Preface

Semiconductors doped with magnetic ions otherwise called as dilute magnetic semiconductors have been studied in an effort to develop spintronics based device. Spintronics, a new class of electronics that seeks to exploit in addition to the charge degree of freedom as in usual electronics, the spin of carriers.[1] Dilute magnetic semiconductors (DMS) based on II-VI compounds such as Mn doped CdTe and ZnSe are the first studied materials but are not useful for devices because of their low T_c (~1K).[2] DMS's based on III-V semiconductor compounds, such as Mn doped GaAs have $T_c \sim 110$ K which is also far below room temperature.[3] Research efforts to discover the room temperature ferromagnetism (RTFM) have led to the discovery of Mn doped compounds such as $CdGeP_2$,[4] $ZnGeP_2$,[5] and ZnO[6]. The discovery of RTFM in Co-doped TiO_2 semiconductor in the year 2001 by Matsumato *et al*. has made it a potential candidate for the application in spintronics.[7] Combination of semiconducting and ferromagnetic property of doped TiO_2 has ignited the field of science to establish its applicability. TiO_2 basically occurs in three polymorphs: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Anatase and brookite are metastable phases that irreversibly transforms to rutile on heat treatment. Anatase to rutile transformation is kinetically defined and it depends on the parameters such as particle size, shape, source effects, atmosphere, and dopants. This phase transformation is basically a nucleation and growth process. It is anticipated that phase transformation could be influenced by defect concentration, grain boundaries, and particle size. The phase of TiO_2 is also crucial for deciding the magnetic ordering.

TiO_2 has been grown in different dimensions such as zero dimensional nanoparticles, one dimensional nanowires or nanorods, and two dimensional thin films. It has been of great challenge to synthesize one dimensional TiO_2 nanowires without any impurity. Thin films of TiO_2 as well as doped TiO_2 on different substrates have been grown by various deposition techniques such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), sputtering and spin coating etc. exhibit diverse structural, magnetic and transport properties. Matsumoto *et al.* have reported ferromagnetism in Co-doped anatase TiO_2 thin films grown by a combinatorial molecular beam epitaxy (MBE) technique that has enhanced the

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1. H. Ohno, Science 281, 951 (1998); 2.J. K. Furdyana and J. Kossut, DMS's, Semiconductors and Semimetals (Academic Press New York, 1988), vol. 25;3. H. Ohno et al., Appl. Phys. Lett. 69, 363 (1996);4.G. A. Medvedkin et al., Jpn. J. Appl. Phys. 39, L949 (2000); 5. S. Cho et al., Phys. Rev. Lett.88, 257203 (2002)6. P. Sharma et al., Nature Material 24, 673 (2003);7. Y. Matsumoto et al., Science 291, 854 (2001) ferromagnetic order upto 400 K.[7] The measured M_s for Co-doped TiO_2 thin film per Co atom has been found to be 0.32 μ_B /Co for dopant concentration upto7%. Chambers *et al*. have further enhanced the ferromagnetic moment upto 1.26 μ_B/Co in oxygen plasma assisted (OPA) MBE.[8]All the films showing ferromagnetism as mentioned above were of anatase phase. However, in the following year, Park *et al*. have grown ferromagnetic Co-doped rutile films by sputtering and T_c has also been found to be above 400 K with saturation magnetisation 0.94 μ_B /Co.[9]

The origin of room temperature ferromagnetism in these systems was described by various models such as Ruderman-Kittel-Kasuya-Yosida (RKKY) model,[10] bound magnetic polaron (BMP) model,[11] and Stoner type model[12]. Still no single model could explain the observed ferromagnetism satisfactorily. For example, samples produced in oxygen rich atmosphere show negligible magnetisation suggesting excess of oxygen as a factor that deteriorates the magnetisation.[13] Kim *et al*.[14] and Shinde *et al*.[15] have observed the presence of Co clusters leading to room temperature ferromagnetism. On the other hand, the experimental results obtained by Suryanarayanan *et al*. in Fe and Co-doped TiO_2 thin films highlight the important role of oxygen vacancies driving the room temperature ferromagnetism.[16,17]It becomes more surprising, when Hong *et al*. and Yoon *et al*. have reported the room temperature ferromagnetism (RTFM) in TiO_2 thin films without adding any dopant.[18,19] In addition, Sundaresan *et al*. have reported room temperature ferromagnetism in nanoparticles of inorganic oxides like ZnO, HfO_2, SnO_2, YBCO etc.[20] as a universal property. In these oxides, ferromagnetism has been explained on the basis of oxygen vacancies.[20-22] As a consequence of oxygen vacancy, the two electrons associated with it will either localize onto one of the Ti ions transforming it into a Ti^{2+}/Ti^{3+} ion or be delocalized in the TiO_2 matrix. While the latter makes the film conducting, the

