height between donor levels to the conduction band resulting into the minimum thermal energy required to raise these electrons (called as activation energy). The average transmission in visible region was found to be 90% for 0.8 at wt% Boron doping. It shows that increasing doping concentration, results into increased transmittance of thin films. The absorption spectra reveal that as deposited films have low absorbance in the visible and near infrared regions while the absorbance is high in the UV region. The 0.8 at wt% B: ZnO thin film show minimum absorbance among all the thin films.

The structural, morphological, optical and electrical characteristics suggest that the sample prepared for 0.8 at wt% Boron concentration shows significant improvement in electrical and optical properties. This indicates the 0.8 at wt% is the optimized doping concentration with highly transparency and low resistivity.

**Effect of Thickness variation on properties of Boron doped ZnO thin films**

Effect of thickness variation was studied for the films prepared with optimum doping concentration (i.e. 0.8 at wt%). The films with varying thickness were obtained by spraying different volumes (100ml to 500ml at a step of 100ml) of spraying solution. The XRD analysis shows no change in preferential orientation. However it shows the increase of grain size with thickness. It can be attributed to the improved crystallinity due to increased ability of adatoms to move towards stable sites in the lattice because of increase in thickness. FESEM micrographs reveal that with increase in thickness the radius of nanospherical shaped morphology increases. At higher thickness the core shell of these microspheres are broken and bowl like morphology is observed. Finally for maximum thickness (486nm) it shows flower like morphology. These results are confirmed with AFM studies. 3D micrographs show increase in smoothness with thickness of thin film.
Arrhenius plot shows that with increase in thickness the activation energy goes on decreasing. Van der Pauw resistivity and Hall Effect measurements are used to measure the electrical parameters. Both the sheet resistance and resistivity are found to decrease with increasing thickness of thin film. It is observed that the Hall mobility and the carrier concentration increase resulting in decrease in resistivity. This improvement of electrical properties of the films can be explained in terms of enhancement of crystallization with increase in thickness. The optical transmission spectra show decrease in average transmittance with increase in thickness of thin film. The optical absorption study reveals that the refractive index increases with increase in thickness. The increased thickness of B doped ZnO thin films causes red shift in the optical band gap. Room temperature photoluminescence spectra shows very intense UV emission peak located at 385nm along with a weak blue emission band located at 475nm. The intensity of UV emission band goes on increasing with increasing thickness on the other hand intensity of blue emission band remains unchanged. It is attributed to the band edge emission or the exciton transition. The amplification of the UV emission indicates that the crystalline defects in the ZnO film have changed after B doping. Strong UV emission depends on microcrystalline structure indicating enhanced crystallinity with increased thickness of thin films. The results reveal that with increasing thickness the resistivity decreases remarkably however the transmittance decreases significantly.

**Effect of Fluorine doping on properties of ZnO thin films**

Fluorine doped ZnO thin films have been deposited by spray CVD technique onto glass substrate. Zinc acetate (dehydrate) and ammonium fluoride were used as a starting material. The solution of 0.075M of Zinc acetate in methanol and that of ammonium fluoride of 1M used for deposition. The 200ml solution of zinc acetate in methanol was used as the main solution. For different concentrations of Fluorine doping, ranging from 0.2 at wt% to 0.8 at wt% corresponding volume of ammonium fluoride was added to the main solution. The films are prepared at previously optimized parameters. XRD analysis implies that the crystallinity and degree of orientation of the ZnO: F films were closely associated with the F doping concentration. The highly orientation along c-axis is observed for 0.2 at wt% doping concentration with enhanced crystallinity. On the other hand, with increase in Fluorine content above 0.2 at % causes to decrease intensity of all peaks. No
significant change in bond length is observed with Fluorine content. Hence the basic crystal lattice of ZnO is not modified by doping. SEM micrographs reveal remarkable change in surface morphology. For 0.2 at wt% of fluorine, the surface morphology was very smooth, more compact, dense with uniform spherical grains supporting the (002) intensity maxima observed for same sample during XRD studies indicates the complete crystallization. 2D AFM topography indicates a reasonably rounded geometry with non porous, regular and uniform texture for all micrographs. It also reveals the increased grain size due to the F doping. Arrhenius plot shows minimum activation energy for 0.2 at wt% F doping. Van der Paw’s measurement indicates 0.2 at wt% be the optimum Fluorine doping concentration showing minimum resistivity due to increase in carrier concentration. The maximum visible average transmission was observed to be 92% for optimum at doping concentration of 0.2 at wt%. This transmission was significantly better than most TCO’s. The refractive index calculated from reflectance spectra indicates that the fluorine incorporation in the films raises the refraction index value for 0.2 at wt% doping concentration. The Fluorine incorporation at ZnO thin films shows optical band gap widening. The photoluminescence measurements exhibited three PL bands centered on 385nm, 440nm and 500nm which correspond to near ultraviolet emission, blue band emission and green emission band respectively. The amplification of UV emission for 0.2 at wt% F doping indicates higher crystalline quality structure. The structural, electrical and optical characteristics reveal that 0.2 at wt% represents optimized Fluorine doping concentration in order to achieve highly transparent conductive films.

