CHAPTER VIII: Conclusions and Suggestions for Future Work

8.1 Summary of the Present Work

In this work, we have discussed the structural, magnetic and transport properties of TiO_2 with controlling the defect concentration by using Co-doping and Swift Heavy Ion irradiation. Defects have been created by different ways such as: (a) reducing the size of TiO_2 to nanoscale, (b) doping Co at Ti site, (c) varying the oxygen partial pressure during growth of the thin films and (d) using Swift Heavy Ion irradiation. For manipulating the defects we have synthesized nanoparticles of $Ti_{1-x}Co_xO_2$ (x = 0, 0.01, 0.03 and 0.05) by controlling the *p*H of precipitation. Phase pure TiO_2 nanowires are grown using hydrothermal technique. Thin films of $Ti_{1-x}Co_xO_{2-\delta}$ are deposited on Si as well as $LaAlO_3$ substrates by PLD technique under different oxygen environment. To explore the magnetic properties in TiO_2, thin films are deposited by e-beam evaporation technique. To have post deposition defects in the films, 100 MeV Ag^{7+} ions are used to irradiate the films with different fluence. We have performed structural, electronic, magnetic as well as transport studies to evaluate the role of defects in the physical properties of the TiO_2 and Co-doped TiO2 nanoparticles and thin films. The main findings of the present work are outlined below:

- TiO_2 nanoparticles prepared by the sol–gel technique at *p*H of precipitation 4.5 and 6.5 show the anatase phase after calcining at 500 °C. While anatase to rutile phase transformation occurs at 650 °C in the case of *p*H 6.5 sample, it elevates to 850 °C for the sample synthesized at lower *p*H. The earlier belief was that smaller the particle size, lower will be the anatase to rutile transformation temperature, and vice versa. Our observation of higher crystallite size and lower anatase to rutile transformation temperature in the case of the higher *p*H sample contradicts the previous reports. X-ray photoelectron spectroscopic studies reveal that oxygen vacancy concentration drives the anatase to rutile transformation temperature to lower values in case of higher *p*H sample compared with the sample synthesized at lower *p*H of precipitation in spite of higher particle size.

- The magnetic properties of TiO_2 nanoparticles doped with 1 and 3 at % Co show anatase phase. However, for 5 at% Co, a $CoTiO_3$ secondary phase appears indicating low solubility of cobalt in TiO_2 matrix. Magnetisation measured as a function of magnetic field and temperature show no evidence of ferromagnetic ordering down to 10 K. However, a diamagnetic material like TiO_2 compared with cobalt doped TiO_2 nanoparticles exhibits higher magnetic moment as well as a nonlinear behaviour in *M-H* plot at low fields. It is realized from the x-ray photoelectron spectroscopic (XPS) studies that the oxygen vacancy plays an important role in showing high magnetic moment in a diamagnetic material like TiO_2. Higher oxygen vacancy in x = 0 sample observed from XPS shows higher magnetic moment as well. Oxygen vacancies are compensated after substituting Co at Ti site as a result, it reduces the magnetic moment in case x = 0.01 and 0.03. This is in contrast with the bulk cobalt doped TiO_2 where Co substitution creates oxygen vacancies and increases the net magnetic moment.
- We have also demonstrated the synthesis of TiO_2 nanowires with high aspect ratio using a two-step hydrothermal process using TiO_2 nanoparticles and 10 M NaOH solvent at a reaction temperature of $180^{o}C$. These nanowires are characterised by FE-SEM, TEM, XRD, and Raman. Phase of these nanowires are found to be anatase, confirmed from both XRD and Raman spectroscopic measurements. High resolution electron microscopy (HREM) further supports the anatase structure and SAED pattern indicates the single crystalline nature of these nanowires. In addition to these techniques, XPS and EDS refute the presence of any impurity elements like Na as reported in the literature. Magnetic properties of these nanowires reveal paramagnetic nature at 300 K. The electronic structures of the nanoparticles and nanowires are studied with maximum entropy method (MEM) using the

XRD tools. Nanowires are found to be more ionic than the nanoparticles evidenced from the MEM simulations.

- TiO_2 and Co-doped TiO_2 (CTO) thin films deposited on Si substrate under various oxygen partial pressure by pulsed laser deposition exhibit room temperature ferromagnetism (RTFM) independent of phase. The ferromagnetism at room temperature is also supported from the MFM results. Films deposited at 0.1 mTorr oxygen partial pressure show a complete rutile phase and confirmed from the glancing angle x-ray diffraction as well as Raman spectroscopic studies. At the highest oxygen partial pressure, i.e. 300 mTorr, although the TiO_2 film shows a complete anatase phase, a small peak corresponding to the rutile phase along with the anatase phase is identified in the case of CTO film. An increase in O to Ti/(Ti+Co) ratio with increase in oxygen partial pressure is observed from the Rutherford's backscattering spectroscopy. X-ray photoelectron spectroscopy (XPS) reveals the higher oxygen vacancies in the CTO film than TiO_2, with valence of cobalt unaltered (i.e. +2). Therefore, the CTO film deposited at 300 mTorr does not show a complete anatase phase unlike the TiO_2 film deposited at the same partial pressure. We have observed RTFM in both films which is not due to impurities/contaminants, as confirmed from the XPS depth profiling and cross-sectional transmission electron microscopy (TEM), rather due to oxygen vacancies. The magnitude of magnetic moment, however, depends not only on the phase of TiO_2 but also on the crystallinity of the films.
- To confirm the universality of ferromagnetism in TiO_2 in nano-dimension, we have deposited thin films by electron beam evaporation technique. These films are annealed in O_2 and Ar atmosphere separately and demonstrate ferromagnetism at 300 K. The pristine amorphous film shows anatase phase after annealing under Ar/O_2 atmosphere at 500 ^{o}C. Magnetic measurements of the pristine films reveal superparamagnetic behaviour at 300 K. On the other hand, both O_2 and Ar annealed films

