Journal of Power Sources 325 (2016) 306–310

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Orientation alignment of epitaxial $LiCoO_2$ thin films on vicinal $SrTiO_3$ (100) substrates

Kazunori Nishio [a, 1], Tsuyoshi Ohnishi [a, b, c], Kazutaka Mitsuishi [a], Narumi Ohta [a, c], Ken Watanabe [c], Kazunori Takada [a, b, c, *]

[a] Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), 1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan
[b] International Center for Materials Nanoarchitectonics (MANA), 1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan
[c] Environment and Energy Materials Division, National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan

HIGHLIGHTS

- $LiCoO_2$ epitaxial thin films are synthesized on vicinal $SrTiO_3$ (100) substrates.
- The (104)-oriented films exhibit single-domain structure on the vicinal substrates.
- The orientation alignment is explainable by step-flow growth mechanism.
- The influence of domain boundaries on electrode performance is discussed.

ARTICLE INFO

Article history:
Received 15 March 2016
Received in revised form
1 June 2016
Accepted 3 June 2016
Available online 16 June 2016

Keywords:
Epitaxial film
Vicinal substrate
Pulsed laser deposition
Lithium cobalt oxide
Thin-film battery

ABSTRACT

$LiCoO_2$ is epitaxially grown on $SrTiO_3$ (100) substrates with (104) orientation. Because the $LiCoO_2$ film is grown with its *c*-axis parallel to four equivalent ⟨111⟩ axes of the $SrTiO_3$, the (104)-oriented film exhibits four-domain structure on the $SrTiO_3$ (100) substrate. Introducing off-cut angle to the substrate surface breaks the equivalency between the four ⟨111⟩ axes of the $SrTiO_3$ substrate to induce preferential growth of specific orientation with the *c*-axis in a descending direction of off-cut surface. Increasing off-cut angle and lowering deposition rate promote the preferential growth, because they facilitate step-flow growth mode, and finally align the *c*-axes in the domains completely into one ⟨111⟩ direction of the $SrTiO_3$ substrate. The $LiCoO_2$ film delivers a discharge capacity of 90 mAh g^{-1} at a low discharge rate of 0.01 C, and 25% of capacity is kept even at a high rate of discharge with 100 C.

1. Introduction

Studies on thin-film batteries started in 1980s [1], and they are growing in importance with the births of new micro-devices, e.g. nonvolatile memories, micro electro mechanical systems (MEMS), etc. Another importance of thin-film systems is originated from their simple geometry. Because electrode/electrolyte interfaces and ion-conduction paths can be simplified in the geometry, thin-film systems are beneficial for fundamental research. Especially, recent materials research has provided new materials with excellent bulk properties. They have often replaced their bulk with their interfaces that govern the battery performance and initiated many studies on interface, where planar interfaces and one-dimensional ionic conduction in the simplified geometry are useful.

Although the electrochemical systems become to have simplified geometry in thin-film systems, more efforts are necessary to gain basic insight into intrinsic interface properties. Grain boundaries affect the ionic conduction, and the interfaces are formed between uncontrolled crystal faces, as far as the films are polycrystalline. Epitaxial films are anticipated to provide ideal interfaces for the fundamental research on the interfaces due to their specified surface. However, even epitaxial films do not always show intrinsic nature of the materials. For example, they often have multi-domain structure, whereas a recent computational study predicts that twin domain boundaries existing in epitaxial films

* Corresponding author. National Institute for Materials Science, 1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan.
E-mail address: takada.kazunori@nims.go.jp (K. Takada).
[1] Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980–8577, Japan.

http://dx.doi.org/10.1016/j.jpowsour.2016.06.015
0378-7753/

affect ion transport in the films [2]. Therefore, ultimate goal is to form these materials in monolithic single-crystal films without domain boundaries, which is equivalent to bulk single crystal, although it is challenging task.

