Discovery of suboxidic coordinate in high-T_C ferromagnetic semiconductor Co-doped TiO_2

High-Curie-temperature diluted ferromagnetic semiconductors (high-T_C DFSs) are strongly desired for the room-temperature operation of semiconductor spintronic devices. Among them, high-T_C DFS oxides have been intensively studied since the discovery of room-temperature ferromagnetism in Co-doped TiO_2 in 2001 [1]. The T_C of Co-doped TiO_2, ~600 K, is extraordinarily high considering the conventional carrier-mediated ferromagnetism seen in GaMnAs (~200 K). However, the microscopic origin of the high-T_C ferromagnetism has remained a mystery for a long time.

X-ray fluorescence holography (XFH) is a powerful tool for resolving a local structure, enabling a 3D atomic environment to be visualized around a selected element within a radius of nanometer orders without assuming any prior models [2]. To date, the advantageousness of XFH has been demonstrated for the evaluation of local lattice distortions around specified elements [3] and for the detection of nanocluster-like structures [4]. In this work, we experimentally determined local structures around the Co atoms in paramagnetic and ferromagnetic rutile Co-doped TiO_2 films by measuring XFH holograms. In addition, first-principles calculations based on density functional theory were carried out to evaluate the validity of the structure model obtained by XFH. In the ferromagnetic Co-doped TiO_2 film, suboxidic coordination around Co embedded in the rutile structure was observed. This suboxidic coordination may generate a ferromagnetic embryo leading to the strong exchange interaction realizing the high-T_C in Co-doped TiO_2 [5].

Two rutile $Ti_{1-x}Co_xO_2$ films with $x = 0.01$ and 0.05 were used, where the former and latter are paramagnetic and ferromagnetic, respectively. The XFH experiment was carried out at beamline **BL39XU**, and XAFS measurements were performed at beamline **BL22XU**. XFH data were recorded at incident X-ray energies of 8.0–12.0 keV in 0.5 keV steps by measuring Co Kα fluorescence (6.9 keV) intensity variation as a function of the incident beam direction. Figure 1(a) shows the hologram pattern of the $Ti_{0.95}Co_{0.05}O_2$ taken at 8.0 keV. The hologram data were symmetrized using the mirror symmetry of rutile TiO_2 (101) and then extended using the rotoreflection symmetry as shown in Fig. 1(b). Such data manipulation is important for providing accurate and high-resolution atomic images. The 3D atomic arrangements around the fluorescent element Co were reconstructed from multiple-energy holograms using Barton's algorithm [6].

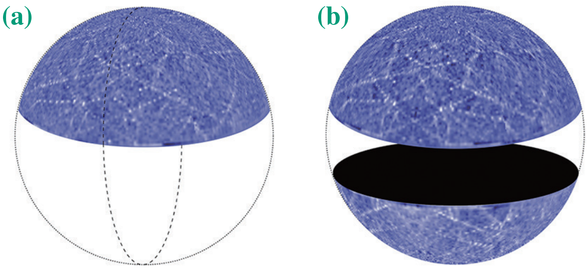

Fig. 1. Co holograms of $Ti_{0.95}Co_{0.05}O_2$ film. **(a)** Raw data and **(b)** symmetrized data. In (b), the data are mirror-symmetrized with respect to the dashed circle and then rotoreflection-symmetrized with respect to the (100) plane.

The 3D atomic images of $Ti_{0.99}Co_{0.01}O_2$ and $Ti_{0.95}Co_{0.05}O_2$ are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(a), the reconstructed 3D atomic images are superposed on the ideal Ti atomic positions of the rutile TiO_2, as marked by open circles, while the images of O atoms are hardly visible owing to their low scattering powers. Since the rutile structure, which shows in Fig. 2(c), is most stable form of TiO_2, the visible images are contributed to Ti atoms. Therefore, the Co atoms in the paramagnetic $Ti_{0.99}Co_{0.01}O_2$ substituted for Ti atoms without a large lattice distortion from the rutile structure. In contrast, the 3D atomic images in Fig. 2(b) are markedly different from the rutile structure. The surrounding atomic arrangement exhibits fourfold symmetry with respect to the normal to the rutile (101) plane (z-axis). Taking into account the very low visibility of O atoms, we can assume that the O atoms are located just above and below the Co atom along the z-axis, as denoted by dashed circles (Fig. 2(d)), corresponding to CoO_2Ti_4 coordination as discussed below.

To confirm the validity of our structure models in Figs. 2(c) and 2(d), we measured the Co K-edge XAFS spectra and calculated the XAFS spectra using the structure models and FEFF. The XAFS spectrum of the $Ti_{0.99}Co_{0.01}O_2$ agrees with that calculated using the rutile structure in Fig. 2(c). The spectrum of the $Ti_{0.95}Co_{0.05}O_2$ was calculated using the structure model in Fig. 2(d). The CoO_2Ti_4 and CoO_2Co_4 structure models were used for the calculation and their XAFS spectra were compared. The CoO_2Ti_4 structure model more closely reproduces the experimental spectrum of the $Ti_{0.95}Co_{0.05}O_2$ film.

