Preface

Transparent conducting oxides (TCO’s) have been known and used for technologically important applications for more than 50 years. The oxide materials such as In$_2$O$_3$, SnO$_2$ and impurity doped SnO$_2$: Sb, SnO$_2$: F and In$_2$O$_3$: Sn (indium tin oxide) were primarily used as TCO’s. Indium based oxides had been widely used as TCO’s for the past few decades. But the current increase in the cost of indium and scarcity of this material created the difficulty in obtaining low cost TCO’s. Hence the search for alternative TCO material has been a topic of active research for the last few decades. This resulted in the development of various binary and ternary compounds. But the advantages of using binary oxides are the easiness to control the composition and deposition parameters. ZnO has been identified as the one of the promising candidate for transparent electronic applications owing to its exciting optoelectronic properties. Some optoelectronics applications of ZnO overlap with that of GaN, another wide band gap semiconductor which is widely used for the production of green, blue-violet and white light emitting devices. However ZnO has some advantages over GaN among which are the availability of fairly high quality ZnO bulk single crystals and large excitonic binding energy. ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO based devices.

Most of the TCO’s are n-type semiconductors and are utilized as transparent electrodes in variety of commercial applications such as photovoltaics, electrochromic windows, flat panel displays. TCO’s provide a great potential for realizing diverse range of active functions, novel functions can be integrated into the materials according to the requirement. However the application of TCO’s has been restricted to transparent electrodes,
notwithstanding the fact that TCO’s are n-type semiconductors. The basic reason is the lack of p-type TCO, many of the active functions in semiconductor originate from the nature of \textit{pn}-junction. In 1997, H. Kawazoe et al reported the CuAlO\textsubscript{2} as the first p-type TCO along with the chemical design concept for the exploration of other p-type TCO’s. This has led to the fabrication of all transparent diode and transistors.

Fabrication of nanostructures of TCO has been a focus of an ever-increasing number of researchers world wide, mainly due to their unique optical and electronic properties which makes them ideal for a wide spectrum of applications ranging from flexible displays, quantum well lasers to \textit{in vivo} biological imaging and therapeutic agents. ZnO is a highly multifunctional material system with highly promising application potential for UV light emitting diodes, diode lasers, sensors, etc. ZnO nanocrystals and nanorods doped with transition metal impurities have also attracted great interest, recently, for their spin-electronic applications.

This thesis summarizes the results on the growth and characterization of ZnO based diodes and nanostructures by pulsed laser ablation. Various ZnO based heterojunction diodes have been fabricated using pulsed laser deposition (PLD) and their electrical characteristics were interpreted using existing models. Pulsed laser ablation has been employed to fabricate ZnO quantum dots, ZnO nanorods and ZnMgO/ZnO multiple quantum well structures with the aim of studying the luminescent properties.

\textit{Chapter 1} presents a brief description on the transparent conducting oxide (TCO). It includes an introduction, general properties, classification of TCO, brief description and a short review of the materials studied in the present
investigation. Introduction to nanotechnology, followed by description of basic nanostructures such as quantum dot, nanorods and quantum well and a short review of ZnO based nanostructures are also presented in this chapter.

Chapter 2 describes in detail the growth techniques and characterization tools employed for ZnO based heterojunction diodes and ZnO based nanostructures. The heterojunction diodes, nanorods and quantum wells were deposited using PLD. The details of PLD technique with a short description on the rf magnetron sputtering and vacuum evaporation are also included in this chapter. Various physical and chemical synthesis techniques of quantum dots, especially liquid phase laser ablation (LP-PLA) technique has been described in this chapter. Thin films grown were characterized by various analytical techniques, thickness measurement using stylus profiler, morphological analysis using scanning electron microscope (SEM) and atomic force microscopy (AFM), composition analysis like energy dispersive x-ray analysis (EDX), inductively coupled plasma.- atomic emission spectroscopy (ICP-AES) analysis and x-ray photoelectron spectroscopy (XPS), structural characterization using x-ray diffraction method, microstructure analysis using transmission electron microscopy (TEM), determination of band gap, Raman spectra studies, photoluminescence, electrical characterization consisting of two probe resistivity method and hall measurement and thermo power measurement are briefly described in this chapter.

Chapter 3 describes the growth and characterization of transparent p-AgCoO2/n-ZnO heterojunction diode by PLD. The PLD of AgCoO2 thin films was carried out using the sintered target of AgCoO2, which was synthesized in-house by hydrothermal process. The band gap of these thin films was found to be
~3.89 eV and they had transmission of ~55% in the visible spectral region. Although Hall measurements could only indicate mixed carrier type conduction but thermoelectric power measurements of Seebeck coefficient confirmed the p-type conductivity of the grown AgCoO₂ films. The PLD grown ZnO films showed a band gap of ~3.28 eV, an average optical transmission of ~85% and n-type carrier density of ~4.6 x 10¹⁹ cm⁻³. The junction between p-AgCoO₂ and n-ZnO was found to be rectifying. The ratio of forward current to the reverse current was about 7 at 1.5V. The diode ideality factor was much greater than 2.

