CHAPTER V
SUMMARY AND CONCLUSION

This chapter summarizes the present research work and the major conclusions derived.

5.1. Summary

In recent years, considerable interest has been generated in the study of compound semiconductors with dimensions in the nanometer range. The opportunity to study the physics in small dimensions added the bonus of novel optical and transport properties exhibited by this material continuously fascinate and hold the interest of researchers worldwide. Over the last 10 years, it has been realized that nanomaterials have some unique properties, which have been attributed to their size dependent bandgap energy. Nano-semiconductor materials that exhibit peculiar properties which are not shown by their bulk counterparts have attracted much interest from both fundamental and technological researchers. ZnO is technologically an important material due to its wide range of optical and electrical properties; also it is a semiconductor crystal with a large binding energy (60 meV) and wide band gap (3.3 eV at 300 K). ZnO nanoparticles are used in a variety of applications such as UV absorption, antibacterial treatment, UV light emitters, and photocatalyst and as an additive in many industrial products. It is also used in the fabrication of solar cells, gas sensors, luminescent materials, transparent conductor, heat mirrors and coatings.

The II–VI compound semiconductor has been studied for a variety of applications such as optical coatings, photoconductors, optic modulators, electro-optic modulators and fabrication of solar cells.. In doped ZnO semiconductors, in contrast with undoped ones, the impurity states play a special role in affecting the electronic energy structures and transition probabilities. For doped nanocrystalline semiconductors, quantum confinement effects in the energy states also produce unusual physical and optical behavior. The doping ions act as recombination centers for the excited electron–hole pairs and result in strong and characteristic luminescence.

A variety of synthesis routes have been reported for the synthesis of metallic nanoparticles, for example thermal decomposition, laser ablation, microwave

irradiation, sonochemical, reverse micelles process, chemical reduction, ultrasonic irradiation, radiolysis, solvothermal and electrochemical. However, controlling the particle size distribution and stability of the particles is extremely difficult and does not provide enough usage of their properties. Another disadvantage in using the nanoparticles alone is due to their potential dangers associated with their size which can affect humans and the environment. Hence we need environment friendly synthesis technique to prepare pure and doped ZnO nanocrystalline films. The chemical bath deposition method has been found to be cost effective and environment friendly method to prepare high quality uniform size nanocrystalline films.

In the present work, we have attempted to prepare and characterize pure and doped (Mn^{2+}, Cu^{2+} and Pb^{2+}) ZnO nanocrystalline films with different dopant concentrations viz. 2.5, 5.0, 7.5 and 10.0 mole % by the simple chemical bath deposition method with the easily available chemicals. The main advantage of this approach is that they are simple, cheaper and convenient. Results obtained indicate that the chemical bath deposition method is a considerable one for the preparation of pure and doped (Mn^{2+}, Cu^{2+} and Pb^{2+}) ZnO nanocrystalline films.

X-ray powder diffraction (PXRD) and energy dispersive X-ray absorption (EDAX) analysis were carried out to characterize the prepared samples chemically and structurally. The crystallite sizes were found to be less than 25 nm for all the prepared nanocrystalline films considered in the present study. The indexed data indicate wurtzite phase for all the samples and the unit cell volume increases with increasing compositions from 2.5 to 10.0 mole % for the Mn^{2+}, Cu^{2+} and Pb^{2+} added nanocrystalline films. The presence of Mn^{2+}, Cu^{2+} and Pb^{2+} is revealed clearly by the EDAX data. The stoichiometric concentration of dopant in ZnO nanocrystalline film is also estimated from EDAX analysis. Atomic force microscopic (AFM), Scanning electron microscope (SEM) and Transmission electron microscopic (TEM) analyses were also carried out. The calculated particle sizes were well matched with the XRD results.