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8. S. A. Chambers et al, Appl. Phys. Lett. 79, 3467 (2001) and Mater Today 5, 34 (2002);9. W. K. Park et al., Appl. Phys. Lett. 91, 8093 (2002); 10 Z. Wang et al, Appl. Phys. Lett.83, 518 (2003); 11.J. M. D. Coeyet al., Nature Mater. 4, 173 (2005);12. J. M. D. Coey et al., New J. Phys. 12, 053025 (2010);13. S. A. Chambers et al., Phys. Rev. B, 67, 100401 (R) (2003); 14. J. Y. Kim et al., Phys. Rev. Lett. 90, 017401 (2003); 15. S. R. Shinde et al., Phys. Rev. Lett. 92, 166601 (2004); 16. R. Suryanarayayanan et al., Solid State Communication, 133, 439 (2005); 17. R. Suryanarayanan et al., J. Phys.: Condens. Matter, 17, 755 (2005);18.N.H. Hong et al., Phys. Rev. B 73, 132404 (2006); 19. S.D. Yoon et al., J. Phys.:Condens. Matter 18, L355 (2006); 20. A. Sundaresan et al. Phys. Rev. B. 74, 161306R (2006);21.A.K. Ruamaiz et al., Solid State Commun.144, 334 (2007); 22. D. Kim et al., J. Phys.: Condens. Mater.21,195405 (2009);

former possibility create local magnetic moment at T^{3+}/Ti^{2+} site.[5,8] The other possibility could be that one of the two electrons localizes onto the neighbouring Ti ion and the other electron is delocalized. Therefore, in the oxygen deficient undoped and magnetic ion doped semiconducting TiO_2 films, the formation of localized moments at Ti and/or at the dopant site may have deeper consequences for the electrical, magnetic and magneto-transport properties. For example, one can find room temperature ferromagnetism in insulating as well as in conducting films. In transport measurements, the temperature dependent resistivity in Fe/Co doped TiO_2 thin films show semiconducting like behaviour below T_{min} and beyond display metallic behaviour.[23,24] The resistivity behaviour below T_{min} has been explained by Kondo like scattering,[23] by thermal activation[25] or could be treated by quantum correction to conductivity (QCC)[26] for the disordered electronic system.

Besides conventional techniques, transition metals like Co,[27] Ni,[28] Mn and Fe[29] have been implanted in TiO_2 using low energy ion beam. But the magnetism observed in these cases is explained on the basis of formation of metal nanoclusters. Magnetism have been triggered by implanting inert ions like Ar/N in TiO_2 single crystals where only the lattice defects mediate the ferromagnetic ordering.[30,31] Another potential method to create defects in a system is by Swift Heavy Ion (SHI) irradiation. SHI can produce structural phase transformation from anatase to rutile,[32] can create amorphized latent tracks or point defects,[33] can transform the film from amorphous to crystalline phase[34] and induce ferromagnetism[35] in a diamagnetic material like TiO_2. Hence, ion irradiation is a powerful tool for creation of defects in a material in a controlled manner.

Owing to the important role of defects like oxygen vacancies in the electrical, magnetic and magneto-transport properties of the TiO_2, it becomes fascinating to study these properties by controlling the defect concentration