display hysteresis at 300 K. Various characterisation techniques like XPS, Raman, RBS, TEM and EDS are used to refute the possible role of impurities/contaminants in showing room temperature ferromagnetism. The saturation magnetisation of the films annealed under O_2 flow is found to be higher than the Ar annealed one. It is revealed from shifting of O 1s and Ti 2p core level spectra as well as from the enhancement of high binding energy component of O 1s spectra that the higher magnetic moment is associated with higher oxygen vacancies. In addition, O_2 annealed film demonstrates better crystallinity, uniform deposition and smoother surface than that of the Ar annealed one from glancing angle X-ray diffraction (GAXRD) and scanning probe microscopy (SPM). We have shown that although ferromagnetism stems from oxygen vacancies, the higher magnetisation in O_2 annealed film is due its higher degree of crystallinity in compared to the Ar annealed film which supports our previous findings.

- Owing to the important role of defects in tailoring the magnetic properties of the material, we have used Swift Heavy Ions (SHI) with varied the ion fluence from 5×10^{11} to 1×10^{12} ions/cm^2 to create post-deposition defects in $Ti_{1-x}Co_xO_{2-\delta}$ thin films deposited on Si substrate. While the film deposited at 0.1 mTorr oxygen partial pressure retains its crystallinity upon irradiation showing radiation-resistant behaviour even at a fluence of 1×10^{12} ions/ cm^2, films deposited at 1 to 300 mTorr oxygen partial pressure becomes almost amorphous at the same fluence. Using Poisson's law, the diameter of the amorphized region surrounding the ion path is calculated to be ~4.2 nm from the x-ray diffraction peak intensity as a function of ion fluence. The saturation magnetisation (M_s) is found to decrease exponentially, following the decreasing trend in XRD peak intensities with fluence, indicating magnetic disordered region surrounding the ion path. The diameter of the magnetically disordered region is estimated to be ~ 6.6 nm which is larger than the diameter of the amorphized latent track indicating significant magnetic disorder than the structural disorder in case of polycrystalline $Ti_{0.985}Co_{0.015}O_{2-\delta}$ films.

- In addition to structural and magnetic properties, we have explored the transport behaviour of epitaxial $Ti_{1-x}Co_xO_{2-\delta}$ (x = 0 and 0.05) thin films grown on $LaAlO_3$ substrate after irradiating with 100 MeV Ag^{7+} ions. Irrespective of deposition condition and irradiation fluence, all films exhibit room temperature ferromagnetism. However, while the TiO_2 and Co-doped TiO_2 thin films grown at lower oxygen partial pressure i.e. 0.1 mTorr are conducting, films deposited at higher oxygen partial pressure are found to be insulating. Resistivity versus temperature plot shows minima for both films deposited at 0.1 mTorr oxygen partial pressure. However, the minima disappear with ion irradiation in case of Co-doped TiO_2 film whereas in case of $TiO_{2-\delta}$ film, it is retained upto a fluence of $1x10^{11}$ ions/cm^2. At 1 $x10^{12}$ ions/cm^2 the minima disappears for $TiO_{2-\delta}$ film. We have discussed the occurrence of resistivity minima considering scattering of conduction electrons by magnetic moments i.e Kondo model, thermally activated electrons model and the possible contribution from Quantum Correction to Conductivity (QCC)). The nonlinear behaviour of ln (ρ) vs. 1/T at low temperature discards the thermally activated carrier's contribution. However, the resistivity data below T_{min} fits well with both Kondo and QCC model. In case of perfect Kondo system ferromagnetism must vanish below T_{min} which is not the case here. Ferromagnetism at 5 K as well as at 300 K in all the pristine and irradiated films thus refutes the Kondo effect. However, QCC model fits well with the resistivity behaviour. In addition to room temperature ferromagnetism, we also observed enhancement of saturation magnetisation in ion irradiated films. The ferromagnetism is governed by the competing RKKY and BMP mechanisms for the pristine and irradiated films at lowest fluence i.e. 1 x 10^{11} ios/cm^2. The films irradiated at highest fluence i.e., 1 x 10^{13} ions/cm^2, demonstrate maximum saturation magnetisation. However, the magnetism in the films irradiated at $1x10^{13}$ ions/cm^2 may be explained on the basis of BMP model.

8.2 Suggestions for Future Work

Our investigation on TiO_2 based nanostructures revealed several interesting findings (as listed above). However, there are several open issues need to be answered/clarified with proper experimentation as well as theoretical investigations. Few important suggestions for future work are appended below.

- The effect of nonmagnetic dopant (like V or Cu) in TiO_2 may be studied related to the magnetism in TiO_2 both in the form of nanoparticles as well as thin film form systematically.
- Meticulously controlling the synthesis parameters, TiO_2 (doped with transition metals) single crystals may be grown using hydrothermal technique to explore the origin of magnetism vividly.
- Low energy inert ions like Ar/N may be used to irradiate thin films of TiO_2 to create defects and their effect may be studied by the magnetic and transport measurements.
- SHI irradiation may be used to tailor the structural, magnetic and transport properties of TiO_2 as well as doped TiO_2 thin films epitaxially grown on $SrTiO_3$ substrates.
- To explore the origin of magnetism and the electronic states, XMCD (at oxygen K, Ti 2p and Co 2p edges), EXAFS and RPES measurements of the pristine as well as irradiated films may be carried out using Synchrotron source.
- To explore the transport behaviour with doing and ion irradiation. Hall effect measurements may give the carrier concentration of these systems.