The prepared samples were optically characterized by carrying out UV-Vis absorption spectra and photoluminescence spectra. The optical bandgap energies are found to be varied from 3.64 to 3.30 eV with the increasing dopant concentrations from 0.0 to 10.0 mole % (in steps of 2.5 mole %) for the Mn^{2+} doped ZnO nanocrystalline film. The addition of Cu^{2+} and Pb^{2+} slightly decreases the bandgap energy values and

are found to be varied from 3.45 to 2.477 eV and 3.36 to 2.81 eV respectively with the increasing dopant concentrations. The pure ZnO nanocrystalline film has no remarkable absorption in visible light region with a wavelength above 400 nm, whereas the Mn^{2+}, Cu^{2+} and Pb^{2+} doped ZnO nanocrystalline film extends the absorption spectrum obviously into the visible region. The result indicates the ability of doped ZnO crystalline films to harvest the visible component of solar radiation. Thus, the doped ZnO crystalline films could be promising photocatalysts under visible light. Moreover, 10 mole % Mn^{2+} and 10 mole % Cu^{2+} doped ZnO nanocrystalline film possesses much stronger visible light absorption than 10 mole % Pb^{2+} doped ZnO nanocrystalline film. The addition of Cu^{2+} and Pb^{2+} in host ZnO, the optical band gap energy is greatly reduced when compared to the addition of Mn^{2+} in ZnO at all concentration (2.5, 5.0, 7.5 and 10.0 mole %) of dopant. Also it reveals that the decreasing band gap energy of doped nanocrystalline film increases the crystallite sizes. It suggests that Cu^{2+} and Pb^{2+} help to slightly tuning the optical bandgap energy. The optical bandgap energy calculation for the fabrication of any optical devices which require optical bandgap ranging from a minimum of 2.77 eV to maximum 3.64 eV, the composition and the methods that been have described will lend a clue to choose an optimum composition. For any major tuning of optical bandgap energy one may change the composition of Cu and Pb and for minor tunings Mn may be incorporated.

The PL spectrum of all the synthesized samples shows the existence of two peaks, a narrow ultra-violet (UV) emission and a broad visible light emission extending from approximately 480 nm to 680 nm with a strong defect emission peak. The narrow ultra-violet emission peak centered at 350 nm (3.54 eV) due to the near band edge emission (NBE) in the wide band gap of ZnO nanoparticles, which resulted from the direct recombination of photo generated charge carriers and is attributed to an exciton-related activity. In the case of Mn^{2+} doped ZnO nanocrystalline films, the position of near band edge emission peak shift systematically from 364 nm to 392 nm (red shift) with the increase of dopant concentration from 2.5 to 10.0 mole % in steps of 2.5. Similar behaviour was observed for Cu^{2+} and Pb^{2+} doped ZnO films. This significant red shift provides clear evidence for the formation of Mn^{2+}, Cu^{2+} and Pb^{2+} doped ZnO nanocrystalline films. The intensity of ultra violet emission was high for pure, Mn, Cu and Pb doped ZnO nanocrystalline films, indicating improvement of the crystallinity of pure and doped ZnO nanocrystalline films due to free exciton emission. Moreover, the band edge emission of pure and doped ZnO nanocrystals has a line width (full-width at

half maximum) less than 34 nm. This small line width indicates that all the synthesized nanocrystals have a very narrow size distribution. The obtained results proved that the dopant entered into the host lattices also their optical properties can be effectively tuned for desired emission wavelengths. The 2.5 and 5.0 mole % Cu^{2+} doped ZnO nanocrystalline film leads to strong enhancement in photoluminescence yield compared to pure ZnO. The doped ZnO nanocrystalline films are the new useful materials for photonic and solar cell applications.

The photocurrent of both pure and doped (Mn, Cu and Pb) ZnO nanocrystalline film is more than the dark current, which is termed as positive photoconductivity. All the synthesized pure and doped ZnO nanocrystalline films considered in the present study are found to exhibit positive photoconductivity. We observed that the ZnO doped with 5.0 mole% Mn^{2+} is more photosensitive as compared to other Mn^{2+} doped ZnO nanocrystalline films. In the case of Cu^{2+} and Pb^{2+} doped ZnO nanocrystalline film, dark (I_d) and photocurrents (I_p) increases with increasing dopant concentrations except in 10.0 mole % Pb^{2+} doped ZnO.

Under steady state illumination, all the nanocrystalline films (considered in the present study) exhibit anomalous behavior. The photocurrent rise and decay curves are governed by trap levels and recombination centers lying in the forbidden region of the photoconductor. Such behavior was observed for all the doped (Mn^{2+}, Cu^{2+} and Pb^{2+}) ZnO nanocrystalline film with different dopant concentrations (2.5, 5.0, 7.5 and 10.0 mole %).