Our previous study on epitaxial growth of $LiCoO_2$ has revealed that $LiCoO_2$ is epitaxially grown with (104), (018), and (001) orientations on $SrTiO_3$ (100), (110), and (111) substrates, respectively [3]. In the study, we demonstrated electrode properties of the (104)-oriented film, because CoO_2 layers in the film are the most upright and thus offer the most accessible interlayers for lithium ions. However, the film has four-domain structures, in which domain boundaries may affect the electrode properties.

Vicinal substrates, surface of which is at off-cut angle to a specific crystal plane, are sometimes utilized in order to improve the crystallinity of epitaxial thin films [4,5], because they are generally believed to enhance step flow growth of thin films and control domain structure. In this study, (104) oriented $LiCoO_2$ epitaxial thin films are grown on vicinal $SrTiO_3$ (100) substrates to promote preferential formation of specific domains.

2. Experimental

Epitaxial $LiCoO_2$ thin films were grown by pulsed laser deposition (PLD). A sintered $Li_{1.2}CoO_{2+\delta}$ pellet (TOSHIMA Manufacturing Co., Ltd.) was used as the PLD target. A KrF excimer laser (COMPex Pro 50, COHERENT, Inc., $\lambda = 248$ nm) was operated at a repetition rate of 2 Hz or 40 Hz for the target ablation. Laser spot size on the target was 0.031 cm^2, and the laser fluence was 0.65 J cm^{-2}. The incident angle of the excimer laser on the target surface was 30°, and the target–substrate distance was set at 58 mm. Oxygen pressure in the chamber and substrate temperature were set at 0.1 Pa and 725 °C, respectively. Detailed information regarding the selection of target composition, laser fluence, and oxygen pressure can be found in Refs. [6,7].

Films were deposited on non-doped $SrTiO_3$ single crystal substrates, which were exactly-cut $SrTiO_3$ (100) substrates and vicinal substrates with 3° off-cut toward in-plane [001] direction, and those with 2° and 4° off-cut toward in-plane [011] direction from (100) plane as illustrated in Fig. 1 in order to investigate the effects of the off-cut directions and off-cut angles from (100) plane of $SrTiO_3$ on the film structure. A vicinal 3 at% La-doped $SrTiO_3$ (La:$SrTiO_3$) single crystal substrate with 5° off-cut toward in-plane [011] direction was used in place of the non-doped insulating ones in order to investigate the electrode properties of the $LiCoO_2$ film grown on the vicinal substrate, because the La-doping provides electronic conduction to the substrates and makes them act as current collectors in the electrochemical measurement. All the substrates were made by SHINKOSHA Co., Ltd., and the substrate size is typically 10 mm in diameter, 10 mm × 10 mm, or 7.5 mm × 7.5 mm with 0.5 mm in thickness.

An X-ray diffractometer (XRD, SmartLab, Rigaku Corp.) equipped with a rotating Cu target was used for crystallographic and thickness analyses of obtained thin films, which include in-plane pole figure measurement [8]. The pole figures were taken for reflections of $LiCoO_2$ 003, as well as $LiCoO_2$ 104, 110 and $SrTiO_3$ 100, 110, and 111 with a step of 1.0°, where non-monochromated X-ray was used to obtain high diffraction intensity. Prior to the pole figure measurement, asymmetric diffraction measurements were performed with 2-bounce Ge 220 monochromated CuKα_1 radiation in order to determine the 2θ value precisely for each reflection.

Transmission electron microscopy (TEM) was employed to investigate the structural features of the films. Cross-sectional samples were made by wedge polishing. Bright field (BF) and dark-field (DF) transmission electron micrographs were taken on using a JEOL ARM-200F microscope at 200 kV acceleration voltage.

