Ferromagnetism in Co-doped Anatase TiO_2 Thin Films

Since a recent discovery of ferromagnetism in III-V based diluted ferromagnetic semiconductors (DMS's) such as $Ga_{1-x}Mn_xAs$, the ferromagnetic DMS have become a hot field because of the possible technological applications utilizing both semiconductor physics and the ferromagnetism, the so-called "spintronics". However most of the Curie temperatures have been reported to be much lower (T_C < 100 K) than the room temperature. Meanwhile, oxide-based DMS's have buoyed up as a candidate of room temperature DMS's. Indeed, Co-doped and Fe-doped ZnO films were reported to show ferromagnetism with T_C ~ 300 K and well above 300 K, respectively. However, it is still questionable whether the ferromagnetism is truly come from the DMS.

Very recently, cobalt doped anatase titanium dioxide, $Ti_{1-x}Co_xO_2$, thin films were reported to be ferromagnetic even above 400 K. The ordered magnetic moment was estimated to be 0.32 μ_B/Co, and the ferromagnetic ordering was explained in terms of the carrier-induced ferromagnetism as in the III-V based DMS. The ferromagnetism of $Ti_{1-x}Co_xO_2$ was reproduced by Chambers *et al.* They reported that the ordered moment is as high as 1.25 (μ_B/Co, and claimed that the ferromagnetism strongly depends on the oxygen deficiency. These results seem to show that the ferromagnetism in $Ti_{1-x}Co_xO_2$ is originated from the ordered low spin Co^{2+} state due to the charge carriers induced by oxygen defects. However, considering the facts that the ferromagnetism strongly depends on the growth condition, the possibility of the Co segregation cannot be excluded completely in this system. Furthermore, it was reported that nano-size defects can be easily created in the anatase TiO_2. Therefore it is important to clarify the origin of ferromagnetism in the oxide based high T_C DMS.

In this article, we report the X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (MCD) results at the Co $L_{2,3}$-edges to clarify the ferromagnetic origin of Co-doped anatase TiO_2 thin films on $LaAlO_3$ (100) substrates. In the study, we have found that in the epitaxially grown $Ti_{1-x}Co_xO$ films, the Co state is a divalent high spin ionic state, $Co^{2+}(3d^7; S = 3/2)$, as in CoO, indicating that the doped Co ions could be well substituted for the Ti sites. However we observed a very small MCD signal at the Co $L_{2,3}$-edges, which corresponds to ~ 0.1 μ_B/Co, and the MCD line shape is nearly identical to that of Co-metal, suggesting that the magnetic origin should be small amount of clustered Co. Furthermore, after thermal treatments at ~ 400 ℃, the MCD signal becomes greatly enhanced, and the moment reaches up to ~ 1.55 μ_B/Co, which corresponds to about 90% of the magnetic moment observed in Co-metal. The field-emitted scanning electron microscope (FE-SEM) image of the post-annealed 10% Co-doped sample shows that Co-clusters were formed randomly in the entire sample with 20 ~ 60 nm in size. These results manifest that the ferromagnetism in the Co-doped anatase TiO_2 is induced by the Co-clustering.

40 nm thick anatase $Ti_{1-x}Co_xO_2$ (x = 0.04, 0.07, 0.10) films were grown on $LaAlO_3$ (001) substrates with laser molecular beam epitaxy (MBE). Each $Ti_{1-x}Co_xO_2$ ceramic target was ablated with a KrF pulsed laser with 2 W/cm^2. The substrate temperature and the oxygen partial pressure during the growth were maintained at 650 ℃ and 10^{-5} ~ 10^{-6} Torr, respectively. The growth rates were less than 1 Å/min the growing surfaces were monitored in-situ with the reflection high energy electron diffraction (RHEED). The structural properties of the films were confirmed by *in-situ* RHEED and *ex-situ* X-ray diffraction (XRD). Fig. 1 shows the RHEED intensity oscillations of the specular spot during the growth of a $Ti_{0.93}Co_{0.07}O_2$ film. After deposition of about 1 unit cell, which corresponds to 4 TiO_2 monolayers, a clear oscillation became observed, indicating that the film was grown epitaxially in the layer-by-layer growth mode. The clear and streaky RHEED

pattern in the inset of Fig.1 confirms that the film be in the anatase phase and has a very flat surface.

