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Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmmX-ray absorption and magnetic circular dichroism characterization of Fe-doped $\text{TiO}_{2-\delta}$ thin filmsEnju Sakai^{a,*}, Kenta Amemiya^b, Akira Chikamatsu^a, Yasushi Hirose^{a,c}, Toshihiro Shimada^{a,c}, Tetsuya Hasegawa^{a,c}^a Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan^b Institute of Materials Structure Science, High Energy Accelerator Research Organization, Oho, Ibaraki 305-0801, Japan^c Kanagawa Academy of Science and Technology (KAST), Kawasaki 213-0012, Japan

ARTICLE INFO

Article history:

Received 12 September 2012

Available online 2 January 2013

Keywords:

Dilute magnetic semiconductor

X-ray absorption spectroscopy

X-ray magnetic circular dichroism

Thin film

ABSTRACT

We report x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements of both paramagnetic and ferromagnetic $\text{Ti}_{1-x}\text{Fe}_x\text{O}_{2-\delta}$ thin films. Fe $L_{3,2}$ edge XAS spectra showed that the Fe ions in our samples were in mixed valence states and that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreased with increasing oxygen partial pressure. Finite XMCD signals were observed only for the Fe^{2+} state in the ferromagnetic sample. These findings indicate that the observed ferromagnetism in $\text{Ti}_{1-x}\text{Fe}_x\text{O}_{2-\delta}$ originates from ferromagnetic interactions between Fe^{2+} local spins.

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1. Introduction

Since the discovery of transparent ferromagnetism in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$, transition-metal-doped TiO_2 has been extensively studied in order to establish diluted magnetic semiconductors (DMSs), which are indispensable for spintronics [1–5]. The detailed mechanism of the ferromagnetic ordering, however, remains controversial [6]. Empirically, conducting samples prepared under relatively reducing atmospheres tend to exhibit ferromagnetism. Recent experimental results actually confirmed that metallic electronic state is indispensable for the emergence of the ferromagnetism [7] and the ferromagnetism can be controlled by carrier injection [8]. These seem to favor a p – d exchange model, in which free carriers in the oxygen $2p$ -nature conduction band interact with the localized d states of transition metal dopants, as originally postulated in conventional DMSs with hole carriers [9]. However, several groups have reported that ferromagnetism can appear even in highly insulating samples [4,10], strongly suggesting that a simple carrier-mediated mechanism is not applicable to TiO_2 -based DMS, and that oxygen vacancies introduced during sample preparation or post-annealing play a significant role in the ferromagnetic ordering of the $3d$ local spins [11,12]. Recently, we reported that Fe-doped TiO_2 films also exhibit room temperature ferromagnetism, but only in samples deposited under reducing conditions. Notably, free carriers introduced by Nb doping did not induce

ferromagnetic ordering [5]. This implies that oxygen vacancies rather than free electrons are indispensable for the ferromagnetism of Fe-doped TiO_2 . Therefore, magnetic interaction between oxygen vacancies and local $3d$ moments is a key to room temperature ferromagnetism in transition-metal-doped TiO_2 , as pointed out by several groups [10,13], and such interactions may be very sensitive to the valence state of the $3d$ ions.

In this paper, we report x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements of ferromagnetic and paramagnetic Fe-doped $\text{TiO}_{2-\delta}$ films. XMCD is a powerful tool in investigating the origins of ferromagnetism, because of its element-specific and valence-orbit-selective nature [14–17]. The Fe L_3 and L_2 edge XAS spectra contained two characteristic peaks, which were attributable to Fe^{2+} and Fe^{3+} states, respectively. A comparison of the intensity ratio of these two peaks with those of Fe^{2+} and Fe^{3+} reference materials indicated that the Fe ions in our samples were in mixed valence states. XMCD signals were observed only for the Fe^{2+} peaks of a ferromagnetic sample, indicating that the ferromagnetic interaction between Fe^{2+} local spins plays an essential role in Fe-doped $\text{TiO}_{2-\delta}$. To interpret the magnetism of Fe-doped TiO_2 as influenced by Fe valence, we propose a model in which Fe ions are coupled with oxygen vacancies to satisfy local charge neutrality.