Chapter 4 deals with the fabrication of p-Si/ZnO heterojunction diode by the PLD of ZnO at different oxygen pressures. These heterojunctions were found to be rectifying with the maximum forward to reverse current ratio of about 1000 in the applied voltage range from -5 to +5 V. Turn-on voltage of the heterojunctions was found to depend on the ambient oxygen pressure during the growth of the ZnO film. The current density-voltage characteristics and the variation of the series resistance of the n-ZnO/p-Si heterojunctions were found to be in line with the Anderson model and Burstein-Moss (BM) shift.

Chapter 5 presents the studies on luminescent ZnO based multiple quantum wells and nanorods. ZnO/ZnMgO Multiple Quantum Well (MQW) of well layer thickness of 2 nm was grown on sapphire (0001) substrate by PLD at a substrate temperature 400°C. Efficient room temperature photoluminescence (PL) was observed from these MQW’s, which was found to be blue shifted as compared to the room temperature near band edge PL from ZnO thin film of 200 nm grown at same experimental conditions. ZnO thin films were deposited using room temperature PLD by varying the oxygen pressure and found a pressure window for the growth of (002) oriented polycrystalline ZnO thin films.
Morphological analysis using Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM) demonstrated the formation ZnO nanorods at a particular oxygen pressure in this pressure window. Room temperature violet luminescence was observed from these ZnO nano rods. Temperature dependent photoluminescent studies of both ZnMgO/ZnO MQW and ZnO nano rods were carried out and the results are discussed.

Chapter 6 describes the preparation of highly transparent, luminescent and bio-compatible ZnO quantum dots in water, methanol and ethanol using liquid phase pulsed laser ablation technique without the aid of any surfactant. Transmission electron microscopy (TEM) analysis confirms the formation of good crystalline ZnO quantum dots with uniform size distribution of 7 nm. The emission wavelength was tuned by playing the native defect chemistry ZnO quantum dots and laser fluence. Maximum concentration ZnO quantum dots without loosing the transparency was observed to be 17 μg/ml from inductively coupled plasma - atomic emission spectroscopy (ICP-AES) analysis. Highly luminescent non-toxic ZnO quantum dots have exciting application potential as fluorescent probes in biomedical applications. Chapter 7 summarizes the main results in the thesis and the scope for future works.
Part of the thesis has been published in internationally referred journals

1. Transparent p-AgCoO$_2$/n-ZnO diode heterojunction fabricated by pulsed laser deposition.  

2. Luminescence from surfactant free ZnO quantum dots prepared by Laser ablation in liquids.  

3. Electrical Characteristics of n-ZnO/p-Si Heterojunction Diodes Grown by Pulsed Laser Deposition at Different Oxygen Pressures.  

4. Violet luminescence from ZnO nanorods grown by room temperature Pulsed Laser Deposition.  

5. Photoluminescence studies on ZnMgO/ZnO Quantum well grown by low temperature Pulsed Laser Deposition  

Conference Proceedings

1. Transparent p-AgCoO$_2$/n-ZnO p-n Junction fabricated by pulsed laser deposition  

2. Room temperature Photoluminescence from Low temperature Grown ZnMgO/ZnO Quantum well by Pulsed Laser Deposition  
Other internationally referred journals to which author has contributed


2. Effect of surface roughness on Photoluminescent spectra of silicon nanocrystals grown by off axis pulsed laser deposition

3. p-type electrical conduction α-AgGaO₂ delafossite thin film

4. Growth of Zinc Oxide thin films for optoelectronic application by pulsed laser deposition

5. Pulsed Laser Deposition of p-type α-AgGaO₂ thin films

6. Synthesis of highly luminescent, bio-compatible ZnO quantum dots doped with Na

7. p-AgCoO₂/n-ZnO heterojunction diode grown by rf magnetron sputtering

8. Enhanced nonlinear optical properties of Er doped Si nanoparticles prepared by off-axis pulsed laser deposition
   J. R. Rani, V. P. Mahadevan Pillai, C. S. Suchand Sandeep, Reji Philip, R. S. Ajimsha and M. K. Jayaraj (To be communicated).
Conference proceedings
1 Photoluminescence characteristics of silicon nanoparticles prepared by off axis PLD,
J. R. Rani, R. S. Ajimsha, V. P. M. Pillai and M. K. Jayaraj,
2 Optical characterization of Silicon nanoparticles prepared by off axis PLD.
3 Off axis pulsed laser deposition of silicon nanoparticles,
4 Studies on RF plasma using Optical Emission Spectroscopy