

Surface analysis of topmost layer of epitaxial layered oxide thin film: Application to delafossite oxide for oxygen evolution reaction



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ABSTRACT

Delafossite oxides (ABO_2) have a layered structure with alternating layers of *A* and *B* elements, the topmost layer of which appears to determine their performance, such as the oxygen evolution reaction (OER) activity. In this study, we investigated the topmost layer of single-domain (0 0 1)-oriented $AgCoO_2$ epitaxial thin film for potential use as an OER catalyst. The thin film was confirmed to possess OER activity at a level comparable to the catalyst in powder form. Atomic scattering spectroscopy revealed the topmost layer to be composed of CoO_6 octahedra. *In situ* X-ray absorption spectroscopy showed that the oxidation of Co at the surface did not change under different potentials, which suggests that there is no valence fluctuation of Co in the stable CoO_6 octahedral structure. However, the oxidation number of Co at the surface was lower than that in the bulk. Our density functional theoretical calculations also showed the Co atoms at the surface to have a slightly higher electron occupancy than those in the bulk, and suggests that the unoccupied t_{2g} states of Co at the surface have an influence on OER activity.

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1. Introduction

Delafossite oxides (ABO_2) [1], which have a layered structure with alternate layers of *A* and *B* elements (Fig. 1), have been studied extensively for their potential as *p*-type transparent electrodes [2,3] and thermoelectric materials [4]. These oxides are also likely to be highly active catalysts for water electrolysis anode. Carcia et al. report that delafossite oxides that include precious metals, such as $PdBO_2$ ($B = Co, Cr, Rh$) and $PtCoO_2$, are good catalysts for the oxygen evolution reaction (OER) [5]. In our previous studies, we also found that $CuBO_2$ [6,7] and $AgBO_2$ [8] ($B =$ transition metal) powder catalysts have the OER activity, showing that $AgCoO_2$ has the best catalytic performance. To achieve further improvement of their performance, we need to identify the topmost layer of these catalysts and examine its electronic state, which is likely to be closely correlated with OER activity. However, it is impossible to distinguish the topmost layer of powder-based catalysts, because they include several crystal planes.

Thin-film-based catalysts terminated with well-defined surfaces have been studied to elucidate how crystal planes affect catalytic activity [9,10]. The OER activities of perovskite [9] and rutile oxides [10] are

dependent on their surface orientation, which shows that their unstable surface planes tend to be highly active. On the other hand, much less work has been done on delafossite thin films as OER catalysts [5]. Although the topmost layer of delafossite thin films is the key to the OER process, it is not determined explicitly whether their topmost layer is an *A* or *B* layer. The OER activity of $AgCoO_2$ thin films has never been evaluated, though $AgCoO_2$ appears to be a promising OER catalyst [8].

In this study, we investigated epitaxially-oriented (0 0 1) $AgCoO_2$ thin film to determine the elements in its topmost layer and analyze their electronic states. $AgCoO_2$ thin film was deposited on Nb-doped $SrTiO_3$ (1 1 1) substrate using magnetron sputtering. The thin film was grown epitaxially, as confirmed by X-ray diffraction (XRD) measurements. Electrochemical measurements showed that the film has almost the same OER activity as the powder-based catalyst. We employed atomic scattering spectroscopy to identify the elements in the topmost layer, and found it to be composed of CoO_6 octahedra. To examine the oxidation state of Co in the topmost layer, we measured *in situ* total reflection X-ray absorption near the edge structure (XANES). The oxidation number at the surface was detected as being slightly lower than that in the bulk. Density functional theoretical (DFT) calculations agreed

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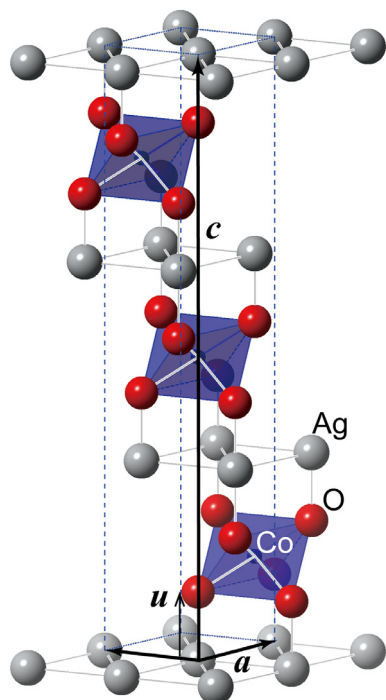


Fig. 1. Crystal structure of 3R-type AgCoO_2 . The 3R-type delafossite has a rhombohedral structure ($R\bar{3}m$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with the results from XANES. Our study reveals that the topmost layer is comprised of cobalt, and suggests that the valence state of the topmost Co layer has an influence on OER activity.

2. Experimental methods

2.1. Powder synthesis

Ag_2O (Wako Pure Chemical Industries) and CoOOH were used as precursors of AgCoO_2 . Here, CoOOH was obtained by heating $\text{Co}(\text{OH})_2$ (Wako Pure Chemical Industries) at 120°C in an oxygen atmosphere for 24 h.

