

Electronic structure and magnetic properties of Co doped TiO_2 thin films using X-ray absorption spectroscopy

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Abstract

The thin film of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ has been grown on LaAlO_3 (100) substrate using pulsed laser deposition method. X-ray diffraction, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray magnetic circular dichroism (XMCD) and magnetic hysteresis loop measurements were used to fully understand the origin of ferromagnetism. Our structural analysis reveals a single phase nature of the film and excludes the presence of any secondary phase. NEXAFS spectra collected at Ti $L_{3,2}$, and Co $L_{3,2}$ -edge infer that Co and Ti ions are in 2+ and 4+ valence states, respectively. Multiplet calculation performed at Co $L_{3,2}$ -edge also support the experimental observations and shows that Co ions are in 2+ valence state in O_h (octahedral) symmetry. Zero field cooled and field cooled magnetization infer that T_C of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film is above room temperature. DC magnetization hysteresis loop study and XMCD measurement at Co $L_{3,2}$ -edge reflect that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film exhibits ferromagnetic ordering at room temperature.

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1. Introduction

In recent years, dilute magnetic semiconductors have attracted a lot of attention due their potential technological applications in spintronics, where the spin of the charge carriers (electron or hole) is exploited to provide the additional functionality in spintronics devices [1,2]. Various semiconducting host matrix doped with transition metal (TM) are expected to play an important role for devices and circuits [3]. However, a big issue which has been discussed controversially at the moment is, understanding the origin of room temperature ferromagnetism (RT-FM) in these

systems. The idea of doping of TM ion in semiconducting host matrix is to generate the magnetic interaction between TM ions, so that these interactions may induce the FM in the host material. However, the most important issue of whether the FM observed in TM doped host material really comes from doped matrix or not, is still a challenge in the condensed matter physics and physics of magnetism.

Among various wide band gap semiconductors, TiO_2 is an important material because of their excellent physical, chemical and mechanical properties such as excellent optical transmittance in the visible and near infrared range, high dielectric constant and low loss tangent and high index of refraction [4,5]. It has various potential technological applications such as photocatalyst, solar cell, gas sensors, optical waveguide in integrated optics, suitable template layers for growing high- T_C superconducting films and electrical device etc. [6,7]. The 3d transition metal doped TiO_2 has been paid a great attention

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after the discovery of RT-FM in Co doped anatase and rutile TiO_2 by Matsumoto et al. [8]. However, among the entire known TM doped TiO_2 , Co doped TiO_2 is probably the most controversial system [9–14]. It is found from the literature that the reported values of magnetic moments vary, and depend on the growth process and subsequent conditions. Therefore, it is very challenging to confirm the observed FM is intrinsic or extrinsic due to the presence of secondary phase or Co metal cluster. These controversial reported results about the intrinsic origin of ferromagnetism motivated us to further study about the origin of RT-FM in Co doped TiO_2 . Here we have used X-ray absorption spectroscopy (XAS) techniques to understand the origin of ferromagnetism and the influence of Co substitution on electronic structure of Co doped TiO_2 . XAS measures the transition between the core levels of a specific atom and the conduction band of the solid. XAS is one of the excellent techniques which probe the unoccupied electronic states as a result of excitation of core electrons into unoccupied electronic states (conduction band). XAS offers the unique information about the crystal field strength and symmetry, hybridization, valence state of the specific ions of interest. Therefore, in order to explain the correlation between the experimentally observed magnetic properties and electronic structure of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film, we have measured the near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, at O K , Co $L_{3,2}$ and Ti $L_{3,2}$ -edge and X-ray magnetic circular dichroism (XMCD) at Co $L_{3,2}$ -edge. The X-ray diffraction (XRD) is also used to confirm the crystal structure of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film. Magnetic behavior has been studied using zero field cooled (ZFC), field cooled (FC), and magnetic hysteresis loop measurements. XRD and NEXAFS studies indicate that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film has a single phase rutile structure and ruled out the presence of a secondary phase. DC magnetization and XMCD measurements show that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film exhibits ferromagnetic ordering at room temperature.