In order to check the Co-state, we performed Co $L_{2,3}$-edge XAS measurements on $Ti_{1-x}Co_xO_2$ (x = 0.04, 0.07, 0.10) thin films with 0.3 eV energy resolution and linear polarization for the incident photon. The base pressure during the measurements was below 1×10^{-9} Torr and the sample temperature was maintained at 300 K. The XAS spectra are presented in Fig. 2, in comparison with the reference spectrum of CoO, which was measured at the same conditions. The XAS spectra, which result from the Co $2p \rightarrow 3d$ dipole transitions, are dominated by the large $2p$ core-hole spin-orbit coupling energy dividing the spectra into roughly the L_3 and L_2 regions at low and high photon energies, respectively. As shown in the figure, the XAS spectra are nearly identical for different x-values, and display a characteristic multiplet structure. In comparison with the spectrum of CoO, one can recognize that the XAS spectra of $Ti_{1-x}Co_xO_2$ are very similar to that of CoO. The absorption white line locates at exactly the same energy and the overall multiplet structure is very similar except minor differences in the relative intensities of the multiplet states at the L_3-edge, which are probably due to a small tetragonal distortion of the CoO_6 octahedron in the anatase structure. The whiteline energy and the multiplet structure represent the valence and the ionic ground state symmetry, respectively. Therefore,

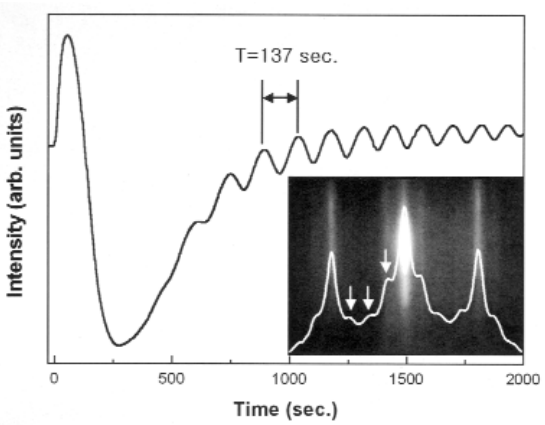

Fig. 1: RHEED oscillations during the deposition. The one oscillation corresponds to growth of the 1/4 unit cell. The inset shows the RHEED pattern and corresponding intensity line-profile. A weak (4×1) surface reconstruction pattern consisting of three additional lines (marked by three arrows in the intensity line-profile) can be clearly seen.

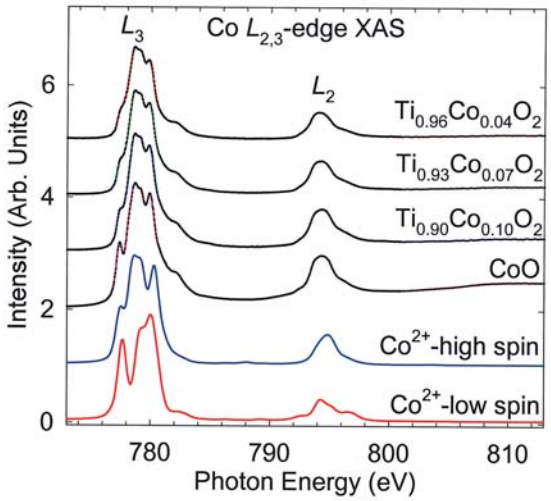

Fig. 2: Co $L_{2,3}$-edge XAS spectra of $Ti_{1-x}Co_xO_2$ (x = 0.04, 0.07, 0.10) in comparison with that of CoO and theoretical calculation spectra for a high spin Co^{2+} ($3d^7$; S = 3/2) and a low spin Co^{2+} ($3d^7$; S = 1/2) states under Oh symmetry.

we can confidently conclude that the ionic ground state of doped Co in $Ti_{1-x}Co_xO_2$ is the high spin divalent state, i.e. Co^{2+} ($3d^7$; S = 3/2), as in CoO. For further confirmation, theoretical multiplet model calculations were carried out for the XAS spectra for a high spin Co^{2+} (S = 3/2) and a low spin Co^{2+} (S = 1/2) ground states under O_h-symmetry. As shown in the figure, the spectra of $Ti_{1-x}Co_xO_2$ and CoO are generally well reproduced by the theoretical calculations for the high spin Co^{2+}. These results show that the Co-state in $Ti_{1-x}Co_xO_2$ is a Co-oxide state with the high spin Co^{2+} as in CoO, different from the previous interpretation of the low spin Co^{2+}.