AgCoO_2 was produced by using hydrothermal reactions [11]. Equimolar reactants of Ag_2O and CoOOH in 2 M NaOH aqueous solution were sealed in a polytetrafluoroethylene (PTFE: Teflon) container. The container was maintained at 210°C for 60 h. The AgCoO_2 powder that resulted was used as the target of magnetron sputtering.

2.2. Film preparation and characterization

A 20-nm AgCoO_2 thin film was fabricated on (1 1 1)-orientated Nb-doped SrTiO_3 (Nb:STO) substrate (K & R Creation) by magnetron sputtering. A mixed flow of Ar and O_2 (Ar: 75%, O_2 : 25%) gases was applied at a back pressure of 4.5 Pa. The substrate was heated to $\sim 400^\circ\text{C}$ and the sputtering power was set to 60 W.

X-ray diffraction (XRD) measurements were performed using a four-circle diffractometer (X'Pert Pro MPD, Panalytical) with $\text{Cu K}\alpha$ radiation. Out-of-plane ($2\theta/\omega$) scanning showed the orientation of the c -axis of the thin film with respect to the normal of the substrate. In-plane (ϕ) scanning provided information on the in-plane arrangement of the thin film relative to that of the substrate.

2.3. Electrochemical measurements

The thin film was fixed to an attachment (Hokuto Denko). The electrical contact was applied to the Nb:STO substrate, which was electri-

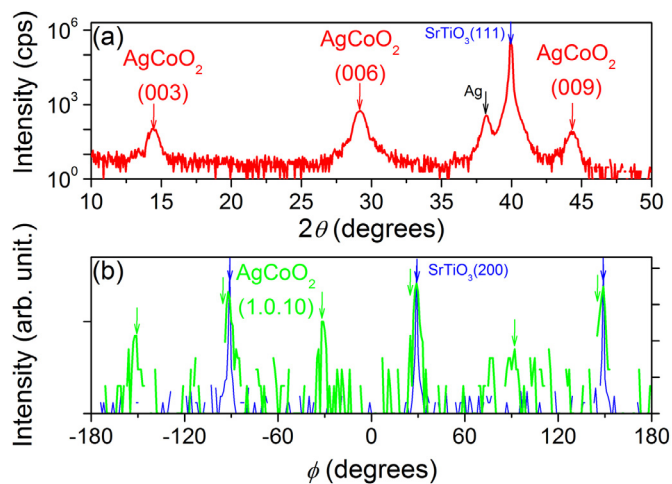


Fig. 2. XRD patterns. (a) 2θ - ω scan of AgCoO_2 thin film, and (b) ϕ scan of AgCoO_2 (1.0.10) and SrTiO_3 (200). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cally conductive. The peripheral edge of the thin film was covered with the cap of the attachment, which made it possible to expose only the catalyst film to the electrolyte (geometric surface area: 0.385 cm^2) [12]. The attachment was inserted into a rotating disk electrode (RDE) system (Nikko Keisoku). In the RDE system, the thin film was used as the working electrode (WE) for electrochemical measurements. The attachment for powder was the same as that used in our previous reports [6–8].

The OER measurements were evaluated in oxygen-saturated 1.0 M KOH aqueous solution (Wako Pure Chemical Industries) in the RDE system to fix the oxygen equilibrium potential. The rotation speed of the WE was set to 2000 rpm. The three-electrode system was controlled using a potentiostat system (ALS-760C, BAS), with a platinum plate and reversible hydrogen electrode (RHE) used as the counter and reference electrodes, respectively. The scan rate of cyclic voltammetry (CV) was set to 50 mV/s. Potentials were corrected for electrolyte resistance ($\sim 6\ \Omega$) by using electrical impedance spectroscopy (EIS).

2.4. Atomic scattering spectroscopy

To identify the elements comprising the topmost layer, atomic scattering spectroscopy was performed with TOFLAS-3000 (Pascal Corporation) [13,14]. The intensity and time-of-flight (TOF) of back-scattered He atoms were detected to analyze the atomic type of the topmost layer of the thin film. The substrate was mounted on a sample stage that could be rotated in any direction. The pole figure of atomic scattering spectroscopy can be used to determine the structure of the topmost layer.

2.5. In situ X-ray absorption spectroscopy

In situ X-ray absorption near edge structure (XANES) was measured at the BL01B1 beamline at SPring-8. The spectra were obtained by detecting Co K-edge fluorescence from the thin-film electrode loaded into a custom-made three-electrode cell in O_2 -saturated 1.0 M KOH aqueous solution. The spectra in the total reflection geometry where the incident angle was $\sim 0.15^\circ$ (referred to as the “surface”) were obtained to examine the contribution of the topmost layer. On the other hand, those in a geometry where the incident angle was $\sim 1^\circ$ (referred to as “bulk”) involved the whole region of the film. The cell setup is described in more detail elsewhere [12].

3. Calculation methods

Our calculations were carried out using “STATE” [15], a first-principles molecular dynamics program. The Perdew-Burke-Ernzerhof

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