2. Experiment

Thin film of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ was fabricated by using a pulsed laser deposition (PLD) technique. TiO_2 target doped with 5 mol% Co was synthesized using a standard solid state reaction method. The stoichiometric amount of CoO and TiO_2 powders (all the chemicals were of 99.99% purity and purchased from Sigma-Aldrich) were mixed using alcohol and calcinated at 800 °C for 12 h and then at 900 °C in air for 24 h with intermediate grinding. Finally, the resulted powder was pressed into the pellets and sintered at a sufficiently high temperature (1200 °C) for 24 h. Before the film deposition, the single phase nature of the target was checked using XRD and it was observed that target shows single phase rutile structure. The composition of Co ions in TiO_2 target was checked by Energy Dispersive X-ray Spectroscopy (EDX) measurement and found that Co has stoichiometric composition in doped TiO_2 target. The Co doped TiO_2 thin film with a typical thickness of ~ 200 nm was deposited on LaAlO_3 (100) substrate by PLD (248 KrF excimer laser, pulse of 10 Hz) from $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ ceramic target. The oxygen partial pressure (PO_2) during the deposition was kept

10^{-6} Torr and the energy density was about 1.8 J/cm². During the film deposition, substrate was kept at 700 °C and after deposition, chamber was cooled slowly to RT at the rate of 5 °C/min. To check the single phase nature of films, we have used a Phillips X'pert (MPD 3040) X-ray diffractometer with a Cu K_α source ($\lambda=1.5406$ Å) was operated at voltage of 36 kV and current 30 mA for collecting room temperature diffraction patterns. Field cooled magnetization and magnetic hysteresis loop measurements were performed using a commercial Quantum Design physical property measurement system (PPMS-6000). The XMCD experiment for 5 mol% Co doped TiO_2 film was performed at 2A MS beam line of Pohang Accelerator Laboratory (PAL) operating at 2.5 GeV with a maximum storage current of 200 mA. This beam line has elliptically polarized undulator with greater than 90% degree of circular polarization. The XMCD spectrum was taken for a fixed helicity of the light by reversing the applied magnetic field (0.8 T) for each photon. The spectrum was normalized to the incident photon flux. The NEXAFS measurements of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ films, along with reference compounds of CoO, TiO (Ti^{2+}), Ti_2O_3 (Ti^{3+}) and TiO_2 (Ti^{4+}), at O K , Co $L_{3,2}$ and Ti $L_{3,2}$ -edges were performed at the soft X-ray beam line 10D XAS KIST (Korean Institute of Science and Technology) of the PAL. The spectra were simultaneously collected in the total electron yield (TEY) mode and the fluorescence yield (FY) mode at room temperature in a vacuum of $\sim 1.5 \times 10^{-8}$ Torr. The spectra in the two modes turned out to be nearly identical, indicating that the systems were so stable that the surface contamination effects were negligible even in the TEY mode. The spectra were normalized to the incident photon flux, and the energy resolution was better than 0.2 eV. The data were normalized and analyzed using Athena 0.8.054/IFEFFIT 1.2.10.

3. Results and discussion

Fig. 1 shows the XRD spectrum of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film. It is found that the film shows peaks corresponding to the rutile phase of TiO_2 and no extra peak could be seen within the detection limit of X-ray diffractometer. The XRD spectrum clearly infers that Co forms a single phase solid solution with TiO_2 and replace Ti position in TiO_2 matrix. From the XRD pattern it is observed that the film shows polycrystalline behavior with maximum intensity for the (210) peak.

Fig. 2 highlights O K -edge NEXAFS spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film along with the reference spectrum of TiO (Ti^{2+}), Ti_2O_3 (Ti^{3+}), and TiO_2 (Ti^{4+}). O K -edge probes the O $2p$ projected unoccupied density of states in the conduction band due to the covalent mixing between O and TM ions. The spectral features at around 530–536 eV are due to the strong Ti/Co $3d - \text{O } 2p$ hybridization and assigned to $3d t_{2g}$ (530.1 eV) and e_g (532.8 eV) states, respectively, because of the crystal field effect. This splitting is very sensitive to the coordination number and extent of the hybridization. The spectral features in the region 538–550 eV are attributed to the O $2p$ orbitals hybridized to Ti/Co $4sp$ orbitals and this region exhibits larger dispersion effects and is more sensitive to long range order. It can be seen from the comparison of the spectral features of Co doped TiO_2 with the