Figure 3 shows the XAS and X-ray absorption magnetic circular dichroism (XMCD) spectra at the Co $L_{2,3}$-edges of $Ti_{0.90}Co_{0.10}O_2$ for different annealing times. The samples were annealed at ~ 400 ℃ under 10^{-6} Torr O_2, which is relatively lower than the growth temperature (i.e. 650 ℃ under 10^{-6} Torr O_2). For the XMCD measurements, the degree of circular polarization of the incident light was set to be 0.85, and a 0.6 T magnetic field produced by an electromagnet was applied along the surface normal of the sample to align the spin moment. In order to minimize the artificial effects caused by decrease of the photon flux with time, the spin direction was flipped to be parallel (ρ_+) and anti-parallel (ρ_-) to the photon helicity vector at each data point. The spectra for

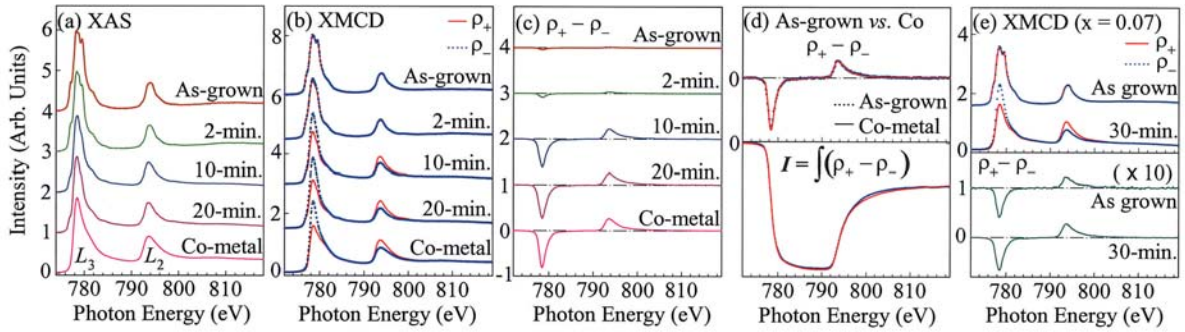

Fig. 3: XMCD spectra of $Ti_{1-x}Co_xO_2$ for the different post-annealing times T_A = 0 (As-grown), 2, 10, and 20-minutes in comparison with those of Co-metal. (a) Co $L_{2,3}$-edge XAS spectra , (b) Co $L_{2,3}$-edge XMCD spectra, and (c) MCD-signal; $\rho_+ - \rho_-$ of the x = 0.10 sample, (d) comparison of MCD signals and their integrations for the as-grown $Ti_{0.90}Co_{0.10}O_2$ and Co-metal, and (e) XMCD results of the x = 0.07 sample.

the different spin directions (ρ_+ and ρ_-), which were normalized by the photon flux, and the dichroism spectra ($\rho_+ - \rho_-$) are presented in the figure, where the degree of circular polarization was taken into account.

One can recognize that the ionic multiplet structure of the Co *L*-edge XAS spectrum is continuously smeared out with increase of the annealing time, T_A. After 20-min. annealing, the spectral line shape rather resembles that of Co-metal. As shown in Fig. 3(c), the very weak MCD signal observed in the as-grown film greatly increases with the annealing time, without any significant change in the MCD line shape. In comparison of the MCD spectrum ($\rho_+ - \rho_-$) and its integration (I) of the as-grown $Ti_{0.90}Co_{0.10}O_2$ with those of Co-metal, Fig. 3(d) shows nearly identical line shapes for both, showing that the magnetic origin of $Ti_{0.90}Co_{0.10}O_2$ is the same as Co-metal. The intensity of the magnetic signal is estimated to be about 6% (~ 0.1 μ_B /Co), 11% (~ 0.2 μ_B /Co), 75% (~ 1.3 μ_B/Co), and 90% (~ 1.55 μ_B/Co) of that of Co-metal (1.72 μ_B /Co) for T_A = 0, 2, 10, and 20-minitues, respectively. These results clearly show that the ferromagnetism in the Co-doped anatase TiO_2 is originated from clustered Co-metal, rather than the ionic oxide Co, and the amount of clustered Co-metal in an as-grown sample increases greatly with the post-annealing. Such behaviors were also observed in the 4% and 7% Co doped samples and Fig. 3(e) presents the results obtained from the 7% sample. Hence, the amount of clustered Co is expected to depend on the growth condition, and the observed strong dependence of the ordered moment on the growth condition is somehow natural in the Co-doped anatase TiO_2. In general, Co-metal surface is easily oxidized even in a low O_2-partial pressure (below 10^{-6} Torr) environment, and thus the Co clustering is somewhat striking in the oxide-based material. However, the anatase TiO_2, which is well known to be a catalyst, yields nano-size defects so easily, and it seems to offer a room for the Co clustering.

