CHAPTER 7

CONCLUSION AND SUGGESTIONS FOR THE FUTURE WORK

7.1 Conclusion

The prime objective of this thesis is to fabricate vertically aligned ZnO NSs without external catalyst by radio RF magnetron sputtering and investigate their structural and optical properties. Manifold 1-D ZnO NSs have been fabricated by various deposition techniques with different growth approaches such as VLS and VS transformations in which the former approach utilizes the external catalyst to manipulate the anisotropic growth of NSs. In VLS approach, the catalyst remain on the apex of the NSs and likely to incorporate as a foreign atoms into the growing lattice. This catalytic droplet is an undesirable external impurity for the fabrication of devices and the incorporated foreign atoms into the host material also reduce the efficiency of the devices. Hence, the alternate VS approach has received a tremendous attention on the fabrication of NSs without external catalyst.

The RF magnetron sputtering is one of the least investigated techniques for the growth of NSs where as it is widely employed for the deposition of thin films. Further, it is one of the controlled deposition techniques in terms of scale-up and mass production which makes it an effective economic approach for the industrial applications. We have investigated the growth of ZnO NSs on Si(111) substrates by varying the growth parameters particularly deposition pressure and substrate temperature without external catalyst. The grown 1-D ZnO NSs were subjected to various characterization techniques to examine the structural and optical properties. Further, we have demonstrated the resistance based NH_3 gas sensors with high sensitivity and the high performance wafer level ZnO NRs based photocatalytic dye degradation under the irradiation of visible and solar light. The significant findings of the thesis are briefly concluded.

In the recent past, wide band gap semiconductor NSs have attracted enormous attention as they are very promising candidate for a variety of applications such as optoelectronics and high-frequency electronics. ZnO, a wide and direct band gap of 3.37 eV with large exciton binding energy (60 meV) at room temperature, have attracted a broad spectrum of interest owing to their potential applications in electronics, optoelectronics, photophysics and sensors. 1-D semiconductor NSs have the potential to be used as both interconnect and functional units for the fabrication of different devices and the detection of various bio-molecules and gases.

The second chapter of the thesis discusses the experimental techniques which have employed for the fabrication and characterization of 1-D ZnO NSs. The first part of the chapter is devoted to describe the experimental techniques involved for the preparation of a 2 in. pure ZnO (99.999%) target by simple solid state reaction technique and fabrication of ZnO NSs by RF magnetron sputtering. The second part of this chapter describes the characterization techniques in which the important methods used for the analysis of ZnO NSs. The crystalline nature and phase orientation of the ZnO NSs are investigated by X-ray diffractometer with Cu K_α radiation of wavelength λ=1.5406 Å. Field emission scanning electron microscope equipped with energy dispersive X-ray spectrometer has used for the morphological and elemental analysis of the NSs. The basic principle and instrumentation of the micro Raman scattering and TDPL have been discussed. Resistance based gas sensor setup was constructed and utilized for the NH_3 gas sensing applications using ZnO NSs. Further, the organic dye degradation study was also carried using ZnO NRs as a catalyst under the irradiation of visible and solar light.

Chapter three consists of the growth and characterization of ZnO NSs on Si(111) substrates under various deposition pressures and substrate temperatures by RF magnetron sputtering. Under pure argon deposition pressure of 0.01 mbar, the vertically aligned ZnO NSs have been successfully grown on silicon substrates at elevated substrate temperatures of 550 and 650 °C. Further, the transition of 1-D ZnO NSs with the pure argon deposition pressure is driven by the change in migration length of the adatoms which promotes the radial growth due to the increased number of collisions between the sputtered and argon gas molecules. The growth of the NSs is governed by the migration length of adatoms which strongly influenced by deposition pressure and temperature. The structural studies suggest that the increase in argon pressure introduces the compressive strain in the NSs which also depends on the footprints of the NSs on the substrate. A blue shift of A_1(LO) Raman phonon mode along with broad band edge emission confirm the enhancement of the free carrier concentration in the NSs due to the point defects. The predominant green emission at 2.28 eV is attributed to the electron transitions between singly ionized oxygen vacancies and photo-excited holes. The anisotropic transformation of vertical to lateral NWs takes place as oxygen reactive gas introduced during deposition due to the change in the migration length of adatoms with respect to the deposition pressure of (Ar + O_2). The structural and optical characterizations reveal the high crystalline nature of the vertically aligned ZnO NRs. TDPL spectra confirm the presence of zinc and oxygen vacancies in the NSs and the oxygen vacancy mediated emission at 2.28 eV quenches with increasing the oxygen deposition pressure whereas the zinc vacancy mediated emission intensity at 3.01 eV is slightly increased.

Chapter four discusses the fabrication and characterization of vertically aligned indium doped ZnO (IZO) NRs on ITO coated glass substrates by RF magnetron sputtering at 550 °C. The anisotropic transformation from lateral NWs to vertical standing NRs has occurred at 550 °C under the (Ar+O_2) pressure range of 0.01 – 0.1 mbar. Uniformly distributed high density (4 x 10^9/cm^2) and well isolated ZnO NRs with homogeneous diameter (90 nm) were achieved by varying the growth parameters such as substrate temperature and pressure. The structural investigation reveals the wurtzite nature of IZO NRs with preferential growth along (002) crystallographic plane. The migration of indium atoms from the ITO coated glass substrate uniformly distributes into ZnO matrix along the axial direction at the growth temperature. The indium incorporation substantially enhances the structural and optical qualities of ZnO NRs. The line shape analysis of the coupled A_1(LO) Raman phonon mode has been used to determine the carrier concentration and mobility of IZO NRs ($n = 1.3 \times 10^{17}/cm^3$ and $\mu = 68\ cm^2/V\ sec$). The origin of the defect mediated orange emission in IZO NRs is expected to be the transition of charged oxygen vacancy state to the photo-excited holes in the valence band.

