Synopsis

Semiconductor devices have become an integral and indispensable part of our daily life. Since the past few years, there have been significant improvements in the quality of thin films of II-VI semiconductors. ZnO thin films have attracted large interest in view of their high exciton binding energy, rich defect chemistry and reasonably large electromechanical coupling, giving rise to a variety of applications. There is strong luminescence in the blue–orange region of the ZnO spectrum and it is suitable as a material for phosphor applications. The *n*-type semiconducting property of ZnO makes it appropriate for applications in vacuum fluorescent displays and field emission displays. The high electrical conductivity and high transparency of ZnO thin films are suitable for Transparent Conducting Oxide [TCO] applications. ZnO has the characteristic property of high thermal conductivity which translates into high efficiency of heat removal in devices. The wide and direct band gap enables applications in optoelectronics in the UV-visible region, including light-emitting diodes, laser diodes and photo detectors. It has been observed that ZnO exhibits exceptionally high radiation hardness and is important for high altitude or space applications.

Native or intrinsic defects are imperfections in the crystal lattice that includes vacancies, interstitials and antisites. Native defects strongly influence the electrical and optical properties of semiconductors. Recent developments in the control of the electrical conductivity of ZnO have extended its applications. While a number of research groups have reported *p*-type ZnO, there are still problems regarding the reproducibility of the results and the stability of the *p*-type semiconductivity. The intrinsic *n*-type semiconductivity in ZnO is still under active research. But in the presence of external impurities/dopants, the situation is highly complex and it requires a thorough correlation of the defect chemistry with the electrical and optical properties. The present study has therefore aimed to understand and establish this correlation.

Lithium (Li) may behave both as a donor and as an acceptor in ZnO depending on the substitution site. Since the ionic radius of Li ion is small, it can easily occupy interstitial positions. When Mn^{2+} ions are incorporated into the Zn sites, there is possibility of mixing between the *s-p* electrons of the host and the d-electrons of the Mn^{2+} ions, resulting in the forbidden transition of $^4T_1$–$^6A_1$ being partially allowed, leading to the characteristic orange emission. As the Mn^{2+}content increases in the host system, the intensity of orange emission is also expected to increase because the Mn^{2+} ions would capture more electron–hole pairs and emit more photons. Therefore, one of the important objectives of the present study is to evaluate the influence of defects like Li^+ in Mn^{2+}-substituted ZnO on the orange emission as well as on NLO properties.

The thesis begins with a general introduction to basic properties of semiconducting systems followed by various intrinsic defects in ZnO. Intrinsic defects and their basic properties are influencing the electrical and optical properties. The introduction of dopants or impurities in the crystalline system results in the breaking of symmetry and modification in crystal structure which are reflected on the band structure. Therefore, the crystal structure and band structure of ZnO are discussed. Photoluminescence is one of the best techniques to study defects. During excitation process, electron-hole pairs are formed and their recombination to emit photons is then discussed. In ZnO, the visible emissions in blue and green regions are discussed along with time-delayed phosphorescence for orange emission. The presence of external impurities is expected to influence the NLO properties. This is discussed in relation to the Two-photon absorption (TPA) process. We also discuss the importance of the NLO properties and its photonic applications. Thus, **C*hapter 1*** concludes with various applications of thin films and significance of this study.

Chapter 2 describes various deposition techniques for the preparation of ZnO thin films and concludes the discussion with a special significance of sol-gel technique. The films are then subjected to various characterization techniques depending on the requirements of particular application. As a first step the evolution of the crystalline phase in the thin films is studied by X-ray diffraction (XRD) analysis using an X-ray diffractometer (XRD, Model D-5005, Bruker, Germany). The refractive index and film thickness are determined from the transmittance spectra using a UV–Visible spectrometer (Model Lambda 35, Perkin Elmer, UK). Film thickness is evaluated from transmittance spectra using the envelope method as discussed by Manifacier. Refractive index is evaluated through Sellmeier dispersion relation from the transmittance spectra. The transverse piezoelectric properties of the ZnO thin films are evaluated using unimorph cantilevers of ZnO/Si. Application of sine wave voltage between upper and bottom electrodes generates the deflection by the transverse inverse piezoelectric effect, and the tip displacement is measured using a Laser Doppler vibrometer (AT-3500, Graphtec, Germany) and a laser interferometer (AT-1100, Graphtec, Germany). Microstructures of the thin film are determined using a high resolution scanning electron microscope (HR-SEM, Model FEI Quanta FEG 200, USA). For Non Linear Optical studies, z-scan technique is one of the best techniques in the open aperture configuration. This technique is employed to understand the basic mechanism behind the NLO properties. Electrical characterization is carried out by four probe method using Hall measuring system (Ecopia Model HMS 3000, South Korea). Photoluminescence (PL) spectra are recorded with a PL spectrometer (Model Lab Ram HR, Horiba Jobin Yvon, France) using a 325 nm excitation wavelength of He–Cd laser (Spectra Physics, USA). Then, phosphorescence measurements are carried out on a PL spectrometer using a pulsed laser (Model SPEX Fluorolog, HORIBA Jobin Yvon, UK).

