DESIGN, GROWTH, AND CHARACTERIZATION OF ZnO-BASED MATERIALS FOR OPTOELECTRONICS

A THESIS

Submitted in partial fulfillment of the

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by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Design, Growth, and Characterization of ZnO-Based Materials for Optoelectronics"** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DISCIPLINE OF ELECTRICAL ENGINEERING, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from **3rd January 2011** to **31st March 2014** under the supervision of Dr. Shaibal Mukherjee, Assistant Professor, Electrical Engineering, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

15/7/14

Signature of the student with date

(SAURABH KUMAR PANDEY)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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SAURABH KUMAR PANDEY has successfully given his Ph.D. Oral Examination held on **Date/2014**.

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Signature of PSPC Member

Date: 15/07/14.

Signature of PSPC Member

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Signature of External Examiner

Date: 15/07/14

ABSTRACT OF THE DISSERTATION

Design, Growth, and Characterization of ZnO-Based Materials for Optoelectronics

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ZnO-material system has been the subject of research for many applications for the past several years, because the material is nontoxic, abundant, chemically stable, and biocompatible. In order to understand and explore the behavior and characteristics of zinc oxide (ZnO) and ZnO based alloys, it is essential to grow high quality thin films of them. The main objective of this dissertation was to study the growth and characterization of ZnO based thin films by dual ion beam sputter deposition (DIBSD) system for the realization of ZnO based double heterostructure light emitting diode (DH-LED). The material study in this work focused on optimal deposition conditions of ZnO related thin film epilayers (ZnO, ZnO: Mg, ZnO: Ga) by using dual ion beam sputtering technique and the structural, morphological, optical and electrical properties of these thin films has been studied for the potential applications in optoelectronic devices. Brief description of detailed experimental work and preliminary work on device fabrication concerning the II-VI ZnO based thin films were discussed. Deposition conditions, such as substrate temperature, oxygen partial pressures etc were studied to optimize the growth parameters of the ZnO based thin films and subsequent characterizations were carried out to evaluate the various properties of the thin films

Theoretical realization of ZnO based double heterostructure light emitting diode has been studied in order to optimize the device parameters such as thickness, doping, and alloy composition of various constituent layers to achieve superior electrical and optical

performances. The optimized device with active region of CdZnO layer having composition emits bluish electroluminescence around 430 nm, at room temperature internal quantum efficiency (IQE) of ~55% at anode current 0.22 A. Further increase in Cd content in turn diminished the intensity of the blue emission band. Rigorous theoret investigation has been performed for the device parameter optimization; more specific optimization of device barriers and contact layers along with active region. Different aspe of band gap engineering and confinement has been considered to identify the optimizat criteria for the design of ZnO based LEDs.

ZnO thin films were grown on p-type Si (100) substrates at different oxygen partial pressu by DIBSD system at a constant growth temperature of 400 °C. The crystallinity, surfa morphology, optical, elemental and electrical properties of these ZnO thin films was studi The minimum value of full-width at half-maximum (FWHM) of the θ-rocking curve obtain from x-ray diffraction (XRD) of the ZnO (002) plane, was reported to be 0.1865° from Zr film grown at 50% oxygen partial pressure. Photoluminescence (PL) measuremer demonstrated sharp near-band-edge emission at ~381 nm at room temperature. Electric resistivity of ZnO was found to increase with the increase in oxygen partial pressure.

The structural, morphological, elemental, and electrical properties of ZnO: Mg thin film grown on p-Si (100) substrates by DIBSD system at different substrate temperature we thoroughly investigated. The FWHM of (002) plane was the narrowest with a value of 0.22 from ZnO: Mg film grown at 400 °C. X-ray photoelectron spectroscopy (XPS) analysis c ZnO: Mg film confirmed the presence of Mg^{2+} at 49.6 eV in MgZnO lattice. ZnO: Mg film grown at 400 °C, was observed to have the highest carrier mobility of 15.7 $cm^2/V.sec$ at roo temperature with a resistivity value of 0.583 Ω-cm and electron concentration of 1.07×10^{18} cm^{-3} Correlation between calculated grain sizes, as evaluated from XRD measurements and roor temperature carrier mobility, obtained from Hall measurements, were established for ZnO Mg films, grown at different growth temperature.

Ternary ZnO: Mg thin films grown on p-Si (100) substrates by DIBSD at constant growth temperature of 600 °C were studied, focusing on the influence of different oxygen partial pressures on the structural, morphological and electrical properties of the films. XRD spectra revealed that the deposited ZnO: Mg films were polycrystalline in nature with preferred (002)

crystal orientation. The minimum value of full-width at half-maximum of the ZnO: Mg (002) plane was reported to be 0.2399° from film grown at 40 % O_2. The maximum electron concentration was found to be 5.79×10^{18} cm^{-3} with resistivity of 0.116 Ω cm and electron mobility of 9.306 $cm^2/V.s$ at room temperature, for ZnO: Mg film grown with 20 % O_2. Raman spectra showed a broad peak at 434 cm^{-1} corresponded to E_2 high phonons mode of ZnO: Mg wurtzite structure. The peak at560 cm^{-1} was associated with oxygen deficiency [E_1 (LO) mode] in ZnO: Mg films. Raman intensity at 560 cm^{-1} reduced, on increasing oxygen partial pressure.

Ga-doped ZnO (GZO) transparent conducting films were deposited on sapphire (0001) substrates using DIBSD system. The impact of growth temperature on the structural, morphological, elemental, optical, and electrical properties was thoroughly investigated and reported. XRD measurements explicitly confirmed that all GZO films had (002) preferred crystal orientation. The film deposited at 400 °C exhibited the narrowest FWHM of 0.24° for (002) crystalline plane and the lowest room temperature electrical resistivity of 4.11×10^{-3} Ω-cm. The Raman spectra demonstrated the vibrational modes at 576 and 650-670 cm^{-1}, associated with native oxygen vacancies and elemental Ga doping in ZnO lattice, respectively. The reduction of carrier concentration and mobility was observed in Ga doped ZnO films, which was attributed to the decline in crystallinity and enhancement of charge-carrier scattering at grain boundaries at higher growth temperatures. All the Ga doped ZnO thin films shows exceeded ~95% optical transmissions and sharp absorption edges in the visible region. These results confirmed that the film grown at 400 °C was suitable for bottom contact layer in double hetero structure light emitting diode.