

LIST OF FIGURES

- Fig.1.1** TiO_6 polyhedra showing the three polymorphs of TiO_2 : rutile (a), anatase (b) and brookite (c). Ti is represented as white and O as red spheres. [2]
- Fig.1.2** Various steps involved in sol-gel process to synthesize nanostructured material. [6]
- Fig.1.3** A donor electron in its hydrogenic orbit couples with its spin antiparallel to impurities with a 3d shell that is half-full or more than half-full. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares. [20]
- Fig.1.4** Schematic illustration of (a) the distribution of magnetic cations in a dilute magnetic oxide and (b) the resulting magnetic susceptibility. [20]
- Fig.1.5** The charge transfer involved in a system with a ferromagnetic instability. [21]
- Fig.1.6** Curves showing the variation of electronic and nuclear energy loss corresponding to the inelastic and elastic collisions respectively of silver beam passing through YBCO at various energies. [23]
- Fig.2.1** Magnetisation as a function of applied magnetic field for (a) $\text{Ti}_{0.93}\text{Co}_{0.07}\text{O}_{2-\delta}$ film and [Matsumoto et al. (2001)] (b) $\text{Ti}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ film [After Chambers et al. (2001)] [30]
- Fig.2.2** M-H of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ (a) Metallic, intermediate, and insulating anatase samples. (b) Metallic rutile sample. [34]
- Fig.2.3** Hall voltage versus applied magnetic field at 300 K for $x = 0.06$. The extraordinary Hall effect dominates at low fields and shows hysteretic behaviour as shown in the inset. [39]
- Fig.2.4** Electrical properties of anatase TiO_2 and Co: TiO_2 . The inset shows the resistivity versus $1/T$ of the anatase TiO_2 and Co: TiO_2 . [41]
- Fig.2.5** A representation of a thin film of Co: TiO_2 in which ferromagnetism arises because titanium 3d electrons (green) travel around the material aligning the spin of cobalt atoms (pink) so that they all point in the same direction. The blue and brown spheres correspond to titanium and oxygen atoms, respectively. [44]
- Fig.2.6** (a) Splitting of d levels in an octahedral crystal field and (b) possible occupation schemes for a $\text{Co}^{2+}(3d^74s^0)$ atom. Unpaired spins are highlighted. [45]
- Fig.2.7** TEM image of $\text{Ti}_{0.98}\text{Co}_{0.02}\text{O}_{2-\delta}$ film at different magnifications. [46]
- Fig.2.8** Ti 2p core-level PES of Co: TiO_2 thin film by Hard x-ray PES (blue) and soft x-ray PES (red), respectively. The inset is the magnetisation vs. magnetic field curve of the same film measured at room temperature. [47]

Fig.3.1 Experimental scheme for synthesis of TiO₂ nanoparticles. [50]

Fig.3.2 Experimental scheme for synthesis of Co-doped TiO₂ nanoparticles. [50]

Fig.3.3 Parr autoclave (450 ml: Model 4560, USA) used for the hydrothermal reaction. [51]

Fig.3.4 Experimental scheme for synthesis of TiO₂ nanowires using hydrothermal technique. [52]

Fig.3.5 Schematic representation of PLD system depicting various parts. [53]

Fig.3.6 Photograph of the PLD chamber during deposition of thin films. [55]

Fig.3.7 Electron beam evaporation unit used for the deposition of TiO₂ film. [56]

Fig.3.8 Schematic representation of e-beam evaporation system depicting various parts. [56]

Fig.3.9A schematic diagram showing various parts of the Pelletron Accelerator. [58]

Fig.3.10 RBS spectra of CTO target (black line is the experimental data and the simulated spectrum is shown in red) [64]

Fig.3.11 Typical four probe arrangement. [71]

Fig.4.1 XRD patterns of TiO₂ nanoparticles synthesised at (a) *pH* = 4.5 (sample A), and (b) *pH* = 6.5 (sample B) calcined at different temperatures. [75]

Fig.4.2 Raman spectra of (a) sample A and (b) sample B calcined at different temperatures. [76]

Fig.4.3 FT-IR of sample A-500 and B-500. Inset shows the comparison of samples B-500 with B-650. [78]