To evaluate the stability of the suboxide cluster in the host rutile TiO_2, we carried out a series of first-principles calculations using the VASP code with the HSE06 hybrid functional for several possible atomic configurations. As the first step, to represent an isolated cluster model, the single CoO_2Ti_4+(Ti_8) cluster depicted in Fig. 2(d) was embedded in the rutile supercell structure while keeping the nearest Ti atoms trivalent. The cluster soon changed into an arrangement similar to that of the rutile crystal during the structure optimization process. This result indicates that an isolated CoO_2Ti_4 cluster is very unstable, also supporting the absence of the suboxide cluster in the low Co-doped film. Next, we aligned two CoO_2Ti_4 clusters in the rutile supercell structure ($Co_2O_{64}Ti_{34}$), as shown in Fig. 3(a), with an initial configuration where the O atoms are located above and below the Co atom orthogonal to the cluster alignment, and we obtained the structure in Fig. 3(b) by structure optimization. This structure preserves the original arrangement surrounding the CoO_2Ti_4 cluster, reproducing the XFH result in Fig. 2(b).

In conclusion, the presence of suboxide coordination in rutile $Ti_{0.95}Co_{0.05}O_2$ was revealed by the XFH and XAFS measurements. Possible atomic configurations of the suboxide network were investigated by first-principles calculation, which justified the reason why the clusters appear only at a high Co concentration. Furthermore, the suboxide network might be the source of the strong exchange interaction leading to the high T_C in Co-doped TiO_2.

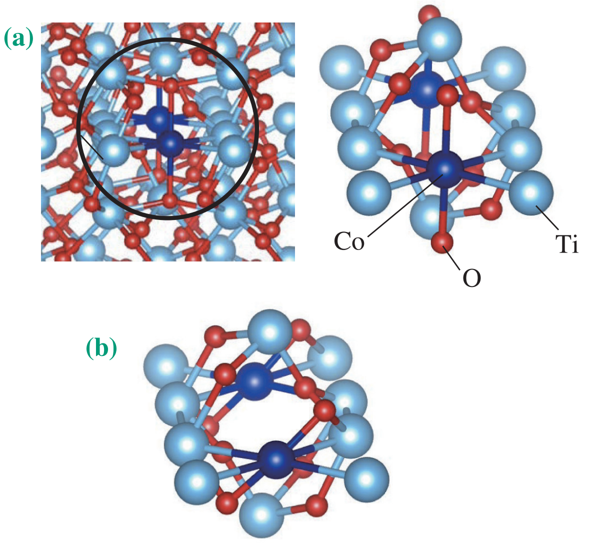

Fig. 3. Possible structures of the suboxide cluster embedded in rutile TiO_2. The structures were obtained by structure optimization based on a first-principles calculation. **(a)** Two aligned suboxide clusters embedded in rutile TiO_2. **(b)** Fully relaxed clusters.

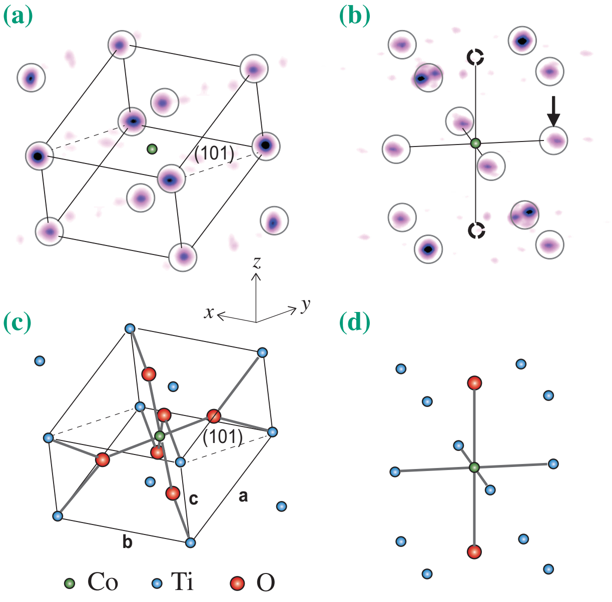

Fig. 2. Reconstructed real-space images around Co in **(a)** $Ti_{0.09}Co_{0.01}O_2$ and **(b)** $Ti_{0.95}Co_{0.05}O_2$ films. **(c)** and **(d)** Structure models obtained from the images in (a) and (b), respectively.

Wen Hu[a], Kouichi Hayashi[b,*] and Tomoteru Fukumura[c]

[a] National Synchrotron Light Source II,
Brookhaven National Laboratory, USA
[b] Department of Physical Science and Technology,
Nagoya Institute of Technology
[c] Department of Chemistry, Tohoku University

*E-mail: khayashi@nitech.ac.jp

References

[1] Y. Matsumoto *et al*.: Science **291** (2001) 854.
[2] K. Hayashi *et al*.: J. Phys.: Condens. Matter **24** (2012) 093201.
[3] W. Hu *et al*.: Phys. Rev. B **89** (2014) 140103(R).
[4] W. Hu *et al*.: Phys. Rev. B **80** (2009) 060202(R).
[5] *W. Hu, K. Hayashi, T. Fukumura, K. Akagi, M. Tsukada, N. Happo, S. Hosokawa, K. Ohwada, M. Takahasi, M. Suzuki and M. Kawasaki: App. Phys. Lett.* ***106*** *(2015) 222403.*
[6] J.J. Barton: Phys. Rev. Lett. **67** (1991) 3106.