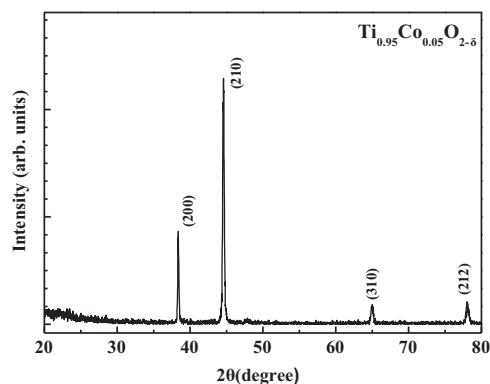


Fig. 1. X-ray diffraction pattern of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film.

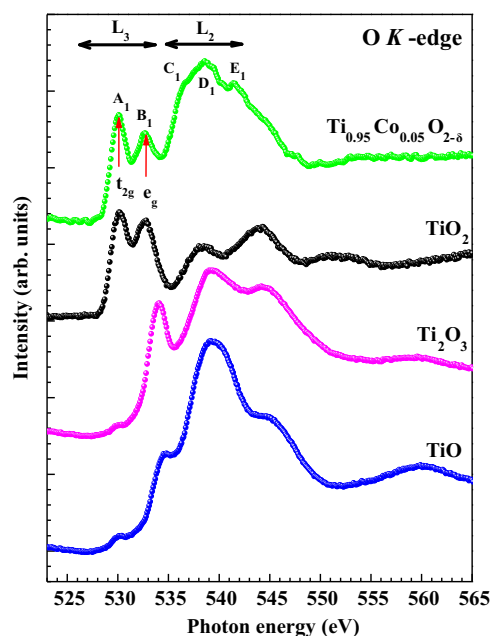


Fig. 2. O K edge NEXAFS spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film along with the reference spectra of TiO , Ti_2O_3 , and TiO_2 .

reference compounds that spectral feature of Co doped film resembles with TiO_2 . From the comparison, it is concluded that Ti ions are in $4+$ valence state in TiO_2 matrix. The spectral features (C_1 and D_1) observed at higher energy is attributed to the lowest unoccupied t_{1u} final states whereas peak E_1 constitutes a transition to higher-lying t_{1u} orbitals. As it is well known that t_{2g} and e_g bands are separated by crystal field [i.e. $E(e_g) - E(t_{2g})$] and can be identified in $3d$ metals [15,16]. In the case of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film, the experimentally observed 10 Dq from the O K edge spectrum was 2.70 eV . The experimentally observed 10 Dq value is similar to the previously reported value of TM doped TiO_2 [3]. Therefore, 10 Dq value observed in O K edge NEXAFS spectrum clearly infers that Co ions are occupying the Ti position in TiO_2 matrix and without changing the valence state of Ti (Ti^{4+}).

Fig. 3 shows the Ti $L_{3,2}$ NEXAFS spectrum of Co doped TiO_2 together with TiO_2 , Ti_2O_3 and TiO as reference spectra. The Ti $L_{3,2}$ edge spectrum displays a significantly more complex structure due to the combination of the atomic interactions and crystal field

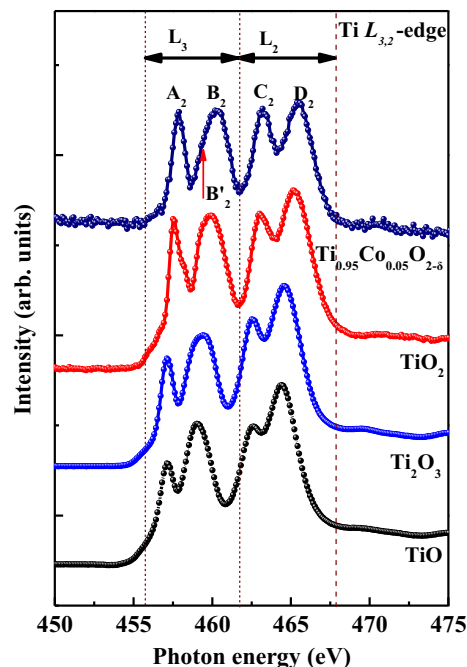


Fig. 3. Ti $L_{3,2}$ -edge NEXAFS spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film along with TiO_2 (Ti^{4+}), Ti_2O_3 (Ti^{3+}) and TiO (Ti^{2+}) as reference spectra.