Fig.4.4 Transmission electron micrographs of (a) A-500 and (b) B-500 samples. SAED patterns of sample A-500 (c) and (d) and B-500. [80]

Fig.4.5 Normalized XPS spectra of samples A-500 and B-500: (a) Ti 2p core levels and (b) O 1s core level. [81]

Fig.4.6 Deconvolution of O 1s core level: Oa and Ob peaks of A-500 and B-500 samples are shown in (a) and (b) respectively. [81]

Fig.4.7 (a) XRD patterns of Ti_{1-x}Co_xO₂ (*x* = 0, 0.01, 0.03 and 0.05) synthesised at *pH* = 6.5 and calcined at 500 °C. (b) A typical Le-Bail profile fitting of TiO₂ (i.e., *x* = 0) [84]

- Fig.4.8** Raman spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.01, 0.03$ and 0.05) calcined at 500°C . [86]
- Fig.4.9** FT-IR spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.01, 0.03$) calcined at 500°C . [87]
- Fig.4.10** (a) Susceptibility as a function of temperature for $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.01, 0.03$) [inset shows the T_N of CoTiO_3] (b) Inverse susceptibility as a function of temperature for $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.01, 0.03$) [inset shows the zoomed in view for $x = 0$] [89]
- Fig.4.11** Magnetisation as a function of applied magnetic field for $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ for (a) $x = 0$, (b) $x = 0.01$ and (c) $x = 0.03$ measured at 10 and 300 K. [91]
- Fig.4.12** Transmission electron micrograph of $\text{Ti}_{0.97}\text{Co}_{0.03}\text{O}_2$ nanoparticles. [92]
- Fig.4.13** XPS core level spectra of (a) Ti 2p, (b) Co 2p ($x = 0.03$) and (c) O 1s of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$. [95]
- Fig.4.14** TEM micrograph of the as synthesised TiO_2 nanoparticles. Inset (a) shows the SAED pattern and (b) particle size distribution histogram of the nanoparticles. [96]
- Fig.4.15** FE-SEM: (a) low magnification image of sample B₁ (b) High magnification image of sample B (c) High magnification image of sample C (inset shows the EDS spectra of the sample C). [97]
- Fig.4.16** (a) TEM image of the sample C (inset shows the HREM image of the nanowire), (b) SAED pattern of the sample C (inset shows the selected bunch of nanowires) and (c) SAED pattern of nanoparticles seen in the sample C (inset shows the selected area). [98]
- Fig.4.17** Profile fitting for (a) Sample A₁ and (b) Sample C from Rietveld Method. [101]
- Fig.4.18** Normalized Raman spectra of sample A and C (inset shows the zoomed view). [104]
- Fig.4.19** Magnetisation (ZFC and FC) as a function of temperature for sample C at a probing field (a) 500 Oe and (b) 1 Tesla. [106]
- Fig.4.20** Three dimensional electron density iso-surface of (a) sample A₁ and (b) sample C. [107]
- Fig.4.21** Two dimensional electron density distribution of (a) sample A₁ and (b) sample C. [107]
- Fig.4.22** One dimensional electron density profile of sample A₁ and sample C between Ti and O atoms. [108]
- Fig.5.1.** GAXRD pattern of TiO_2 thin films deposited at various oxygen partial pressures. [112]

Fig.5.2. GAXRD pattern of CTO thin films deposited at various oxygen partial pressures. Inset shows the XRD spectrum of CTO film deposited at 300 mTorr oxygen partial pressure with $2\theta = 20 - 30^\circ$. [113]

Fig.5.3 Raman spectra of (a) TiO_2 and (b) CTO films deposited at various oxygen partial pressures. [114]

Fig.5.4. RBS spectra of CTO films deposited on Si: (a) vacuum, (b) 0.1 mTorr, (c) 1 mTorr and (d) 300 mTorr. Black line is the experimental data and the simulated spectrum is shown in red. [115]

Fig.5.5 FE-SEM images of CTO thin film deposited at (a) vacuum, (b) 0.1 mTorr, (c) 1 mTorr, and (d) CTO 300 mTorr oxygen partial pressure. [116]

Fig.5.6 FE-SEM image of CTO thin film deposited at 300 mTorr oxygen partial pressure. [117]