2. Experimental details

Fe-doped anatase $\text{TiO}_{2-\delta}$ films were deposited on LaAlO_3 (100) substrates at 600 °C by pulsed laser deposition using a sintered target ($\text{Fe}_{0.06}\text{Ti}_{0.94}\text{O}_2$). The concentration of oxygen vacancies in

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the films was varied by controlling the oxygen partial pressure P_{O_2} during deposition. X-ray diffraction measurements confirmed that the obtained Fe-doped $Ti_{1-x}Fe_xO_{2-\delta}$ films had an anatase structure, with a (004) orientation. The magnetic properties of the films were characterized by a superconducting quantum interference device (SQUID) magnetometer and a magneto-optical Kerr effect (MOKE) spectrometer. A clear insulator-to-metal transition was observed concurrently with ferromagnetic ordering between $P_{O_2} = 2 \times 10^{-6}$ and 3×10^{-6} Torr. The intrinsic nature of the observed ferromagnetism was confirmed by anomalous Hall effect measurements [5]. Details on the transport and magnetic properties of our samples were described elsewhere [5]. All XAS and XMCD experiments were performed at BL-7A at the Photon Factory, Institute of Materials Structure Science (KEK-PF), Japan. In the XAS and XMCD measurements, the incident x-rays and the applied magnetic field were normal to the sample surface. All spectra were measured at room temperature, with a base pressure below 1×10^{-9} Torr in total electron yield mode. XMCD spectra were taken for a fixed helicity of light by reversing the applied magnetic field of 0.1 T. A relatively weak magnetic field of 0.1 T was employed to minimize the signal from the paramagnetic contribution of the samples [18–21].

3. Results and discussion

Fig. 1 shows $M-H$ curves of samples deposited under different P_{O_2} , clearly indicating a paramagnetic-to-ferromagnetic transition between $P_{O_2} = 2 \times 10^{-6}$ and 1×10^{-6} Torr. We also observed a metal-to-insulator transition simultaneous to the ferromagnetic ordering. The negligibly small magnetization of ≤ 3.2 emu/cm³ observed in a sample prepared at $P_{O_2} \geq 2 \times 10^{-6}$ Torr may have been due to contaminants on the reverse side of the substrate [6,22]. Indeed, we have confirmed that the paramagnetic samples did not show a finite Kerr rotation. Furthermore, $LaAlO_3$ substrates that were heat-treated at 600 °C in the PLD chamber generated weak ferromagnetic signals, as shown in the inset of

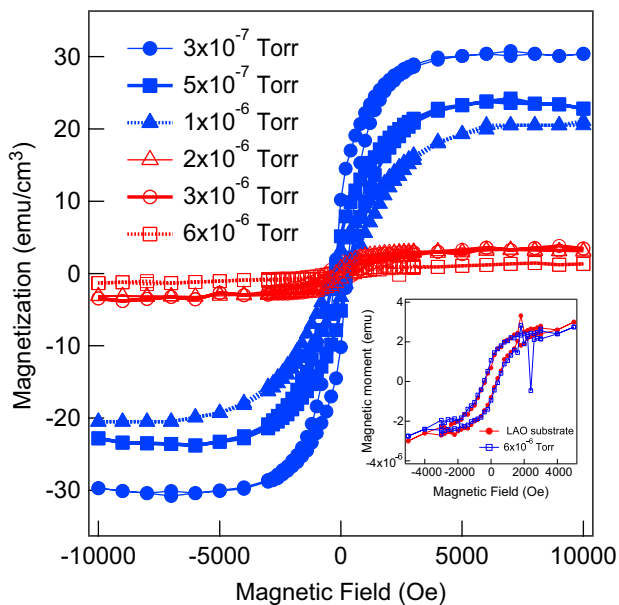


Fig. 1. $M-H$ loops of $Ti_{1-x}Fe_xO_{2-\delta}$ films at 300 K. The inset shows a comparison of raw magnetic moment data between $Ti_{1-x}Fe_xO_{2-\delta}$ films and an $LaAlO_3$ substrate. The substrate was mounted on a sample holder using Ag paint and annealed under UHV (below 3×10^{-8} Torr) before the measurements. The data were corrected by subtracting the diamagnetic component of the $LaAlO_3$ substrate.

Fig. 1, which were comparable to those of paramagnetic samples deposited under $P_{O_2} = 6 \times 10^{-6}$ Torr.