effects. The spectral features in the region L_3 and L_2 corresponds to $\text{O } 2p_{3/2} - \text{Ti/Co } 3d$ and $\text{O } 2p_{1/2} - \text{Ti/Co } 3d$ transition, respectively, due to the spin orbit splitting. Moreover, it can also be clearly seen from the Fig. 3 that L_3 and L_2 edges further split into t_{2g} (A_2 and C_2) and e_g (B_2 and D_2) states due to crystal field. From the close examination of the Ti L_3 edge, we observed a further splitting of the second peaks of L_3 edge (B_2 and B'_2). There are noteworthy differences between the Ti L_3 spectra for anatase and rutile, particularly, in the relative intensities of peaks B_2 and B'_2 . It is reported that peak B'_2 appears as a low energy shoulder for rutile and a high energy shoulder for anatase [17]. The spectral features of L_3 edge clearly infer that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film has rutile structure, which is in well agreement with XRD results. Our main motivation to study the Ti L_3 edge was to study the effect of divalent Co^{2+} ions substitution on the valence state of Ti ions. By comparing the spectral features of the of Ti $L_{3,2}$ edge with reference spectra, it is observed that spectral features clearly match with TiO_2 reference spectra. Furthermore, It is experimentally observed that spin-orbit splitting value of Ti $L_{3,2}$ edges is 5.33 eV , which is similar to the observed value of rutile and anatase TiO_2 [18,19]. In the literature Groot et al. reported a series of absorption spectra calculated for Ti^{4+} in various crystal field strengths [15]. The separation between the experimentally observed peaks matches well with Ti^{4+} spectra in O_h symmetry as calculated by Groot et al. and other mixed perovskite compounds. Experimental values of spin orbit splitting and crystal field splitting clearly indicates that Ti ions are in $4+$ valence state in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film. Therefore, from Ti $L_{3,2}$ edge observation, It can be concluded that charge neutrality in divalent doped TiO_2 may be balanced by formation of oxygen vacancies.

Fig. 4(a) represents the Co $L_{3,2}$ edge NEXAFS spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film. The Co $L_{3,2}$ edge NEXAFS is a very effective tool to confirm the secondary phase such as Co

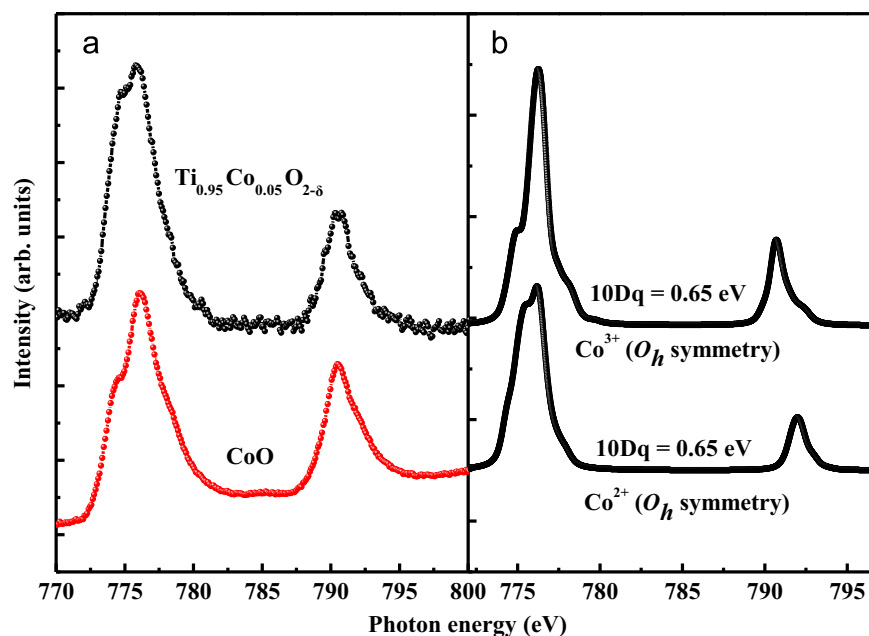


Fig. 4. (a) Co $L_{3,2}$ NEXAFS spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film along with the reference spectra of CoO. (b) Multiplet calculation spectra of Co $L_{3,2}$ -edge for Co^{2+} and Co^{3+} in O_h (octahedral) symmetry with 0.65 eV crystal field value.

