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Fabrication of all-solid-state battery using epitaxial $LiCoO_2$ thin films

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HIGHLIGHTS

- Fabrication of all-solid-state thin film lithium ion secondary battery using epitaxial $LiCoO_2$ thin film.
- Control of crystal orientation of epitaxial $LiCoO_2$ thin film.
- Observation of Li ion insertion/extraction reactions in the thin film battery by cyclic voltammetry measurement.

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ABSTRACT

We demonstrate the orientation control of $LiCoO_2$ epitaxial thin films deposited on (110)-2 × 1 reconstructed surfaces of Au and Pt by using pulsed laser deposition. The epitaxial $LiCoO_2$ thin films have CoO_2 layers tilted with respect to the surface normal, which is suitable for Li-ion insertion/extraction reactions in $LiCoO_2$. We show the successful operation of all-solid-state thin-film Li-ion batteries by employing the epitaxial $LiCoO_2$ thin films as cathodes. The electrochemical properties of epitaxial films in all-solid-state batteries are improved compared to the batteries using liquid electrolyte.

1. Introduction

Lithium ion batteries (LIBs) have attracted great attention for future electrochemical energy storage devices [1]. Among various types of LIBs, thin film LIBs helps to reduce the physical size of sensors and electric device containing the batteries [2,3]. Hence, many efforts have been devoted toward integration, miniaturization and high performance of thin film batteries. Ideal thin film batteries would be all-solid-state LIBs composed of epitaxial thin films from the viewpoint of high power output, high energy density and safety [4]. Recently, epitaxial thin films of electrode materials such as $LiCoO_2$ (LCO) [5–8], $Li_4Ti_5O_{12}$ [9–11], and $LiMn_2O_4$ [12], have been reported. However, many researchers face difficulties in fabricating all-solid-state epitaxial thin film batteries mainly due to weak adhesion and high interface resistance between the stacked films, and internal short circuit between cathode and anode electrodes. Still now, no report has been done on fabrication and electrochemical evaluation of all-solid-state thin film LIBs composed of epitaxial thin films.

In this study, we report to our knowledge for the first time successful battery operation of all-solid-state thin-film LIB composed of epitaxial cathode thin films. In order to fabricate thin film batteries, it is crucial to control crystal orientation of epitaxial thin films, particularly in the case of electroactive materials with anisotropic transport properties. $LiCoO_2$ (LCO) with a layered-rhombohedral α-$NaFeO_2$ structure has been widely used as a cathode material for commercially available LIBs and is still a promising cathode material for all-solid-state LIBs. In the layered structure of LCO, Li ions show a predominant two-dimensional diffusion along the layers, whereas it is unlikely that Li ions jump

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to an adjacent Li diffusion layer. Indeed, epitaxial LCO films showed a difference in the charge/discharge capacity, depending on the crystal orientation of LCO [6]. On a $SrTiO_3$(111) substrate, the epitaxial LCO grows with a crystal orientation that the CoO_2 layer is parallel to the substrate, and shows smaller capacity compared to other crystal orientations. Hence, the CoO_2 layer should not be parallel to the substrate surface in fabricating thin film battery using epitaxial LCO. Furthermore, a substrate with metallic conductivity is required to achieve bottom contact in LIBs. However, there has been no report on the control of the LCO crystal orientation on single crystal metal substrates such as Au and Pt.

Here we first demonstrate the epitaxial growth of LCO films deposited on reconstructed (110)-2 × 1 substrate surfaces of Au and Pt by using pulsed laser deposition (PLD). It is well known that the (110) surfaces reconstruct to so-called "missing row" structures with 2 × 1 symmetry [13]. The reconstructed (110) surfaces consist of alternately-arrayed {111} nanofacets (Fig. 1(a)), which lowers the total surface energy since the close-packed {111} facets have the lowest surface energy in case of face-centered cubic materials. By using the missing-row zigzag structures of surface reconstruction, we established a process to control the LCO crystal orientation in such a way that it becomes suitable for smooth Li-ion insertion/extraction reactions. We evaluate electrochemical properties of the orientation-controlled epitaxial LCO thin films using organic liquid electrolyte. Then, we also fabricate all-solid-state thin-film LIBs by depositing thin films of Li phosphorus oxynitride (LiPON) [14] and Li as solid electrolyte and anode on the epitaxial LCO, respectively. We demonstrate the battery operation, and compare the electrochemical properties of the devices by cyclic voltammetry (CV).