Effect of Aluminium doping on properties of ZnO thin films

Al doped ZnO thin films have been deposited by spray CVD technique onto glass substrate. Dehydrate Zinc acetate and Aluminium Chloride was used as a starting material and dopant source. The solutions of Zinc acetate of 0.075M and Aluminium Chloride of 1M were made in methanol. The 200ml solution of zinc acetate in methanol was used as the main solution. For different concentrations of Aluminium ranging from 1.1 at wt % to 1.6 at wt % in steps of 0.1 at wt % the corresponding volume of Aluminium Chloride was added to the main solution. With previously optimized preparative parameters films were prepared. The result of this study is to provide insight into the structural, morphological, electrical and
optical properties and role is played by Aluminium dopant into ZnO lattice. The first stage of optimization of the growth of Al doped ZnO thin films were to study the dependence of their crystallinity as a function of doping concentration. General examination of XRD patterns shows that the principal line (002) of the hexagonal wurtzite ZnO are the strong in whole spectrum of undoped as well as Al doped ZnO thin films. Among all doping range of Al, the 1.3 at wt% shows enhanced (002) peak intensity which imply the improvement in crystallinity at 1.3 at wt%. Debye Scherrer calculation shows maximum particle size (46nm) for 1.3 at wt% Al doping. The FESEM morphologies exhibited striking dependence on the concentration of dopant ions with transition of shapes from irregular polygonal into well developed, enhanced hexagonal grains. The morphology indicates that the average surface grain size increases with increasing concentration of Al. However, above optimized (1.3 at wt%) doping concentration deterioration in crystallinity is observed with irregular polygonal shaped morphology with average grain size of 100nm diameter. Electrical conductivity measurements reveal enhancement conductivity with increase in Al doping concentration up to optimum doping concentration and then decreases. Higher conductivity value was obtained for 1.3 at wt% Al-doped ZnO film. An initial increase in the conductivity is due to an increase in the free-electron concentration with Aluminium incorporation in the ZnO film. Afterwards, the electrical conductivity decreases with the subsequent addition of Aluminium. It may be due to the reduction in the grain size. Van der Paw's measurements show similar dependence of conductivity on Al doping concentration. The wavelength spectral distribution of transmittance is significantly better than most TCO's (96%) reported earlier. It indicates that the thin films have moderate absorption coefficients and thicknesses with surface uniformity. The Al incorporation at ZnO thin films shows optical band gap widening. The photoluminescence measurements indicate enhanced UV emission in the ZnO film after Al doping. The enhanced crystallite size due to moderate Al doping (1.3 at wt%) causes to decrease in the defects concentration favors the band to band transition which leads to the amplification of this emission.

**Studies on gas sensing properties of undoped and doped ZnO thin films**

The development of gas sensors to monitor toxic and combustible gases is imperative for environmental pollution and safety requirements for the industries.
In view of this these thin films of undoped and doped Zinc Oxide semiconductor are well explored towards the toxic reducing gases like H₂S, and highly flammable reducing gases like LPG. The fundamental sensing principle relies on the change of conductivity of sensor at moderate temperature when exposed to certain target gases. The decrease in resistivity in n-type semiconductor gas sensor when exposed to reducing gases results from desorption of oxygen adsorbed on the surface & grain boundaries of metal oxides at high temperature in air results in a free electron trap. In the present work we have additionally tested as deposited films in sensing harmful reduced gas like H₂S and highly flammable gas like LPG. It is observed that all films are found to be highly sensitive to lower concentration (10ppm) of reduced gases. As deposited films offer response to H₂S gas for operating temperature 300°C however for liquid petroleum gas the operating temperature shifts to the higher side i.e. at 325°C. The optimized parameters observed in sensing H₂S and LPG gas, have been mentioned in following Table 8.1. By observing sensing properties of undoped and doped ZnO thin films, it is concluded that 1.5 at wt % Al doped ZnO thin films show measurably good sensitivity among the other films deposited with boron and aluminum doping.

**Table 8.1 Comparison of H₂S and LPG gas sensing properties of optimized undoped and doped ZnO thin films**

<table>
<thead>
<tr>
<th>Optimized conc. for gas sensing</th>
<th>H₂S gas</th>
<th>LPG gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Response Time (sec.)</td>
<td>Recovery Time (sec.)</td>
</tr>
<tr>
<td>ZnO</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>0.4at% B:ZnO</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>0.4at% F:ZnO</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>1.5at% Al:ZnO</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>