Fig.5.7. XPS core level spectra of: (a) O 1s level of TiO_2 , (b) O 1s level of CTO film (c) Ti 2p level of TiO_2 and CTO film and (d) Co 2p level of CTO film deposited at 300 mTorr. [118]

Fig.5.8 XRD pattern of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films deposited on LaAlO_3 substrate at different oxygen partial pressures. [120]

Fig.5.9 XRD pattern of $\text{TiO}_{2-\delta}$ films deposited on LaAlO_3 substrate at different oxygen partial pressures. [121]

Fig.5.10 Raman spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ ($x = 0, 0.05$) films deposited at 0.1 mTorr oxygen partial pressure. [122]

Fig.5.11 Oxygen resonance RBS result of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ and $\text{TiO}_{2-\delta}$ film deposited on LaAlO_3 substrate at 0.1 mTorr oxygen partial pressure. The inset shows the RBS/channeling results for $\text{TiO}_{2-\delta}$ film. [123]

Fig.5.12 SPM images of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films deposited on LaAlO_3 at (a) 0.1 mTorr, (b) 10 mTorr and (c) 300 mTorr oxygen partial pressure. [124]

Fig.5.13 A typical SPM image of $\text{TiO}_{2-\delta}$ film deposited at 0.1 mTorr oxygen partial pressure. [124]

Fig.5.14 Magnetisation (M) vs. applied magnetic field (H) of: (a) TiO_2 film deposited at 0.1 mTorr, 1mTorr and 300 mTorr (at 300 K) (b) CTO films deposited at 0.1 mTorr, 1 mTorr and 300 mTorr oxygen partial pressure (at 300 K) and (C) CTO films deposited at 0.1 mTorr, 1 mTorr and 300 mTorr oxygen partial pressure (at 5 K). [125]

Fig.5.15 ZFC and FC magnetisation (M) vs. temperature (T) at 50 Oe of (a) CTO films deposited at 0.1 mTorr, 1 mTorr and 300 mTorr oxygen partial pressures (b) TiO_2 films deposited at 0.1 mTorr oxygen partial pressure. [127]

Fig.5.16 Magnetisation (M) vs. applied magnetic field (H) at 300 K of (a) CTO (b) TiO₂ films deposited at 0.1 mTorr, 1mTorr and 300 mTorr. (c) A typical M vs. H plot for CTO film deposited at 0.1 mTorr oxygen partial pressure under ZFC and FC condition. [129]

Fig.5.17 Magnetisation (M) vs. applied magnetic field (H) of (a) Si substrate measured at 300 K and 5 K and (b) LaAlO₃ measured at 300 K and 1.8 K. Inset of (b) shows the M vs. H plot of the sample holder. [132]

Fig.5.18. XPS Core level spectra of CTO film deposited at 300 mTorr: (a) Ti 2p (b) O 1s and (c) Co 2p region with 2keV Ar⁺ ion sputtering for 40 and 80 minutes. [134]

Fig.5.19 Topographic (left panel: (Height)_{max}~60 nm) and corresponding MFM image (right panel: (Height)_{max}~ 40 Hz) of the film Ti_{0.985}Co_{0.015}O_{2-δ} deposited at (a) 0.1 mTorr and (b) 1 mTorr oxygen partial pressure. [135]

Fig.5.20. A typical high resolution cross sectional transmission electron micrograph of CTO film. Inset shows the high resolution electron microscopic image corresponding to (110) plane of rutile phase of TiO₂. [136]

Fig.5.21 Typical EDS spectra recorded over the (a) film and (b) substrate of Ti_{0.985}Co_{0.015}O_{2-δ} film with elemental compositions as inset. [136]

Fig.6.1 Oxygen resonance RBS data of the pristine thin film deposited on Si substrate from Co-doped TiO₂ target. [140]

Fig.6.2 GAXRD pattern of TiO₂ thin films deposited on Si substrate (film P), annealed in O₂ (film A) and Ar (film B) atmosphere. [141]

Fig.6.3 FE-SEM micrograph of TiO₂ thin film annealed in (a) O₂ (film A) and (b) Ar (film B) atmosphere @ 500 °C. Inset of (b) represents a typical EDS spectrum of the film measured at 20 kV. [142]