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23. R. Ramaneti et al., Phys. Rev. B 76, 195207 (2007); 24. K. Bapna et al., J. Phys.: Condens. Matter 24, 056004 (2012); 25.Shinde et al. Phys. Rev. B.67, 115211 (2003) 26. Patrick A. Lee and T. V. Ramakrishnan Rev. Mod. Phys. 57, 287(1985); 27.N. Akdogan et al., J. Phys. D: Appl. Phys. 42, 115005 (2009); 28. D. Bin-Feng et al, Chin. Phys. Lett. 28, 107802 (2011);29.H. P.Gunnlaugsson et al., J. Phys. D: Appl. Phys. 47, 065501(2014);30. R. P. Borges et al. Journal of Physics: Conference Series 153, 012044 (2009);31.L. Chun-Ming et al.,Chinesse Phys. Letter 28, 127201 (2011);32.H. Rath et al, J. Appl. Phys. 105, 074311 (2009);33.N. Ishikawa et al., Nucl. Inst. Meth.Phys. Res. B 250, 250 (2006); 34.M. Thakurdesai et al.,Nucl. Inst. Meth. Phys. Res. B 266, 1343 (2008)35.H. Thakur et al., Applied Physics Letters 98, 192512 (2011) through various ways which is the broad objective of our present work. In particular, we have studied (i) the anatase to rutile phase transformation in presence of oxygen vacancies by reducing the size to nanoscale range and have discussed the magnetic properties in TiO_2 nanoparticles doped with Co, (ii) the microstructure and magnetic properties of TiO_2 nanowires synthesized by two step hydrothermal process, (iii) the structure and magnetic properties of oxygen deficient TiO_2 and Co-doped TiO_2 thin films deposited on various substrates by pulsed laser deposition technique (iv) the observation of room temperature ferromagnetism in electron beam evaporated TiO_2 films annealed in Ar/O_2 atmosphere (v) the evolution of structural, magnetic, transport and magneto-transport properties by enhancing the defect concentration through swift heavy ion irradiation.

The thesis is organised into VIII chapters as follows:

Chapter I gives a brief introduction about the structure, properties and applications of TiO_2. The different methods used to synthesize or deposit nanostructured TiO_2 have been given. It also highlights some general concepts and mechanisms responsible for the observed magnetism in DMS systems. Brief information about the ion matter interaction has also been discussed.

Chapter II presents the literatures related to TiO_2 based dilute magnetic semiconductors. The structural, magnetic and transport properties of TiO_2 and different transition metal doped TiO_2 have been discussed. The effect of ion irradiation or implantation in TiO_2 is also reviewed.

Chapter III gives an overview of the experimental methodology that has been followed for the present work. The sol-gel synthesis of TiO_2 and Co-doped TiO_2 nanoparticles as well as the process to synthesize TiO_2 nanowires using hydrothermal reaction technique has been discussed. It also accounts for the deposition methods like pulsed laser deposition (PLD) and e-beam evaporation technique to deposit TiO_2 and Co-doped TiO_2 films on different substrates. Brief information regarding the ion beam irradiation facility used at IUAC, New Delhi and the characterization techniques used in the present work are also incorporated in this chapter.

Chapter IV deals with the structural transformation in nanoparticles of TiO_2 synthesized through sol-gel technique at various *p*H of precipitation and their magnetic properties. The structural and magnetic properties of anatase TiO_2 nanowires grown from the nanoparticles using two step hydrothermal process are discussed.

Chapter V addresses structural and magnetic properties in TiO_2 and Co-doped TiO_2 (Co 1.5 at %) films deposited on Si and $LaAlO_3$ (Co 5 at %) substrate with varying oxygen partial pressure. An anomaly in phase formation and ferromagnetism at room temperature has been observed. The presence of foreign impurities like Co clusters or any secondary magnetic phase in the films causing the RTFM have been discarded through various characterisation tools.

Chapter VI emphasizes the problem of magnetism in TiO_2 thin films deposited on Si substrate by e-beam evaporation technique. Magnetic measurements reveal room temperature ferromagnetism irrespective of the post annealing conditions. The role of oxygen vacancies as well as crystallinity on the magnetic properties of TiO_2 is addressed.

Chapter VII focuses on the evolution of magnetic properties of $Ti_{1-x}Co_xO_{2-\delta}$ thin films deposited on Si and $LaAlO_3$ substrate by PLD technique irradiated with 100 MeV Ag^{7+} ions. The possible reasons behind the differences in magnetic behaviour with ion dose for the film deposited on Si and $LaAlO_3$ are examined. The occurrence of resistivity minima in TiO_2 and Co-doped TiO_2 films deposited on $LaAlO_3$ substrate are analyzed considering the effect of thermal activation, Kondo scattering and QCC approach. It is realized that the competition between RKKY and Bound Magnetic Polaron (BMP) model leads to the observed ferromagnetism. The possible role of ion irradiation on structural, magnetic, transport and magneto-transport properties are discussed.

Chapter VIII summarises the key findings of the present work. Here, we establish that observation of room temperature ferromagnetism is a universal property of TiO_2 or doped TiO_2 thin films either deposited in oxygen rich or oxygen deficient condition. Finally, we present the future work to be done in this area.