Chapter five describes the investigation on the ferromagnetic behaviour of vertically aligned ZnO NRs grown on Si substrates by RF magnetron sputtering technique under pure argon atmosphere. XRD patterns of the ZnO NRs indicate the existence of the residual compressive strain which is partially relaxed by the post growth treatments. Further, micro-Raman spectra provide a conclusive evidence for the partial relaxation of the compressive strain in NRs from the peak position of the non-polar phonon mode E_2^{high}. The intra-band optical transitions provide a strong evidence for the existence of vacancy mediated point defects which is found to be responsible for the enhancement of room temperature ferromagnetism in undoped ZnO NRs as corroborated by a clear hysteresis loop from the M-H curve. The ferromagnetism decreases with post growth treatment of ZnO NRs in both oxygen and vacuum atmospheres owing to the compensation of point defects and it provides a strong confirmation that the enhancement of room temperature ferromagnetism is attributed to the vacancy mediated exchange interactions between the unpaired electron spins in undoped ZnO NRs.

Chapter six deals with the applications perspective of ZnO NSs. The wafer level 1-D ZnO NSs were subjected to the NH_3 gas sensing property and photocatalytic dye degradation. A resistive based NH_3 gas sensor is fabricated on the 1-D ZnO NSs grown under various argon sputtering pressures (0.01, 0.035

and 0.1 mbar) at the substrate temperature of 550 °C. Despite low coverage and surface area, the NSs grown under higher argon pressure of 0.1 mbar exhibit excellent NH_3 gas sensitivity due to the enhancement of oxygen vacancies as compared to other counterparts. The sensitivity is greatly enhanced to 98% at the operating temperature of 150 °C. The surface defects provide active sites for gas adsorption and desorption which strongly influences the ZnO bands thereby changing the conductivity. The response and recovery times of the ZnO NSs grown under argon sputtering pressures of 0.1 mbar are 49 and 19 sec respectively. The observed responses are highly reliable and comparable with the undoped ZnO NSs grown by various techniques. Hence, the defect engineered ZnO NSs can be used to detect low level of NH_3 gas at room temperature. Further, the photocatalytic activity of the ZnO NRs is demonstrated by the degradation of various organic dyes such as MB, RhB and MO under visible and sunlight irradiations. The combined mechanism of dye excitation along with the surface defects mediated photo-excitation of electrons in high density of ZnO NRs is expected to be responsible for the enhanced decay of MB molecules (97%) under solar irradiations. The photocatalyst is stable (10 cycles) with almost constant percentage of degradation under visible light irradiation evidencing the practical reusability of ZnO NRs as a standard semiconductor photocatalyst.

7.2 Suggestions for the future work

At present, the nucleation, growth, characterization and some applications of ZnO NRs grown without any external catalyst on n-Si(111) and ITO coated glass substrates by RF magnetron sputtering have been demonstrated. In continuation, the ZnO NRs grown on n-Si(111) substrates is to be considered as a potential candidate for the photocatalytic water splitting and hydrogen production. Further, the NRs can be surface functionalized by various nanoparticles such as Au, Ag, Pt and graphene to achieve maximum efficiency of the water splitting ability and hydrogen production. Extensive investigations will be carried out to optimize the parameters to enhance the water splitting ability of ZnO NRs as a photocatalyst under visible light. In addition, ZnO NRs can be grown on the p-Si substrates or p-GaN coated sapphire substrates for the formation and demonstration of hybrid n-ZnO NRs based LEDs in the visible region. As the vertically aligned 1-D NSs have smaller footprints on the substrate, it is expected that the large lattice mismatch does not affect the quality of the 1-D NSs. However, the lattice mismatch between silicon and ZnO is about 40%. Hence, the selection of the substrate plays a crucial role on the quality of NSs as due to introduction of residual strain. Therefore, the fabrication of homo-junction based optoelectronic devices will be subject of future study. However, the fabrication of p-ZnO is very difficult due to various technical reasons. Attempted p-type dopants may be compensated by the low energy native defects such as interstitial site of zinc (Zn_i) and oxygen vacancies (V_o). This compensation problem is the most challenging phenomenon in ZnO. The experimental data show instability of p-type conductivity in ZnO which is reverting to n-type conductivity within a matter of days. The above problems on the fabrication of homo-junction based optoelectronic devices can be overcome by the use of heterostructures where the electrons from the other p-type material are injected into the n-type ZnO material. Mostly, p-GaN will be employed as an alternative material in this regard by considering the similar crystallographic and electronic properties of ZnO and GaN. Hence, n-ZnO NRs/p-GaN thin film hybrid heterostructures may be utilized in order to increase the extraction efficiency of the LEDs by virtue of the wave-guiding properties of the NRs and the large surface to volume ratio can really be exploited for energy efficient solid state white lightening applications.