All the samples prepared were subjected to DC and AC electrical measurements in order to characterize them electrically. The DC electrical conductivity (σ_{dc}) increased with the increase in temperature (30 to 150°C). The addition of Mn^{2+}, Cu^{2+} and Pb^{2+} in the host matrix could increase the DC electrical conductivity. The electrical parameters, viz. dielectric constant (ε_r), dielectric loss factor (tanδ) and AC electrical conductivity (σ_{ac}) increase with the increase in temperature for all the nanocrystalline films studied. The AC electrical conductivities were found to be increased with increasing frequencies for all the 13 nanocrystalline films. All the doped nanocrystalline ZnO film prepared (twelve films) are found to have high AC electrical conductivity when compared to pure ZnO film. The addition of dopant increases the σ_{ac} value at all temperatures considered in the range 30 to 150 °C and all frequencies

considered in the range 100 Hz to 1 MHz for all the systems studied. The AC electrical conductivity values are found to be more than DC electrical conductivity values.

5.2. Conclusion

The results obtained in the present study indicate the possibility to prepare good quality pure and 2.5, 5.0, 7.5 and 10.0 mole % Mn^{2+}, Cu^{2+} and Pb^{2+} doped ZnO nanocrystalline films by using simple chemical bath deposition method. Also, the method is found to be fast and high purity. The unit cell volume expansion is found to be increased with the increasing dopant concentrations for the Mn^{2+}, Cu^{2+} and Pb^{2+} added nanocrystalline film. It reveals that the dopant Mn^{2+}, Cu^{2+} and Pb^{2+} incorporated with the host ZnO matrix. The present study shows a significant increase in bandgap energy when compared to that observed for bulk. The addition of Mn^{2+}, Cu^{2+} and Pb^{2+} minutely tuned the optical bandgap energies. The Mn^{2+}, Cu^{2+} and Pb^{2+} added nanocrystalline films have very high PL yield compared to pure ZnO film. The small amount of dopants in the host ZnO lattices highly enhances the photocurrent. The rise and decay of photocurrent of the ZnO nanocrystalline film is highly changed with the change in concentration of dopants in the host ZnO film. The results obtained in the present electrical conductivity study indicate the occurrence of nano-confirned states in the case of all the thirteen systems studied which may substantially contribute to the electrical properties. Hence it is clearly understood that the space charge contribution plays an important role in charge transport process and polarizability in the case of all the systems considered in the present study. The prepared pure and doped ZnO nanocrystalline film shows a weak quantum confinement effect.

5.3. Future Scope

In the present research work Pure and Mn^{2+}, Cu^{2+} and Pb^{2+} doped nanocrystalline films have been prepared and characterized with limited measurements only. PXRD, EDAX, UV-Vis, PL, photoconductivity and electrical measurements (AC, DC) have been carried out on all the thirteen nanocrystalline films prepared. However, the other measurements like, AFM, SEM and TEM have been carried out on a few selected nanocrystalline films prepared inorder to illustrate the importance of these materials. It would be interesting if these measurements are extended to other samples also. Other characterizations like magnetic measurements (electron paramagnetic

resonance, vibrating sample magnetometer, etc.) crystallite size and shape measurements at different annealed temperature should be carried out to understand further the importance of these films. Cyclic voltametry study should be carried out to study the reduction of a disulphide-based redox couple for dye-sensitised solar cells by using ZnO nanoparticles.

The addition of dopant decreases the bandgap energy. This is an interesting feature observed in the present study. So, it is expected to obtain new interesting optical materials, based on the results obtained in the present study, if other transition metals and rare earth metals are used as dopants. Also it is expected to get interesting materials if pure ZnO films are co-doped with a transition metal and a rare earth metal.

The present study indicated a strong enhancement in the photoluminescence yield for the Mn^{2+} and Cu^{2+} added nanocrystalline films when compared to that for the pure ZnO film. This aspect can be used to fabricate and characterize new light emitting diodes. The photocurrents (I_p) increases with increasing dopant concentrations in all the systems considered in the present study except in 10.0 mole % Pb^{2+} doped ZnO. This can be used to fabricate solar cell with good efficiency.