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The Recovery of a Magnetically Dead Layer on the Surface of an Anatase (Ti,Co)O_2 Thin Film via an Ultrathin TiO_2 Capping Layer

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Abstract: The effect of an ultrathin TiO_2 capping layer on an anatase $Ti_{0.95}Co_{0.05}O_{2-\delta}$ (001) epitaxial thin film on magnetism at 300 K was investigated. Films with a capping layer showed increased magnetization mainly caused by enhanced out-of-plane magnetization. In addition, the ultrathin capping layer was useful in prolonging the magnetization lifetime by more than two years. The thickness dependence of the magnetic domain structure at room temperature indicated the preservation of magnetic domain structure even for a 13 nm thick film covered with a capping layer. Taking into account nearly unchanged electric conductivity irrespective of the capping layer's thickness, the main role of the capping layer is to prevent surface oxidation, which reduces electron carriers on the surface.

Keywords: ferromagnetic oxide semiconductor; Co-doped TiO_2; room temperature ferromagnetism; magnetically dead layer; capping layer; magnetic domain structure; surface oxidation

1. Introduction

A ferromagnetic oxide semiconductor (Ti,Co)O_2 attracts much attention due to its high Curie temperature, promising for room temperature semiconductor spintronics [1–4]. In this compound, the carrier-mediated exchange interaction plays an important role evidenced by its ferromagnetism controlled via electric-field gating [5], chemical doping [6], and the Curie temperature changed by carrier density [7]. Recently, we observed the magnetic domain structure in (Ti,Co)O_2 at room temperature with a magnetic force microscope [8], indicating a possibility of manipulating magnetic domains. However, a magnetically dead layer at the surface observed via X-ray magnetic circular dichroism showed significantly reduced magnetization on the surface [9], which is an obstacle for the implementation of various thin film devices.

A magnetically dead layer on a surface or interface has already been reported in various magnetic thin films. For example, NiFe films showed a magnetically dead layer on a NiFe/Cu interface caused by interfacial mixing [10]. (La,Sr)MnO_3 showed a magnetic disorder on a surface, which was probably associated with a structural disorder [11]. In the case of (Ti,Co)O_2, the magnetically dead layer was at least ~5 nm thick [9] and could be attributed to a surface oxidation and/or a depletion layer due to the different surfaces and bulk electronic structures observed via soft and hard X-ray photoemission spectroscopy [12]. X-ray photoemission spectroscopy under ultraviolet illumination suggested that

photoinduced carriers at a depleted layer intermediate exchange coupling between Co spins [13]. These results suggest that surface depletion possibly caused by oxidation plays a major role in reduced magnetization in (Ti,Co)O_2, since the oxygen vacancies serve as an electron donor to induce the ferromagnetism [6].

In order to recover the magnetically dead layer, the capping layer is known to be effective to protect surface oxidation [14,15]. In this study, we developed a nonmagnetic ultrathin TiO_2 epitaxial capping layer for an anatase (Ti,Co)O_2 epitaxial thin film. Only with the 2-nm-thick capping layer was the magnetization significantly improved, mainly due to enhanced out-of-plane magnetization. In addition, the magnetization lifetime was prolonged by at least two years.

2. Materials and Methods

An anatase $Ti_{0.95}Co_{0.05}O_{2-\delta}$ epitaxial thin film was grown on a $LaAlO_3$ step substrate via pulsed laser deposition. The $LaAlO_3$ substrate was firstly buffered with an insulating 5-unit-cell-thick anatase TiO_2 layer according to a procedure previously reported [16]. After cooling down to room temperature, the $Ti_{0.95}Co_{0.05}O_{2-\delta}$ epitaxial thin film was grown on a buffer layer at 250 °C with an oxygen pressure during growth (P_{O2}) of 1–3 $\times$ 10^{-6} Torr to control carrier density [6]. A nonmagnetic TiO_2 capping layer (0–5 nm thick) was in situ deposited epitaxially on the $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film at 250 °C with a P_{O2} of 1 $\times$ 10^{-4} Torr, and was cooled down to room temperature under the same P_{O2}. Reflection high energy electron diffraction (RHEED) was in situ monitored during growth. The thickness of the $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film was typically 30–40 nm unless otherwise stated. Based on X-ray diffraction measurements, all films were in a pure anatase phase and epitaxially grown in a *c*-axis orientation. The electrical transport properties were evaluated by four-probe and Hall effect measurements of the Hall bar patterned samples. The magnetization was measured with a superconducting quantum interference device magnetometer at 300 K in the range of $\pm$2 T. The topographic and magnetic images of the films were observed with a magnetic force microscope at room temperature in a vacuum of 10 Pa without an external magnetic field [8].