Fig. 2 compares Fe L edge spectra of ferromagnetic ($P_{O_2} = 5 \times 10^{-7}$, 1×10^{-6} Torr) and paramagnetic ($P_{O_2} = 3 \times 10^{-6}$ Torr) samples. The figure also includes a spectrum of Fe_2O_3 as a reference oxide with trivalent Fe. The observed spectra can be separated into two regions, the L_3 edge (705–15 eV) and the L_2 edge (715–30 eV), due to core–hole spin orbit interaction. The L_3 and L_2 edges were composed of two peaks each, with different intensities: a (~ 707 eV) and b (~ 709 eV) for L_3 and c (~ 720 eV) and d (~ 722.5 eV) for L_2 . This split in the Fe L_3 and L_2 edges is usually attributed to a mixed valence of Fe^{2+} and Fe^{3+} [23–28]. In the following discussion, we will focus on the L_3 edge. Fe^{3+} ions in an octahedral crystal field exhibit a main peak at ~ 709 eV with a weak peak or a shoulder structure on the lower energy side (~ 707 eV) [25,29]. The Fe L_3 edge spectrum of Fe_2O_3 obtained in our experiment also exhibited these features. In contrast, the intensities of the two peaks were reversed for Fe^{2+} : the main peak was located at 707 eV with a faint structure around 709 eV [24,25,28,29]. Therefore, the intensity ratio of the 707 eV and 709 eV peaks, corresponding to peaks a and b, respectively, is an indicator of the Fe valence state. As can be seen in Fig. 2, the intensity ratio $r_{ab} = I_b/I_a$ decreased with increasing P_{O_2} , indicating that the Fe^{2+}/Fe^{3+} ratio decreased with increasing P_{O_2} . It is difficult to distinguish metallic Fe from Fe^{2+} on the basis of the peak positions in XAS, because they are close to each other [29]. However, they are distinguishable from the branching ratio I_{L_3}/I_{L_2} of the XAS spectrum: the I_{L_3}/I_{L_2} value of metallic iron is known to be ~ 2 , while FeO has a value of $I_{L_3}/I_{L_2} \sim 3$ [29]. The branching ratio of the $Ti_{1-x}Fe_xO_{2-\delta}$ sample deposited under $P_{O_2} = 5 \times 10^{-7}$ Torr was estimated to be 3, as shown in Fig. 3, indicating that most of the Fe ions in the sample were divalent with octahedral symmetry. In fact, the peak shape was almost identical to that of FeO [27,29]. Therefore, metallic iron did not precipitate in our samples.

Fig. 3 shows μ^+ and μ^- XAS and the corresponding XMCD ($\mu^+ - \mu^-$) spectra, where μ^+ (μ^-) refers to the absorption

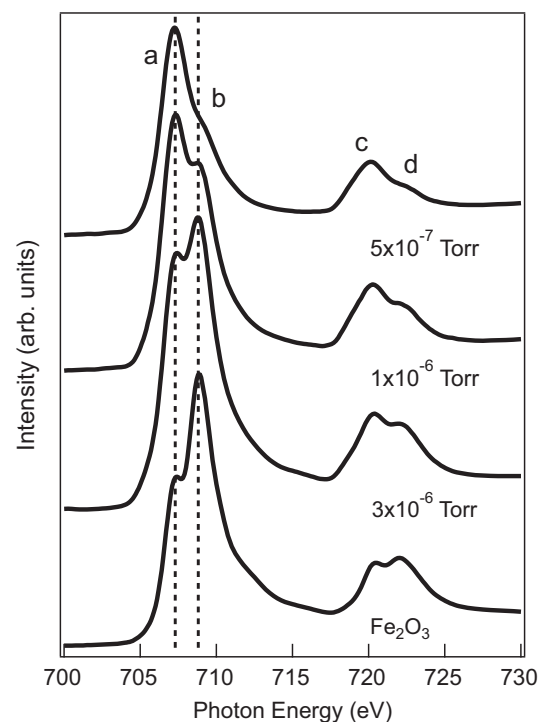


Fig. 2. Fe $L_{2,3}$ edge XAS spectra of anatase $Fe_xTi_{1-x}O_{2-\delta}$ prepared at various P_{O_2} and of the Fe_2O_3 powder.

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