Fig.6.4 SPM images of TiO₂ thin film deposited on Si and annealed in (a) O₂ (film A) and (c) Ar (film B) atmosphere. (b) and (d) represents the 3D view of the film A and B, respectively. [143]

Fig.6.5 Transmittance as a function of incident wavelength (λ). The inset shows the (αhv)^{1/2} as a function of incident photon energy (hv). [145]

Fig.6.6 RBS data of the film A and B indicating Ti, Si and O edges. [146]

Fig.6.7 Magnetisation as a function of applied magnetic field for the Si substrate. [147]

Fig.6.8 Magnetisation as a function of applied magnetic field for the film P at 300 and 5 K (inset shows the zoomed view of the M-H loop at low fields). [147]

Fig.6.9 Magnetisation as a function of applied magnetic field for the film A and B at (a) 300 and 5 K (b) (insets show the zoomed view of the $M-H$ loops at low fields). [148]

Fig.6.10 (a) XPS survey scan of TiO_2 films annealed in O_2 and Ar (b) Oxygen 1s core level spectra of the films: Inset shows the O 1s core level spectra for bulk TiO_2 with Gaussian fitting with Shirley background (c) Ti 2p core level spectra of the films. [154]

Fig.6.11 High resolution cross-sectional transmission electron micrograph of the TiO_2 film on Si substrate. The inset shows the EDS of the Si substrate.[154]

Fig.7.1 Electronic and Nuclear energy loss as a function of energy for silver ion on TiO_2 target.158

Fig.7.2 Glancing angle x-ray diffraction (GAXRD) of the TiO_2 film deposited at (a) vacuum, (b) 0.1 mTorr (c) 1 mTorr and (d) 300 mTorr oxygen partial pressure followed by ion irradiation with different fluence. [159]

Fig.7.3 Glancing angle x-ray diffraction (GAXRD) of the film deposited at (a) vacuum, (b) 0.1 mTorr (c) 1 mTorr and (d) 300 mTorr oxygen partial pressure followed by ion irradiation with different fluence. [160]

Fig.7.4 SPM image of the film CTO film deposited at 0.1 mTorr oxygen partial pressure with irradiation fluence (a) pristine, (b) 5×10^{10} ions/cm², (c) 5×10^{11} ions/cm², (d) 5×10^{12} ions/cm². Figures (e) to (h) depict the 3D representation of the respective films. [162]

Fig.7.5 Particle size histogram of Co-doped TiO_2 film deposited under 0.1 mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ion with fluence (a) pristine, (b) 5×10^{10} ions/cm², (c) 5×10^{11} ions/cm², and (d) 1×10^{12} ions/cm². [163]

Fig.7.6 Logarithm of the intensity of (110) peak of anatase TiO_2 , $\ln(I/I_0)$, plotted against fluence, ϕ , where $I = I(\phi)$ is the peak intensity for the irradiated sample and I_0 is the peak intensity before irradiation. Straight line is to demonstrate that peak intensity decreases following Poisson's law according to Eq. (7.1). [165]

Fig.7.7 Magnetisation (M) as a function of applied magnetic field (H) for the pristine and irradiated Co-doped TiO_2 film deposited at 0.1 mTorr oxygen partial pressure. The inset (a) shows the exponential decrease in the saturation magnetisation with increase in ion fluence. [166]

Fig.7.8 Logarithm of the saturation magnetisation (M_s) of anatase TiO_2 film deposited at 0.1 mTorr oxygen partial pressure, $\ln(M/M_0)$, plotted against fluence, ϕ , where $M = M(\phi)$ is the saturation magnetisation of the irradiated sample and M_0 is the saturation magnetisation of the pristine film. Straight line

fitting in inset (b) is to demonstrate that saturation magnetisation decreases following Poisson's law according to Eq. (7.2). [168]

Fig.7.9 Schematic representation of the ion track regions. The red core indicates the amorphized latent track region whereas the black circle represents the extent of magnetic disordered region over the surface of the film. [168]