3. Results

RHEED patterns of the buffer layer, the (Ti,Co)O_2 film, and the capping layer showed a streak pattern with the flat sample surface observed via AFM (Figure 1), indicating the epitaxial growth and sharp interface between each layer.

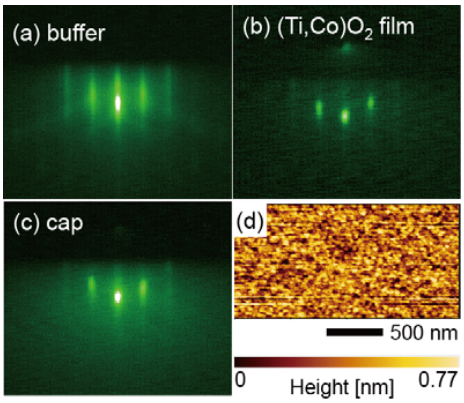

Figure 1. Reflection high energy electron diffraction (RHEED) patterns of (**a**) the buffer layer; (**b**) the (Ti,Co)O_2 film; (**c**) the capping layer. (**d**) Typical topographic image of the sample surface.

Figure 2 shows the temperature dependence of resistivity for $Ti_{0.95}Co_{0.05}O_{2-\delta}$ films with different capping layer thicknesses. The resistivity was calculated from the thickness of the $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film assuming the insulating capping layer because of the lower oxygen vacancy. All resistivity values were

approximately equivalent. The carrier density and mobility at 300 K for non-capped, 3 nm capped, and 5 nm capped films were 4.8×10^{19} cm^{-3} and 5.4 cm^2·V^{-1}·s^{-1}, 5.1×10^{19} cm^{-3} and 5.1 cm^2·V^{-1}·s^{-1}, and 4.7×10^{19} cm^{-3} and 4.5 cm^2·V^{-1}·s^{-1}, respectively. These small variations in carrier density and mobility, irrespective of capping layer thickness, might rule out a possibility of intensive carrier doping at the interface, as was observed in $TiO_2/LaAlO_3$ and $TiO_2/LaTiO_3$ interfaces [17].

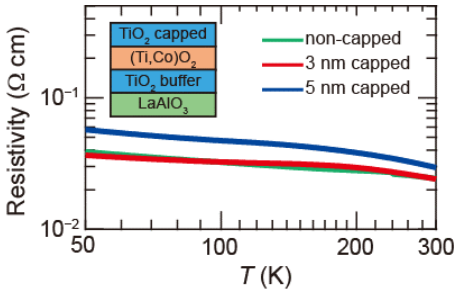

Figure 2. Temperature dependence of resistivity for $Ti_{0.95}Co_{0.05}O_{2-\delta}$ epitaxial thin films with the capping layer of nonmagnetic TiO_2 epitaxial thin films. The capping layer thickness was 0, 3, and 5 nm.

Figure 3 shows out-of-plane and in-plane magnetization curves at 300 K for $Ti_{0.95}Co_{0.05}O_{2-\delta}$ films with and without a capping layer. In case of the films without a capping layer, the out-of-plane and in-plane magnetizations were approximately the same for $n = 4.5 \times 10^{19}$ cm^{-3} (Figure 3a), while the out-of-plane magnetization was slightly larger than the in-plane magnetization for $n = 6.7 \times 10^{19}$ cm^{-3} (Figure 3b), indicating their insignificant magnetic anisotropy. In case of the films with a capping layer, the out-of-plane magnetization was nearly doubled for $n = 4.5 \times 10^{19}$ cm^{-3} (Figure 3c), representing significantly enhanced out-of-plane magnetization and perpendicular magnetic anisotropy (Figure 3c). For $n = 6.7 \times 10^{19}$ cm^{-3}, the out-of-plane magnetization was slightly increased (Figure 3d). It is noted that the in-plane magnetization in saturation was scarcely changed by the capping layer. However, the difference in magnetization slope between the in-plane and out-of-plane magnetization was enhanced (insets of Figure 3), indicating enlarged perpendicular magnetic anisotropy by the capping layer.

