Chapter - 6

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6.1 Summary and Conclusions

In the present study, undoped, transition metal (Co, Fe) doped ZnO nanoparticles and Al doped thin films are prepared through different preparation techniques and their physical properties have been investigated for their feasibility towards spintronics as DMS material, TCO’s and sensor applications.

New fuels (L-Valine, L-Glutamine and Leucine) were reported to synthesize the ZnO nanoparticles by solution combustion technique (SCT) and the fuel to oxidizer combinations on the characteristic properties of ZnO was investigated. The correlations were established between adiabatic temperatures ($T_{ad}$) and the amount of gases liberated which were obtained from thermodynamic theoretical calculations with the characteristic properties of the product (ZnO) obtained from SCT. It was observed that, the compositional dependent exothermicity ($T_{ad}$) influences the quantity of gases liberated with F/O ratio, which influences the crystallinity of the combustion product (ZnO powder). The lattice parameters obtained from the structure refinement by Rietveld refinement on XRD data are in agreement with the literature reported values. It was also observed that, the morphology of as-synthesized ZnO powders were strongly dependent on the exothermicity of the F/O ratio and wide distribution of the particles with possible agglomeration were observed which is evidenced from TEM studies. These agglomerations were attributed to the nature of combustion reaction due to the evolution of enormous amount of gases during combustion process. Furthermore, the structural investigation was carried out to understand the effect of fuel on the structure of the as-formed ZnO and it was found that, the estimated lattice parameters from TEM-SAED patterns were found in good agreement with those obtained from Rietveld refinement of XRD data.
Single phased Co:ZnO and Fe:ZnO samples were synthesized using L-Valine as fuel for the first time and the effect of dopants (Co and Fe) on the physical properties and intrinsic room temperature ferromagnetism (RTFM) were investigated. Single phased and polycrystalline samples were achieved at as-synthesized form. Rietveld refinement on PXRD data confirms the absence of any possible impurities (oxide phases and metallic clusters) in both Co:ZnO and Fe:ZnO samples. Significant changes in the lattice parameters are observed due to the relative difference in the ionic radii of Co$^{2+}$ / Fe$^{2+}$ and Zn$^{2+}$. The optical band gap energy, $E_g$ decreases in both the cases with dopant concentration. In particular, Co:ZnO samples show an emission in blue region and could be the potential candidates for the blue light emitting devices. The undoped ZnO samples exhibit diamagnetic nature while both Co:ZnO and Fe:ZnO samples exhibit RTFM with increasing coercivity with Co/Fe concentration. Particularly, the electronic structure was determined for Co:ZnO samples through NEXAFS and the atomic multiplet calculations / simulations performed at Co $L_{3,2}$ edge, hence determined the valance state, symmetry and crystal field splitting. The spectral features of the experimentally observed NEXAFS spectra compared with the all possible calculated (simulated) spectra of ‘Co’ in 2+ and 3+ valence states with different values of crystal field splitting (10Dq). It was found that, the experimentally observed NEXAFS was in better agreement with the simulated spectra of Co$^{2+}$ in tetrahedral symmetry with 10Dq = - 0.6 eV and the spectral features of Co:ZnO are entirely different from those related to Co metal and other oxide phases, which rules out the presence of impurity phases and Co clusters. Further, XMCD spectra at RT confirm that, the magnetic contribution in Co:ZnO samples is due to Co$^{2+}$ ions, not due to the Co metal cluster. The temperature-dependent XMCD studies shows the existence of weak paramagnetic contribution in Ferromagnetic Co:ZnO samples at RT. The spectroscopic results confirms that RTFM in Co:ZnO is intrinsic, feasible candidates as DMS’s for spintronics applications.

The AZO thin films prepared by RF- sputtering technique (RF-AZO) exhibits single phased and polycrystalline nature with majority of crystallites are orienting along c-axis. No traces of impurities were observed. The thickness of the thin films found to increase with RF power and the surface of the films found to be smooth and uniform. Further the smoothness of the film increases with RF power. The optical band gap energy found to decrease with RF
power. Both low temperature (77 K) and room temperature (300 K) PL spectra were compared. In both cases, greater peak shift of NBE to 405 cm\(^{-1}\) was observed, further this peak shifts towards higher wave number region with increase of RF power. Four distinct characteristic emission peaks are observed in the blue region. The intensities of these peaks found to decrease with RF power at 77 K PL spectra, while it increases in 300 K PL spectra. However, the PL emission intensity at 300 K is less as compared to that of 77 K, due to the non-radiative recombination of electrons with holes at 300 K. The films at higher RF power exhibit lower structural defects preferably the oxygen vacancies. RF-AZO films show n-type conductivity and film deposited at 50 W RF (AZO50) power exhibit a huge response towards NO\(_2\) at 350 °C, whereas the response of AZO films of higher RF power reduces drastically. Particularly, AZO50 film show huge sensitivity about 300% for 100 ppm NO\(_2\) and 6770% for 600 ppm of NO\(_2\) gas at 350 °C. The detailed analysis of the experimental results suggest that the great response of AZO50 film arises from low thickness and higher oxygen vacancies, in comparison to other films deposited at higher RF powers. These results make them better candidates for application in NO\(_2\) sensor devices.

The AZO thin films prepared by spin coating technique (SC-AZO) exhibits single phased and polycrystalline nature and no traces of impurities were observed. SC-AZO thin films exhibit good adhesivity nature with the glass substrates. The thickness of the thin films found to decrease with Al concentration. It was observed that, Al incorporation in ZnO induces nucleation and reduced surface roughness indicates the films are smooth, uniform and homogeneous surface. The absorption peak shifts towards shorter wavelength and optical band gap energy found to increases with Al doping, which is attributed to Durstein-Moss shift. The transparency of the films found to increase with Al doping and in particular, films with > 2% Al doping show transmittance ~ 90% in the visible region, which makes them potential candidates for TCO applications. Also, Al substitution influences the defect density in the films, which affects the luminescence process. Based on the observed photoluminescence in SC-AZO, thin films with > 2% Al doping are the potential candidates for applications in optoelectronic devices such as LED’s.
6.2 Scope for the future work

The work presented in this thesis gives us a qualitative understanding on the effect of various parameters on the characteristic properties of the nanomaterials and thin films. The work was limited to investigate the effect of few parameters (such as, fuel, Co, Fe, Al doping, RF power) on the characteristic properties and for the applications in spintronics devices, sensors, TCO’s and opto-electronics. However, there are few areas need to be considered for a complete and comprehensive understanding and for the possible application of both nanomaterials and thin films. The further below prescribed work may be extended in the following directions in future.

1. The detailed quantitative study involving the correlations between the theoretical thermodynamic calculations and characteristic features of ZnO nanomaterials.

2. Spectroscopic studies such as, NEXAFS and XMCD may be helpful further to investigate the intrinsic RTFM in Fe:ZnO samples.

3. As the presented work focused on only Co and Fe doped ZnO, future work is carried out to understand / investigate RTFM in other transition metals such as, Ni, Mn, V, Cr and Cu doped ZnO nanomaterials. Also, the effect of co-doping may be carried out to tune RTFM in these systems.

4. RF-ZnO thin films were tested only for NO$_2$ gas towards their possible sensing applications. Future work may be carried out to test other toxic gases also.

5. In the presented work, Al doped ZnO thin films have shown very good optical and luminescence properties, further work may be extended to investigate or enhance these properties by doping / co-doping other dopants such as In, Ga and Sn in ZnO thin films.