Fig.7.10 (a) X-ray diffraction pattern of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films deposited on LAO substrate under 0.1mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ion with various fluence. (b) x-ray diffraction pattern of $\text{TiO}_{2-\delta}$ films deposited on LaAlO_3 substrate under 0.1mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ion with various fluence. [170]

Fig.7.11(a) Raman spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films deposited on LAO substrate under 0.1mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ion with various fluence. (b) Raman spectra of $\text{TiO}_{2-\delta}$ films deposited on LAO substrate under 0.1mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ion with various fluence. [172]

Fig.7.12 SPM images of: pristine $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film (a) and film irradiated with 1×10^{13} ions/cm² (b); pristine $\text{TiO}_{2-\delta}$ film (e) and film irradiated with 1×10^{13} ions/cm². Corresponding 3D images are shown as (c), (d), (g) and (h), respectively. [173]

Fig.7.13 Magnetisation as a function of temperature of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ (a) and $\text{TiO}_{2-\delta}$ films deposited on LAO substrate under 0.1mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ions with various fluence. [176]

Fig.7.14(a) Magnetisation of pristine (deposited under 0.1 mTorr oxygen partial pressure) and irradiated $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films as a function of applied magnetic field at 300 K. (b) Magnetisation of pristine (deposited under 0.1 mTorr oxygen partial pressure) and irradiated $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films as a function of applied magnetic field at 5 K. [177]

Fig.7.15(a) Magnetisation of pristine (deposited under 0.1 mTorr oxygen partial pressure) and irradiated $\text{TiO}_{2-\delta}$ films as a function of applied magnetic field at 300 K. (b) Magnetisation of pristine (deposited under 0.1 mTorr oxygen partial pressure) and irradiated $\text{TiO}_{2-\delta}$ films as a function of applied magnetic field at 5 K. [178]

Fig.7.16 Resistivity as a function of temperature (a) CTO pristine, (b) CTO 1×10^{11} ions/cm², (c) CTO 1×10^{12} ions/cm², (d) $\text{TiO}_{2-\delta}$ pristine, (e) $\text{TiO}_{2-\delta}$ 1×10^{11} ions/cm² and (f) $\text{TiO}_{2-\delta}$ 1×10^{12} ions/cm². Red symbols indicate resistivity measured as 8Tesla. [184]

Fig.7.17 $\ln(\rho)$ as a function of $1/T$ (K^{-1}) for (a) CTO pristine, (b) CTO 1×10^{11} ions/cm², (c) CTO 1×10^{12} ions/cm², (d) $TiO_{2-\delta}$ pristine, (e) $TiO_{2-\delta}$ 1×10^{11} ions/cm² and (f) $TiO_{2-\delta}$ 1×10^{12} ions/cm². [187]

Fig.7.18 Resistivity as a function of temperature of $Ti_{1-x}Co_xO_{2-\delta}$ ($x=0$ and 0.05) thin film deposited under 0.1 mTorr oxygen partial pressure and irradiated with 100 MeV Ag^{7+} ions: (a) $Ti_{0.95}Co_{0.05}O_{2-\delta}$ (pristine), (b) $TiO_{2-\delta}$ (pristine) (c) $TiO_{2-\delta}$ irradiated with 1×10^{11} ions/cm² fitted with WL and REEI model for 3D system and Kondo equation. [189]

Fig.7.19 Magnetoresistance of $Ti_{1-x}Co_xO_{2-\delta}$ thin film ((a) $x = 0.05$ and (b) $x = 0$) at 5 K. [194]

LIST OF TABLES

Table 1.1 Structural parameters for the three crystalline phases of TiO_2 . [3]

Table 4.1 Lattice parameters and unit cell volume of $Ti_{1-x}Co_xO_2$ ($x = 0, 0.01, 0.03$). [85]

Table 4.2 Structural parameters for Sample A₁ and C. [102]

Table 4.3 Reliable indices from Rietveld analysis. [103]

Table 4.4 Mid bond electron density between Ti and O atoms. [109]

Table 5.1 Thickness and composition of $Ti_{0.985}Co_{0.015}O_{2-\delta}$ films deposited at various oxygen partial pressures. [115]

Table 7.1 Fitting parameters of resistivity data considering Kondo equation.[190]

Table 7.2 Fitting parameters of resistivity data considering QCC. [190]