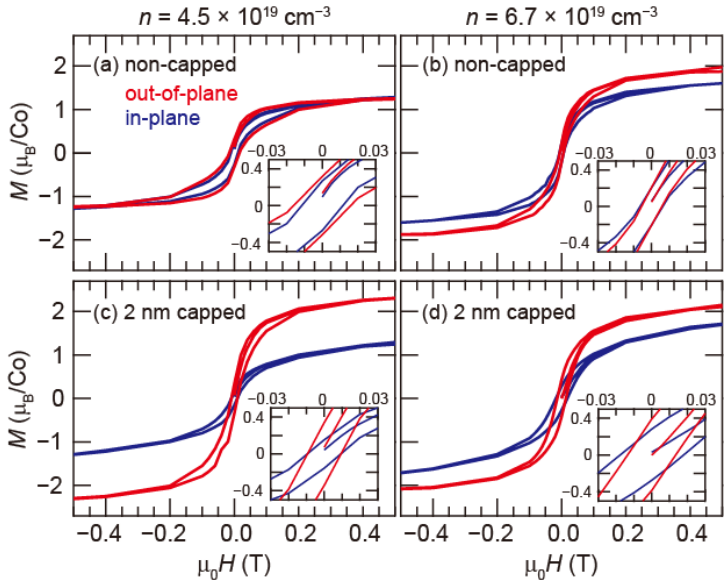

Figure 3. Out-of-plane (red) and in-plane (blue) magnetization curves at 300 K for anatase $Ti_{0.95}Co_{0.05}O_{2-\delta}$ epitaxial thin films with different carrier density. (**a**) $n = 4.5 \times 10^{19}$ cm^{-3} and (**b**) $n = 6.7 \times 10^{19}$ cm^{-3} without capping layer; (**c**) $n = 4.5 \times 10^{19}$ cm^{-3} and (**d**) $n = 6.7 \times 10^{19}$ cm^{-3} with a 2-nm-thick capping layer. Insets denote magnified views at around a zero magnetic field.

The stability of the films without a capping layer and with a 2-nm-thick capping layer was examined as the aging of magnetization. During aging, the films were kept in a desiccator at ambient condition. Figure 4 shows the aging effect of the out-of-plane magnetization curve for the $Ti_{0.95}Co_{0.05}O_{2-\delta}$ thin films ($n \approx 6$–7×10^{19} cm^{-3}) with and without a capping layer at 300 K. The film without a capping layer showed a gradual decrease in magnetization within a two-year period. On the other hands, the film with a capping layer showed almost no change in magnetization or its magnetic hysteresis even after two years. This result indicates that the capping layer protected the film surface against the surface oxidation, which causes decreased magnetization owing to reduced carrier density. Similar decreased magnetization was also reported previously in (Ti,Co)O_2 nanopowders [18].