Electrode performance of the obtained films was investigated in an all-solid-state cell. Powder $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ (*thio*-LISICON [9]) was used as the solid electrolyte. An In–Li alloy was selected as the counter electrode and formed by attaching a piece of lithium (2 mg) to an indium foil (60 mg). The surface of $LiCoO_2$ film was coated with a 20-nm-thick Li_3PO_4 layer to reduce the interfacial resistance to be low enough for the electrochemical measurement [10,11] The Li_3PO_4-coated $LiCoO_2$ film on the La:$SrTiO_3$ substrate and the In–Li alloy were attached to respective sides of a *thio*-LISICON layer (150 mg) and they were pressed together at around 500 MPa to form a three-layered pellet with a 10 mm diameter.

The cell was charged and discharged at room temperature using a potentio-galvanostats (VSP, Bio-Logic SAS, and PS-08, Toho Technical Research Co., Ltd.). Because the electrode potential of the In–Li alloy counter electrode is 0.62 V *vs.* Li^+/Li, the upper cutoff voltage was set at 3.58 V in order to charge the epitaxial $LiCoO_2$ thin film up to 4.2 V *vs.* Li^+/Li. The charging rate was fixed at 0.01 C, while the discharging rate was varied from 0.01 C to 100 C, where the rate of 137 mA g^{-1} was defined as 1 C. The specific capacity was estimated based on the film thickness determined by X-ray reflectivity measurement and the theoretical density of 5.0 g cm^{-3}.

3. Results and discussion

Our previous study, in which exactly-cut $SrTiO_3$ substrates were used, has revealed that $LiCoO_2$ epitaxial thin films grow on $SrTiO_3$ (100) surface with (104) orientation. The films exhibit four-domain structure, in which the four kinds of domains whose *c*-axes of $LiCoO_2$ are parallel to the four equivalent ⟨111⟩ directions of $SrTiO_3$ substrates appear with equal probability [3]. The $LiCoO_2$ films in this study are also (104) oriented regardless of the exactly-cut or vicinal $SrTiO_3$ (100) substrates; however, the four kinds of domains do not appear with equal probability on the vicinal substrates.

Fig. 2 shows X-ray pole figures for 003 reflections of the $LiCoO_2$ films, and Fig. 3 indicates azimuthal phi scan curves ($\alpha = 36°$ and phi = β, α: angle from substrate surface) extracted from the pole figures with off-cut angle adjustment. The $LiCoO_2$ film grown on the exactly-cut $SrTiO_3$ (100) substrate gives four poles in ⟨111⟩ directions with an equal intensity, as indicated in Fig. 2a and the bottom curve in Fig. 3, which support that the four kinds of domains appear with the equal probability.

Such domain structure is dramatically changed on the vicinal $SrTiO_3$ (100) substrates, while the out-of-plane (104) orientation is preserved. The off-cut toward [001] direction prefers two orientations out of the four, as can be recognized in the pole figure in Fig. 2c and the second curve from the bottom in Fig. 3. The XRD data obtained from the $LiCoO_2$ thin film grown on a 3° off-cut substrate toward [001] direction at a laser repetition rate of 40 Hz clearly indicate that the off-cut promotes two orientations with the *c*-axis parallel to [111] and [$1\bar{1}1$] directions of the $SrTiO_3$ substrate, i.e. in a descending direction of in-plane off-cut direction (arrows in Fig. 1)

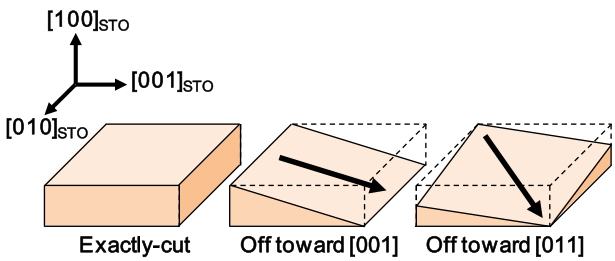

Fig. 1. Schematics of $SrTiO_3$ single crystal substrates with "Exactly-cut", off-cut toward [001] direction, and off-cut toward [011] direction.