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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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film is above room temperature. DC magnetization hysteresis loop study and XMCD measurement at Co $L_{3,2}$ -edge reflect that $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film exhibits ferromagnetic ordering at room temperature.

Keywords: C. Magnetic properties; Electronic material; Thin film; PLD; NEXAFS

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 mater 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 photo-catalyst, solar cell, gas sensors, optical waveguide in integrated optics, suitable template layers for growing high-T_C super-conducting films and electrical device etc. [6,7]. The 3*d* 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film has a single phase rutile structure and ruled out the presence of a secondary phase. DC magnetization and XMCD measurements show that $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film exhibits ferromagnetic ordering at room temperature.

2. Experiment

Thin film of $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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/cm^2. 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 (λ=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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 difftactometer. 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 $Ti_{0.95}Co_{0.05}O_{2-\delta}$ 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 2*p* 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 3*d* – O 2*p* hybridization and assigned to 3*d* 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 2*p* orbitals hybridized to Ti/Co 4*sp* 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