HYBRID OPTOELECTRONIC MATERIALS AND DEVICES BASED ON CADMIUM ZINC OXIDE

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **HYBRID OPTOELECTRONIC MATERIALS AND DEVICES BASED ON CADMIUM ZINC OXIDE** 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 July 2011 to November 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.

Shruti 28/11/2014

Signature of the student with date
(SHRUTI VERMA)

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

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SHRUTI VERMA has successfully given her Ph.D. Oral Examination held on 25 March 2015

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ABSTRACT OF THE DISSERTATION

Hybrid Optoelectronic Materials and Devices Based on Cadmium Zinc Oxide

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Cadmium Zinc Oxide (CdZnO) based hybrid optoelectronics materials and devices are studied and discussed in this dissertation. CdZnO thin films with a nominal thickness of ~200 nm were grown on c-plane sapphire substrates by using dual ion-beam sputtering deposition technique. The effect of substrate temperature and gas ambience on structural, morphological, compositional and opto-electronic properties was studied. X-ray diffraction patterns confirmed that all the films were polycrystalline in nature and were preferentially oriented along the c-axis. It was revealed that the films grown at Ar/O_2 ratio of 4:1 were structurally more ordered and the film quality was found to be best at 500 °C. The compositional studies specified that approximately 11.8 at.% of cadmium was present in the film deposited at 300 °C in $Ar\text{-}O_2$ mixture. Investigations on optical properties by photoluminescence (PL) and absorption studies indicate band gap shrinkage with the increase in argon partial pressure and substrate temperature. The CdZnO thin films showed broad PL spectra indicating its possible application as white light emitters. The photosensitivity was found to be 5000-fold higher for CdZnO film grown at 600 °C in $Ar\text{-}O_2$ ambience as compared to the best reported result on the material. These results were promising to realize opte-electronic devices such as multiple quantum well light-emitting diodes utilizing these CdZnO films. Blue multiple quantum well light-emitting diodes (LEDs) comprising of *p*-ZnO/ ($Cd_{0.12}Zn_{0.88}O$/ZnO) quantum wells/ *n*-ZnO were grown on *n*-Si substrates. X-ray diffraction of individual thin films revealed growth preferentially in *c*-axis direction perpendicular to the substrate and high crystallinity of each film. Photoluminescence studies indicated blue emission ~ 440 nm (2.81 eV) from CdZnO and UV emission ~384 nm arising from ZnO thin films. The quantum well LEDs showed a rectifying current-voltage behavior with a turn-on voltage of ~2 V at room temperature. The LEDs emanated a room temperature prominent blue electroluminescence (EL) peak centered at 442 nm due to quantum wells, along with shoulder peak at 380 nm in ultra-violet region associated with the recombination in ZnO layers of structure. It was found that with the increase in injection current the blue EL intensity

increases and UV emission decreases, leading to improvement in successful radiative recombination in quantum wells. The results indicate prospects of fabrication of ZnO-based blue multiple quantum well LEDs. Apart from this, the scope of work was stretched from inorganic structures to hybrid structures based on II-O/III-N and CdZnO/organic. We proposed II-O/III-N hybrid light-emitting diode (LED) design comprising of *p*-MgZnO/ InGaN/ *n*-MgZnO sandwiched structure and emanating green electroluminescence centered at 560 nm. Different design strategies for optimizing the internal quantum efficiency (IQE) through 2-D numerical simulation were proposed. Moreover, the feasibility of device realization was also reviewed. Detailed study of the effects of alloy composition, dopant concentration, and thickness of the electron blocking layer (EBL) and hole blocking layer (HBL) on the IQE was carried out. The optimization in selecting materials for EBL, HBL, and active layer was addressed while maximizing device IQE and reducing the efficiency droop. The impact of Auger non-radiative recombination on luminous power and quantum efficiency was discussed. It was found that the hybrid LED showed the highest IQE of 93% with minimum efficiency droop as compared to ZnO based and GaN based LEDs for similar design parameters. Hybrid Cd-doped ZnO/organic nanostructures with photosensitive nature are also discussed in this dissertation. Lamellar hybrid inorganic/organic nanostructures comprising of alternating layers of benzo[ghi] perylene monoimide and Cd-doped ZnO called BPyM/CZO nanohybrids were electrochemically synthesized on Ga-doped ZnO/Si. In order to study the effect of organic surfactant, inorganic CZO nanorods were also electrochemically synthesized. The role of annealing and organic surfactant on morphology, structure, composition and opto-electronic properties was analyzed. Annealed BPyM/CZO nanohybrids showed visible orange photoluminescence emission while unannealed nanohybrids and inorganic CZO nanorods emitted white emission at room temperature. The annealed nanohybrids and inorganic nanorods tend to follow Varshni equation with temperature variation from 80 K to 300 K. It was found that annealing expanded the band gap by 50 meV in case of inorganic CZO nanorods, but shrunk the band gap by 20 meV for BPyM/CZO nanohybrids. Temperature dependent photosensitivity measurement revealed that BPyM/CZO nanohybrids were highly photosensitive ~8 fold and ~4 fold higher than inorganic CZO nanorods at 80 K and 300 K, respectively. The studies indicated that BPyM/CZO nanohybrids hold potential as photosensors and light emitters.