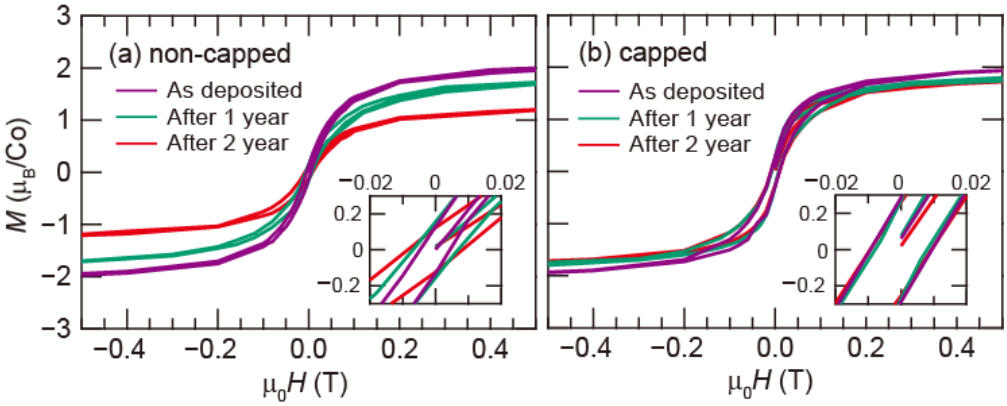

Figure 4. The aging of out-of-plane magnetization curves at 300 K for $Ti_{0.95}Co_{0.05}O_{2-\delta}$ thin films (**a**) without a capping layer and (**b**) with a 2-nm-thick capping layer. Insets denote magnified views at around a zero magnetic field.

The effect of the 2-nm-thick capping layer on the magnetic domain structure in $Ti_{0.95}Co_{0.05}O_{2-\delta}$ films with thicknesses from 13 nm to 38 nm was examined. Magnetization curves were almost the same with open hysteresis for all films, representing similar magnetization in a unit of Bohr magneton per Co site. The magnetic domain structure showed a weaker contrast with a smaller domain with decreasing thickness as a result of decreased thickness (Figure 5a–c), where the average domain width evaluated by a stereological method [19] was 160, 120, and 80 nm with decreasing thickness. It is noted that the magnetic domain structure was observed even for a thickness of 13 nm. On the other hand, a 15-nm-thick film without a capping layer showed smaller and irregularly shaped magnetic domains, probably caused by a magnetically dead layer on the surface and/or weak perpendicular magnetic anisotropy.

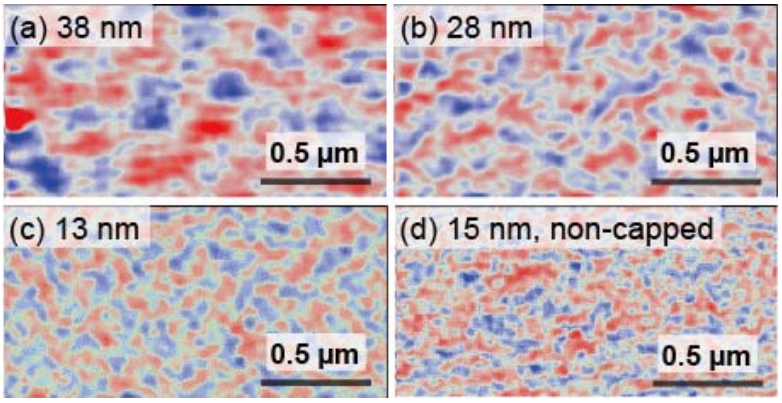

Figure 5. Magnetic images at 300 K for $Ti_{0.95}Co_{0.05}O_{2-\delta}$ thin films with different film thicknesses (**a**–**c**) with a 2-nm-thick capping layer and (**d**) without a capping layer.

4. Discussion

The capping layer works to protect (Ti,Co)O_2 films from surface oxidation. However, significantly enlarged perpendicular magnetic anisotropy might be attributed to not only the carrier density dependence of magnetic anisotropy briefly reported in previous reports [5] but also other effects such as the varied 3d orbital occupancy of Co ions in (Ti,Co)O_2 caused by interfacial effects [20,21]. The influence of ferromagnetism in the capping layer (if any) on the enlarged magnetization can be ruled out because of the layer's significantly lower thickness in comparison with that of the (Ti,Co)O_2 film.

5. Conclusions

In conclusion, an ultrathin TiO_2 epitaxial capping layer was developed for an anatase $Ti_{0.95}Co_{0.05}O_{2-\delta}$ (001) epitaxial thin film. As a result, the magnetization was concomitantly recovered with enlarged perpendicular magnetic anisotropy, resulting in the observation of a magnetic domain structure for the 13-nm-thick $Ti_{0.95}Co_{0.05}O_{2-\delta}$ film. In addition, the magnetization was almost unchanged for at least two years. One major role of the capping layer is to prevent surface oxidation, and other mechanism such as varied 3d orbital occupancy might play a role as well.

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Author Contributions: T.F. and T.H. conceived and designed the experiments; T.S.K. performed the experiments; T.S.K. and T.F. analyzed the data; all authors wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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