clusters, Co oxide phase, whether it is substituting Co at Ti position in the TiO_2 film or not. The Co $L_{3,2}$ -edge spectral features result from the Co $2p \rightarrow 3d$ dipole transitions and are strongly influenced by the large $2p$ core-hole spin coupling energy, which divide the spectra into L_3 and L_2 regions at low and high photon energies, respectively. The Co L -edge spectra of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ do not match with the Ti L -edge spectra, which is to be expected due to the different electronic configurations of $\text{Co}^{2+}(d^7)$ and $\text{Ti}^{4+}(3d^0)$. Therefore, a simple spectral feature comparison with Ti spectra cannot determine whether Co dopants are substitutional in the rutile TiO_2 lattice. It can be seen from the Co $L_{3,2}$ -edge spectra that Co $L_{3,2}$ -edge spectra display fine structure at both L_3 and L_2 edges, in contrast to the L edge spectra of Co metal, where any fine structure at L_3 , and L_2 edges is absent. Furthermore, in order to clarify the valence state and site symmetry of Co ions in TiO_2 thin film, we have performed multiplet calculation and simulated Co $L_{3,2}$ -edge spectra for different valence states of Co ions in different symmetries (here results are shown only for octahedral symmetry). Fig. 4(b) shows the simulated spectra for Co^{2+} and Co^{3+} ions in octahedral symmetry with crystal field ($10 Dq$) value of 0.65 eV. The experimentally observed multiplet structure at Co $L_{3,2}$ - edge of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film clearly resembles with the simulated Co $L_{3,2}$ -edge spectra for Co^{2+} ions in O_h symmetry with 0.65 eV crystal field value. Also by looking at the Fig. 4(a), it is clear that the spectral feature of Co $L_{3,2}$ - edges in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film clearly matches with that of CoO, which indicate the absence of Co metal cluster. The theoretically simulated and experimentally observed Co $L_{3,2}$ -edge spectra clearly indicate that Co ion in $2+$ valence state.

Fig. 5 shows the XMCD spectrum of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film measured at room temperature. XMCD study was performed to know the intrinsic origin of ferromagnetism in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$

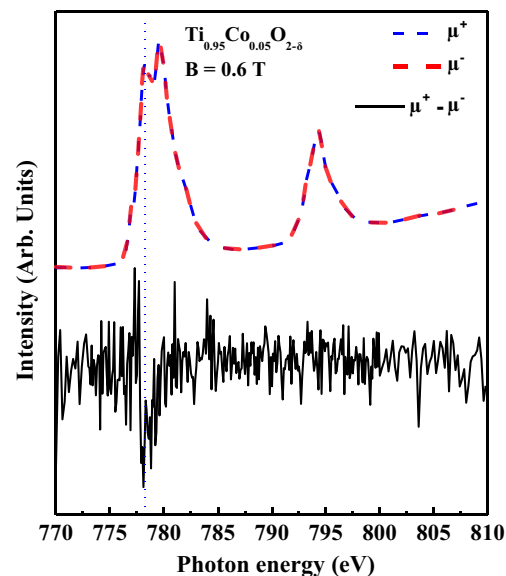


Fig. 5. X-ray magnetic circular dichroism spectrum at Co $L_{3,2}$ -edge for $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film.

film at room temperature. It is well known that the magnetization of the sample is proportional to the XMCD signal. The XMCD signal results from the difference between XAS spectrum recorded for the parallel (μ^+) and antiparallel (μ^-) alignment of the photon helicity with applied field. The XMCD ($\mu^+ - \mu^-$) signal with a negative sign at energy ($h\nu$) 778 eV confirms the intrinsic origin of ferromagnetism in the Co doped TiO_2 films. The XMCD signal observed at 778 eV indicated that ferromagnetism is due to Co^{2+} ion, which also confirms that Co ions are in $2+$ valence state in TiO_2 matrix.

