CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

8.1 CONCLUSIONS

Systematical studies were carried out to investigate the structural, optical and electrical properties of pure, doped and surface modified ZnO NR thin films synthesized using simple chemical route. After the deposition of ZnO seed layer via spin coating technique, the growth of pure ZnO NRs was investigated by varying the growth parameters like precursor concentration, growth temperature and time. Based on the morphological studies, the most favorable growth parameters (20 mM precursor concentration, 90 °C growth temperature and 3 h growth time) were identified to yield vertically aligned ZnO NRs with a high aspect ratio. Therefore, these selected growth parameters have been used for the subsequent synthesis of doped and surface modified core/shell-type heterostructure ZnO NRs.

Characterization studies using XRD showed a strong diffraction peak corresponding to (002) planes indicating the growth of the ZnO NRs was primarily along the c-axis direction. HRTEM analysis established that the rod-like structure of ZnO nanorod has a diameter of ~50 nm and the corresponding SAED pattern showed sharp diffraction spots reinforcing the single crystalline nature of the ZnO nanorod. FTIR analysis inferred the presence of Zn-O stretching vibration mode at 454 cm⁻¹. From the UV-visible studies, the optical energy band gap value of pure ZnO NR thin film was determined as 3.24 eV. Enhancement in optical properties was established by the PL spectrum with a dominant NBE emission peak at 380 nm over the broad defect level visible emission at 574 nm. I-V measurements recorded the lowest resistivity value of 5.43 x10⁻³ Ω cm under light illumination compared with a value of 2.86 x10⁻² Ω cm in dark condition.
Effect of doping group III elements (Al, Ga and In) on ZnO NR thin films has been investigated at different concentrations (1, 2, 3%). From the structural studies, it was found that the incorporation of dopants induced a distortion in the ZnO lattice in all doped films. Again, GZO NR thin films showed an improved crystalline nature while AZO and IZO films had a declination in crystallinity beyond 2% dopant concentration. The morphological studies depicted that the diameter and length of the ZnO NRs were greatly influenced by doping. Further, incorporation of dopants above 2% induced a reduction of diameter in AZO and IZO NR thin films whereas GZO NR thin films showed a gradual increase in diameter with increasing Ga concentration. EDX analysis confirmed the presence of all the constituent elements in Al, Ga and In doped ZnO NR thin films. UV-visible studies displayed the widening of energy band gap with respect to dopant content for all doped ZnO NR thin films due to the well-known Burstein-Moss effect. The luminescence spectra of all the doped films have both NBE and DLE peaks in which, an improved NBE intensity was observed for AZO and IZO NR thin films while reduction in intensity was detected in GZO films with the increase of dopant concentration. Among all the doped films, Ga 2% doped film exhibited the lowest resistivity value of 1.88x10^{-3} \, \Omega \, \text{cm} under light illumination which is 65% lower than that of pure ZnO NR thin film. Hence, the 2% Ga doped film can be used to replace the ITO substrate for fabricating solar cells.

Surface modification has been successfully demonstrated on core ZnO NRs with CdS and C_{60} shell layer. XRD studies showed the presence of mixed crystal structures of both hexagonal crystal structure of ZnO and cubic structure of CdS for ZnO/CdS whereas hexagonal ZnO along with face-centered cubic C_{60} for ZnO/C_{60}. FTIR studies gave evidence for successful functionalization of ZnO NRs by C_{60}. HRTEM results confirmed the formation of \sim{}5 nm thickness of CdS and \sim{}3 nm thickness of C_{60} nanocrystal shell layer on the surface of ZnO nanorod core. The corresponding SAED pattern revealed that ZnO nanorod was single crystalline and the shell layer corresponding to both CdS and C_{60} was polycrystalline in nature. HRSEM images depicted the decoration of CdS or C_{60} nanocrystals on the surface.
of hexagonal ZnO NRs. The EDX spectra confirmed the presence of Zn, O, Cd, S for ZnO/CdS and Zn, O, C elements for ZnO/C₆₀ heterostructures. From the UV visible studies, it was observed that the absorption edge of ZnO/CdS got red-shifted and the energy band gap was narrowed from 3.24 to 2.46 eV on increasing the number of SILAR coatings. Two distinct absorption edges and energy band gap values related to ZnO (3.05 eV) core and C₆₀ (1.83 eV) shell was observed in surface modified ZnO/C₆₀ core/shell structure indicating the spatial separation of two semiconducting phases. The PL measurement for both surface modified ZnO/CdS and ZnO/C₆₀ core/shell NR thin films displayed an enhanced NBE emission intensity with reduced defect emission intensity displaying exemplary improvement in optical quality of the film due to surface modification. I-V measurements of surface modified core/shell heterostructure exhibited the electrical resistivity value under illumination as 1.25x10⁻³ Ω cm for ZnO/CdS and 2.23x10⁻³ Ω cm for ZnO/C₆₀.

Among bare, doped ZnO and surface modified ZnO/CdS and ZnO/C₆₀ NR thin films, ZnO/CdS core/shell NR thin film recorded the lowest resistivity of 1.25x10⁻³ Ω cm under illumination with visible light. Therefore, from the results it is recommended that the surface modified ZnO/CdS core/shell-type heterostructured NR thin film can be considered for optoelectronic applications.

8.2 SUGGESTIONS FOR FUTURE WORK

Future directions associated with the continuation of the present work are given below:

- To study the surface morphology of the pure and doped samples using atomic force microscopy (AFM) in order to infer the variation in heights of the nanorods.
- X-ray photoelectron spectroscopy (XPS) could be carried out to find the chemical composition and chemical bonding of doped samples.
- To investigate the structural property and material quality of the films by performing Raman measurements.
Apart from CBD method, some other advanced techniques like pulsed laser deposition or molecular beam epitaxy could be employed to synthesize well aligned ZnO NRs in order to compare their properties.

The incorporation of dopants at a lower concentration less than 1% into the growth of doped ZnO NRs may be used for preparing the best ITO free TCO substrate.

Doped ZnO NRs could be used as core structure for preparing surface modified core/shell heterostructure, like GZO/CdS in order to probe the possibility of reduction in the resistivity of core/shell heterostructure which can be tested for enhanced performance in solar cell application.

Conversion of nanorods into nanotubes could be carried out along with the formation of ZnO nanotube based surface modified heterostructure for some special applications.