SYNTHESIS AND CHARACTERIZATION OF ZnO: THIN FILMS, NANOSTRUCTURES, POLYMER/NANO ZnO COMPOSITES AND ZnO BASED HETEROJUNCTION

By

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Dedicated to

My Father

CERTIFICATE

I certify that the PhD thesis entitled **"Synthesis and Characterization of ZnO: Thin Films, Nanostructures, Polymer/Nano ZnO Composites and ZnO Based Heterojunction"** submitted by Mr. Bhupendra Kumar Sharma is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of the original and bonafide research work carried out by him under my guidance and supervision. The work presented in the thesis has not been submitted in part or full to any other university or institute for award of any degree or diploma.

August, 2010

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ABSTRACT

ZnO, a semiconductor having direct wide band gap (~ 3.2 eV) and large exciton binding energy (~ 60 meV) has created a substantial interest in the research community due to its potential applications in optoelectronic devices.

ZnO normally show n-type of conductivity due to presence of Zinc interstitials (Zn_i) and oxygen vacancies (V_O) defects. The n-type conductivity in ZnO can be further improved by doping with group III elements (e.g., B, Al, Ga and In). Among these dopants, Al has been found an efficient n-type dopant for realizing high quality samples with strong ultraviolet/blue light emission and high transparency to visible light. For making efficient optoelectronic devices using ZnO, it is necessary to understand the correlation between structural, optical and surface properties of the Al-doped ZnO films. To carry out work in this direction ZnO and Al-doped ZnO films are deposited on quartz substrates using ultrasonically assisted chemical vapor deposition and detail study of its structural, optical and electrical properties is carried out. The undoped ZnO film is found to be subjected to stress which increases initially for a 3% Al doping and then a slight decrease is observed for 5% Al doping. The band gap of Al-doped ZnO films shows a blue shift as compared to the undoped ZnO. The blue shift in the band gap of Al-doped ZnO films can not be understood in the framework of Burstein Moss shift and has been attributed to increase in the stress present in the Al-doped ZnO film. The photoluminescence spectra of undoped ZnO film shows a wide peak in the visible region which suppress with a small red shift for the Al doping in ZnO film. The detail analysis of photoluminescence and X-ray

photoelectron spectra of ZnO and Al-doped ZnO films indicates suppression of Zinc interstitials (Zn_i) and oxygen vacancies (V_O) defects after Al doping in ZnO films.

In recent years, the growth of ZnO in various shapes and sizes at nano scale has been a subject of intensive research because it is expected that devices based on nano ZnO can have better performance. Therefore, to carry out work in this direction ZnO nanostructures are synthesized by chemical solution method at different growth temperatures (130–200 °C). A shape transition from nanoparticles to nanorods is observed in ZnO nanostructures with the increase in the growth temperature from 130 °C to 200 °C. The effect of shape change on the structural properties like crystallite sizes and lattice strain, optical absorption and luminescence properties of ZnO nanostructures are investigated. XPS analysis of core level spectra of Zn and O indicates that defects are more prominent at intermediate (150 °C and 170 °C) and less prominent at 130 °C and 200 °C growth temperatures. The movement of Fermi energy level (E_F) with respect to valence band edge for different growth temperatures is investigated and it is attributed to the different defect contributions of ZnO nanostructures of different shapes.

ZnO nanorods are grown on seedless and seeded glass substrates by hydrothermal method. Investigation of structural, morphological, optical and electronic properties of ZnO nanorods are carried out. Presence of tensile stress has been observed in the vertically aligned nanorods and a correlation between stress and blue shift in the band gap has been suggested. Photoluminescence studies indicate the dominance behavior of zinc vacancies (V_{Zn}) defects, which creates the shallow acceptor level. Valence band analysis shows that the difference between Fermi level (E_F) and valence band maxima (VBM) is less than the half of the band gap of ZnO and E_F moves towards conduction band minimum for vertically aligned nanorods as compared to horizontal nanorods.

The development of polymer/nano inorganic composite material has been receiving significant interest due to wide range of potential applications of these composites in optoelectronic devices and electromagnetic interference (EMI) shielding. In the present study, in this direction films of Polyaniline and Polyaniline/ZnO composite have been synthesized by solution casting technique and investigation of dielectric behavior in the microwave frequency range (8.0–12.0 GHz) have been carried out. Fourier transform infrared spectroscopic studies of PANI and PANI/nano ZnO composite films indicated the presence of interaction between nano ZnO particles and molecular chains of PANI. The real part of permittivity ($\varepsilon^{/}$) and loss factor (tan δ) are found to decrease in PANI/nano ZnO composite films which has been attributed to the presence of interaction between nano ZnO particles and PANI molecular chains. The interaction between PANI chains and surface of ZnO nanoparticles restricts the motion of the dipoles and leads to the decrease of $\varepsilon^{/}$ and tan δ of the composite films.

For realizing the ZnO based optoelectronic applications, p-type ZnO is required, which is difficult in making. An alternative approach is to use the p-type conducting polymer with n-type ZnO for fabricating p-n junction In the present study, the organic/inorganic heterojunction is fabricated by spin coating p-type polymer poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on the n-type ZnO film. The ZnO film is deposited on patterned Indium Tin Oxide coated glass substrate and Gold is deposited on the top of the PEDOT:PSS film. The current-voltage (I-V) characteristic of PEDOT:PSS/ZnO shows diode like behavior. The I-V characteristic is examined in the frame work of thermionic emission model. The ideality factor and barrier height are obtained as 3.8 and 0.63 eV respectively. Higher value of ideality factor is attributed to the existence of multiple current pathways due to the presence of surface states in ZnO.

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