For many opto-electronic applications like optical limiting and switching, the knowledge of the NLO properties of materials is necessary. Density of defect states within the bandgap of ZnO thin films are directly related to visible emissions as well as NLO characteristics of the transparent semiconducting system. ***Chapter 3*** discusses the influence of dopants like Li on the density of the defect states, and therefore on the NLO characteristics. Thin films of $(Zn_{1-x}Li_x)O$; x = 0, 0.01, 0.02, 0.05 and 0.10 are prepared on glass substrates by sol-gel method by adopting the spin coating technique. In the ZnO-based thin films, the structural characterization is done using XRD. The presence of defect states is also confirmed from absorption spectra recorded using UV visible spectrophotometer as well as from the PL spectra. Consequently, the influence of defects on the photoluminescence emission process is discussed using defect chemistry. Variation of Reverse Saturable Absorption [RSA] observed in open aperture z-scan method is discussed to establish correlation between blue emission and NLO behavior of Li doped ZnO thin films.

Transition metal ions-doped ZnO thin films have attracted interest because of spintronic applications. Most of the researchers have paid their attention on the magnetic properties. However, the optical properties of the transition metal doped ZnO semiconductor is not fully understood, which is mandatory for the design of modern opto-electronic devices. ***Chapter 4*** describes preparation of $(Zn_{1-x}Mn_x)O$; x = 0, 0.005, 0.01, 0.02 and 0.05 thin films on glass substrates by sol-gel technique by adopting the spin coating procedure. Photoluminescence spectra of the Mn doped ZnO reveals the influence of Mn doping on the intensity of green emission. Open aperture z-scan method in RSA is discussed to establish a correlation between the mechanism for green emission and their NLO properties.

Mn^{2+} is a deep donor in ZnO and creates donor levels 0.31 eV below the conduction band. This donor state is expected to influence the typical orange emission of the Mn doped ZnO thin films. It is reported that there is interaction between the Mn dopant and intrinsic defects such as oxygen vacancies in ZnO and optical nonlinearities increase with the increase in dopant concentration. Therefore, the addition of deep donors like Mn could be effectively used to control the density of the defect states, thereby tailoring defect emission along with NLO characteristics. Li substitution in the Zn site creates an acceptor state around 0.5 eV above the valence band. So co-doping lithium and manganese in ZnO may create donor and acceptor levels within the bandgap and this is expected to influence visible emissions, especially spin-forbidden orange emissions. The influence of the defect states on the orange emission has been studied by altering the defect density through appropriate Li substitution. $(Zn_{0.99-x}Li_x Mn_{0.01})O$; x= 0, 0.005, 0.01, 0.02 and 0.04 is the composition we opt for this studies. In the present study, the Mn-content is kept constant to prevent the influence of variation of Mn-content on the band gap. The defect-mediated mechanism gets importance in the orange emission of Li. and Mn. co-doped ZnO thin films and are discussed in detail in ***Chapter 5***.

In ZnO lattice, lithium ions $[Li^+]$ substituting Zn^{2+} ions act as acceptors enhancing the electrical resistivity. It is also known that, in order to achieve good piezoelectric activity, the films should have preferred (002) orientation. Therefore, we have prepared $[Zn_{1-x}Li_x]O$; x=0, 0.05, 0.10 and 0.20 thin films on platinum coated silicon substrates by sol-gel method. ***Chapter 6*** is dedicated to the piezoelectric applications of lithium doped ZnO thin films. Piezoelectric micro-actuators operate at relatively low frequencies [less than 1 kHz] requiring high resistivity. Transverse piezoelectric coefficient, $|e_{31}^*|$, of the thin films are evaluated from the deflection of $(Zn_{1-x}Li_x)O$/Pt/Ti/SiO2/Si cantilevers by applying unipolar sine wave voltage. The measurement method of e_{31}^* and the basic principles are briefly discussed in this chapter.

The outcome of this research includes the following four research publications in international journals.