As discussed above, the post-annealing greatly accelerates the Co-clustering in Co doped anatase TiO_2 systems, and the ordered moment reaches up to ~ 1.55 (μ_B/Co, indicating that the sizes of the Co clusters become considerably large. Figure 4 shows the *ex-situ* field-emitted scanning electron microscope (FE-SEM) pictures of the $Ti_{1-x}Co_xO_2$ (x = 0.00, 0.10) after the 20-min. post-annealing. The picture of the x = 0.00 sample shows just dark back-ground due to the insulating character, while that of the x = 0.10 sample clearly shows small islands of the clustered Co, which are almost randomly distributed in the entire range. The metallic character of Co makes the image quite outstanding. The size of the Co-island ranges from 20 nm to 60 nm.

Figure 5 shows the magnetic hysteresis (*M vs H*) curves, which were obtained from the XMCD intensity at the Co L_3- white line, of the 20 min. post-annealed $Ti_{1-x}Co_xO_2$ (x = 0.04, 0.07, 0.10) films at ~ 400 ℃ under 10^{-6} Torr O_2. For all three samples, there is not much difference in the *M vs H* for the applied magnetic field in the plane and along the surface normal, indicating no considerable magnetic anisotropy of these systems. However, the magnetic coercivity

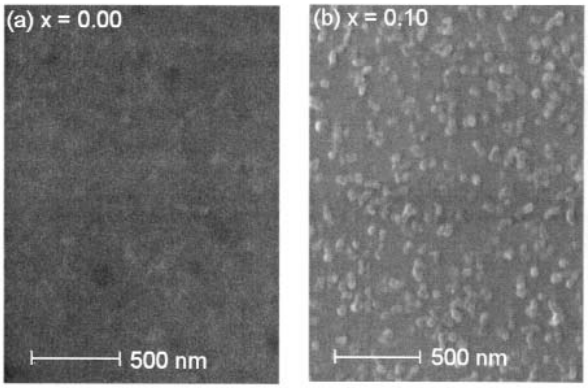

Fig. 4: FE-SEM images of anatase (a) TiO_2 and (b) $Ti_{0.90}Co_{0.10}O_2$ after the post-annealing.

increases with the amount of Co. The coercive fields are estimated to be about 150 Oe, 250 Oe, and 400 Oe for x = 0.04, 0.07, and 0.10, respectively. At this moment, we are not sure whether the coercive field results from that of each island or from the magnetic correlation between islands. In order to clarify its origin, more comprehensive studies are required.

In conclusion, we have investigated the origin of ferromagnetism observed in Co doped anatase TiO_2 films using the X-ray magnetic circular dichroism at the Co $L_{2,3}$-edges. The substituted Co has a high spin Co^{2+} as in CoO, but the magnetic signal, which contributes to ~ 0.1 μ_B/Co in average, was found to be identical to that of Co-metal, showing that the magnetic origin is a partial amount of clustered Co. The magnetic signal was enhanced greatly with thermal treatments, and the magnetic moment reached up to ~ 1.55 μ_B/Co, which corresponds to about 90% of the moment in Co-metal, indicating that most of Co becomes clustered during the post-annealing process. The Co clusters, which have sizes in a range of 20 nm to 60 nm, are distributed randomly in the entire surface region.

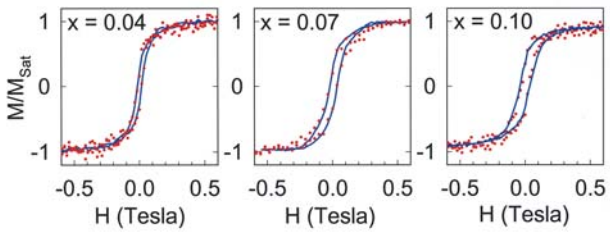

Fig. 5: In-plane (dotted lines) and along the surface normal (solid lines) magnetic hystersis curves of anatase $Ti_{1-x}Co_xO_2$ (x = 0.04, 0.07, 0.10) after the post-annealing. The in-plane and along the surface normal hysteresis curves were obtained from XMCD by using fluorescence and total electron yield measurements, respectively.

Beamline:

11A1 Dragon beamline

Experimental Station:

MCD chamber

Authors:

J.-Y. Kim

Pohang Acceleration Laboratory, Pohang University of Science and Technology, Pohang, Korea

J.-H. Park and B.-G. Park

Department of Physics, Pohang University of Science and Technology, Pohang, Korea

H.-J. Noh, S.-J. Oh, J. S. Yang, D.-H. Kim, S. D. Bu, and T.-W. Noh

School of Physics, Seoul National University, Seoul, Korea

H.-J. Lin, H. H. Hsieh, and C. T. Chen

National Synchrotron Radiation Research Center, Hsinchu, Taiwan

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