2. Experimental

We employed single crystal (110) substrates of Au and Pt, and prepared (2 × 1) reconstructed surfaces by extensive sputtering–annealing cycles in ultrahigh vacuum (UHV) [13]. The surface reconstruction was confirmed by low energy electron diffraction (LEED) and reflection high-energy electron diffraction. The LCO thin films were deposited by using PLD with a polycrystalline $Li_{1.2}CoO_2$ target (Toshima Manufacturing). A KrF excimer laser (wavelength: 248 nm) with a repetition rate of 5 Hz and a fluence of 1.0 J cm^{-2} at the target surface were used for the deposition. During the deposition, the oxygen partial pressure was kept at 1×10^{-6} Torr and the substrate temperature was room temperature (RT). The as-grown samples are epitaxial films, but Li and Co cations are randomly distributed along the c-axis, as discussed by Wang et al. [15] and Bouwman et al. [16]. Hence the as-grown films were subsequently annealed at 650 °C in air to obtain high temperature LCO phase [7]. The LCO films were typically 200 nm thick. The crystal structures of the films were characterized by X-ray diffraction (XRD) (NEW D8 Discover, Bruker), transmission electron microscopy (TEM), and scanning TEM (STEM) (JEM-2010HC and JEM-2100F with an aberration corrector, JEOL Ltd.) [17]. The crystal structures of LCO are indexed on the basis of hexagonal setting, throughout this letter. The electrochemical properties of epitaxial LCO films were examined with coin type Li cells using Li metal foils as anode. The electrolyte used was EC (ethylene carbonate)-DEC (diethyl carbonate) with a molar ratio of 3:7 as a solvent and supporting electrolyte of 1 M $LiPF_6$. The CV measurements were carried out in the voltage range between 3.0 and 4.3 V at a scan rate of 0.1 mV s^{-1}. The cut-off voltages in charge and discharge measurements were 3 and 4.3 V, and the current was set at 1.2 μA (approximately 0.33C). Furthermore, we fabricated all-solid-state thin film batteries using the epitaxial LCO films. A schematic image of the all-solid-state thin film batteries is shown in Fig. 2. The solid electrolyte, LiPON, and anode Li thin films were deposited on the epitaxial LCO films by RF magnetron sputtering (RFMS) and vacuum thermal evaporation (VTE), respectively [3,18,19]. An active area was 5 × 5 mm. After the deposition of LiPON onto LCO, the films were annealed at 180 °C for 30 min in Ar atmosphere to reduce the interface resistance

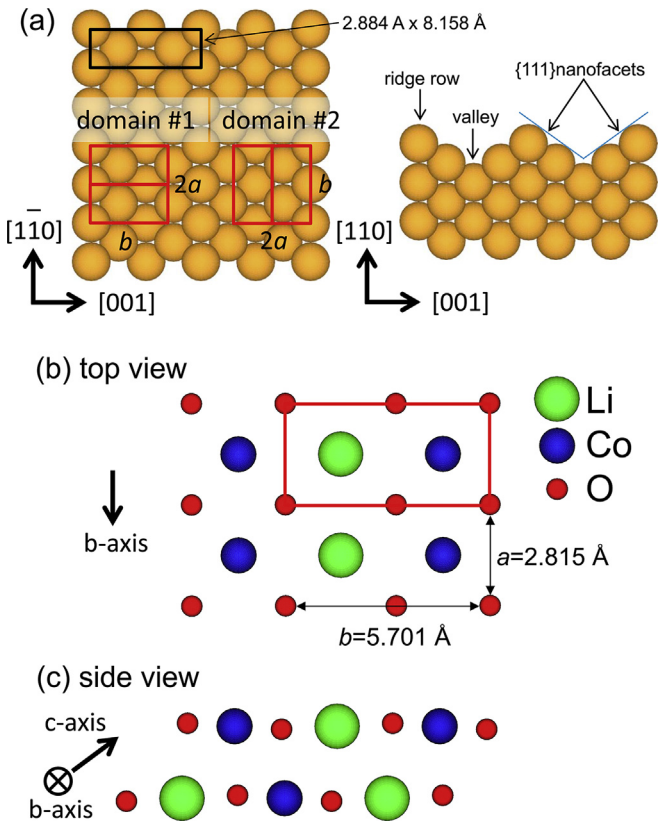

Fig. 1. (a) Schematic view of Au(110)-2 × 1 reconstructed surface and proposed alignment of domains #1 and #2. (b, c) Schematic views of plane of $LiCoO_2$.

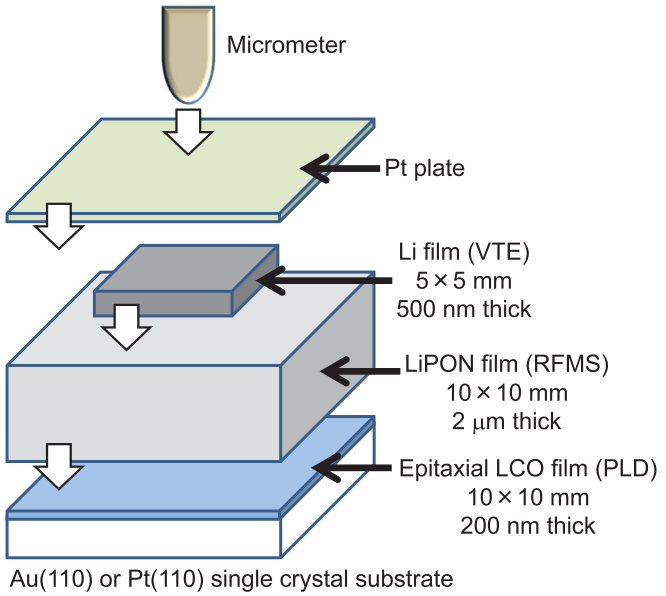

Fig. 2. Schematic image of all-solid-state thin film batteries using epitaxial $LiCoO_2$ thin films on single crystal (110) substrates of Au and Pt.