Fig. 6 highlight the magnetic hysteresis loop (M - H) measurements of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film, measured at different temperatures.

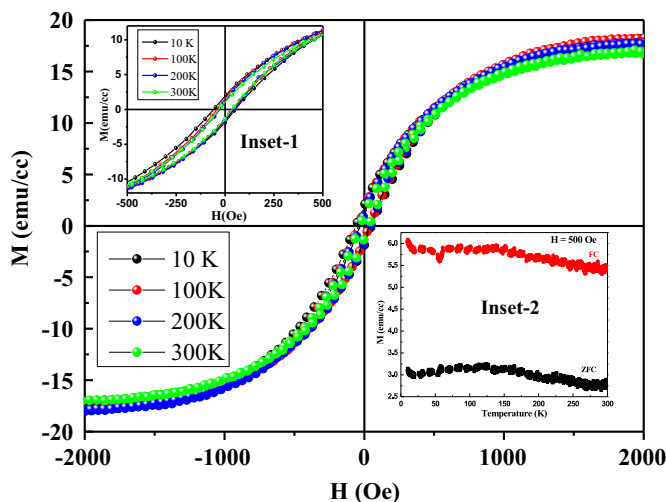


Fig. 6. Magnetic hysteresis curve of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin film measured at 300 K. Inset 1 shows magnetic hysteresis curve at low field and Inset 2 shows the zero field cooled and field cooled magnetization curve.

Notably, Inset-1 shows the low field M - H curve measured at different temperatures, which clearly shows that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film exhibits the ferromagnetic ordering at room temperature, which is analogous to the XMCD results. The saturation magnetization of the film was calculated using the M - H curve by extrapolation $M \rightarrow 1/H$ curve. The saturation magnetization values were found 20.0 emu/cc and 18.6 emu/cc at 10 K and 300 K, respectively. The coercive field observed from the M - H curve were 58 and 30 Oe at 10 K and 300 K respectively. Inset-2 shows the ZFC and FC magnetization of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film. In ZFC process, the film was cooled in absence of magnetic field from 350 K to 10 K and then magnetization was measured in presence of 500 Oe applied magnetic field from 10 K to 350 K. In FC process, however the film was cooled in presence of 500 Oe applied magnetic field from 350 K to 10 K and then magnetization measurement was performed in the presence of the same field during the warming up cycle from 10 K to 350 K. It can be clearly seen from the ZFC and FC curve that the transition temperature of the $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film is above room temperature. The ferromagnetism observed in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film is intrinsic and indicate that Co ions are occupying the Ti position in TiO_2 host matrix. Origin of ferromagnetism due to secondary phase such as Co metallic cluster or its oxide phase has been easily ruled out by the XRD, NEXAFS and XMCD results. The ferromagnetism observed in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film can be explained using bound magnetic polaron model (BMP). According to BMP model, the oxygen vacancies locally exist around magnetic ions i.e. Co ions substitute for Ti in TiO_2 matrix. The electrons trapped by the oxygen vacancies undergo orbital coupling with the d shells of the adjacent Co^{2+} ions and form the BMPs. In each BMP, the neighboring Co^{2+} cations create a spin-alignment of $\text{Co}^{2+}/\text{Co}^{2+}$ magnetic exchange coupling. When a large number of BMPs overlap, a continuous chain of $\text{Co}^{2+}/\text{Co}^{2+}$ magnetic exchange coupling is shaped, and ferromagnetic ordering in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film is established. A higher density of oxygen vacancies results in a greater overall volume being occupied by BMPs, thereby,

increasing the probability of overlapping more Co ions into the ferromagnetic domains, which will enhance the ferromagnetism.

4. Conclusions

We have successfully grown thin films of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ using PLD technique. XRD results infer that film has single phase nature. XMCD and magnetic hysteresis loop studies indicate that $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ film shows the RT-FM. ZFC and FC magnetization results infer that T_C is above room temperature. NEXAFS spectra measured at Ti $L_{3,2}$ - edge confirms that Ti ions are in 4+ valence state. Multiplet structure calculation done at Co $L_{3,2}$ -edge also support the experimentally Co $L_{3,2}$ -edge and confirms that Co ions are in 2+ valence state in $\text{Ti}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}$ thin films.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgments

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