11A/2007G685

Cobalt charge states in cobalt doped anatase titanium dioxide thin films

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Introduction

Cobalt doped anatase titanium dioxide (Co:TiO_2) has attracted much attention as an oxide ferromagnetic diluted magnetic semiconductor (DMS). Because the Curie temperature of Co:TiO_2 is much higher than room temperature, Co:TiO_2 has been expected as a promising material for spintronics devices which can work at room temperature. However, absolute proof of its DMS nature is very difficult and the origin of its ferromagnetism is still under discussion.

In order to investigate the origin of ferromagnetism of Co:TiO_2, it is necessary to clarify charge states of cobalt atoms. Thus, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were carried out for Co:TiO_2 films.

Experiments

Co:TiO_2 films with thickness 31 nm were prepared using pulsed laser deposition (PLD) method. Target pellets used were TiO_2 and $Co_{0.05}Ti_{0.95}O_2$. $LaAlSrO_4$ (LSAO) (001) single crystals were used as substrates. In the fabrication process, first, pure TiO_2 seed layer was deposited onto each LSAO substrate having temperature (T_s) of 650 °C at oxygen partial pressure (P_{O2}) of 5×10^{-3} Torr. Then, each sample was cooled to 300 °C and Co:TiO_2 was deposited onto the seed layer at various P_{O2} (5×10^{-7}, 1.0×10^{-6} and 1.0×10^{-4} Torr). XRD measurements confirmed the growth of (001)-oriented anatase TiO_2 without any impurity phases.

The magneto-optical and transport properties of the prepared samples were measured by magneto-optical Faraday effect and Hall effect, respectively. The charge states and relative concentration of cobalt atoms in the samples were measured by XAS and XMCD at BL-11A of the Photon Factory, KEK.

Results and Discussion

Magneto-optical Faraday effect measurements revealed that samples prepared at P_{O2} = 5×10^{-7} and 1.0×10^{-6} Torr were ferromagnets. Anomalous Hall effects were also observed in these two ferromagnetic samples. The sample prepared at P_{O2} = 1.0×10^{-4} Torr was, however, paramagnet. Figure 1 shows cobalt *L*-edge XAS spectra of these three samples. The shapes of the spectra are similar to that of previously reported metallic cobalt spectrum[1, 2]. This suggests that small clusters of cobalt metal exist in our Co:TiO_2 films and the ferromagnetism of our Co:TiO_2 films is induced by these clusters. XAS spectra also revealed that the cobalt concentration in the samples depend on P_{O2}. This suggests that cobalt atoms are hardly taken into the TiO_2 films at low P_{O2}. And cobalt concentrations of ferromagnetic samples were far less than 5at.%. XMCD measurements were carried out for all samples, but no clear XMCD signal was observed. This may be due to the low cobalt concentration in samples.

Conclusion

The XAS measurements showed that cobalt exists in the form of metal clusters in both ferromagnetic and paramagnetic Co:TiO_2 films. Cobalt concentration in the target was 5at%, but that of our Co:TiO_2 films decreased with decrease of P_{O2}. It is probable that these cobalt clusters are the origin of ferromagnetism, observed as magneto-optical Faraday effects and anomalous Hall effects, in our Co:TiO_2 films.

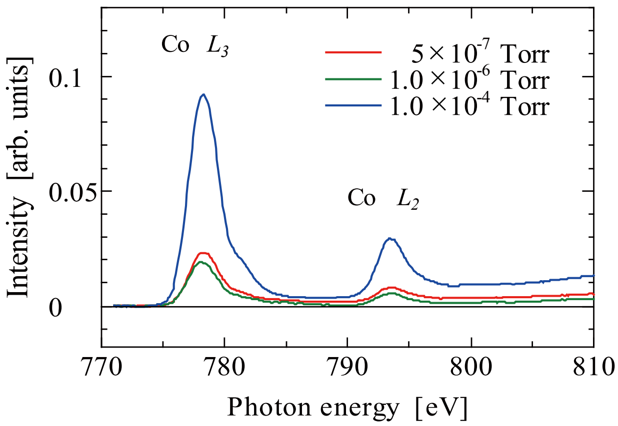

Figure 1
XAS spectra of Co:TiO_2 fabricated with various P_{O2}.

References

[1] J.-Y. Kim. et al., Phys. Rev. Lett. 90, 017401 (2008).
[2] K. Mamiya et al., Phys. Rev. Lett. 89, 062506 (2006).