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Synthesis of $LiCoO_2$ epitaxial thin films using a sol–gel method

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HIGHLIGHTS

- Epitaxial $LiCoO_2$ films are synthesized from aqueous solutions using a sol–gel method.
- Preheating on a hotplate notably promotes the orientation.
- The crystal orientation is controllable on different planes of the substrates.

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ABSTRACT

Epitaxial $LiCoO_2$ films are synthesized using a sol–gel method. The precursors are aqueous solutions of acetates or nitrates of Li and Co with polyvinylpyrrolidone as a thickener. The $LiCoO_2$ films prepared from the solutions by spin coating are epitaxially grown on sapphire (0001) substrates with *c*-axis orientation and in-plane alignment of $LiCoO_2$ $[1\bar{1}0]$||sapphire [100]. A two-step heat treatment of the spin-coated films consisting of preheating on a hotplate at the crystallization temperature followed by a high-temperature treatment notably promotes the *c*-axis orientation. In addition, the crystal orientation is controllable on different planes of the $SrTiO_3$ substrates; the $LiCoO_2$ films are grown with epitaxial relationships of $LiCoO_2$ (001)||$SrTiO_3$ (111), $LiCoO_2$ (018)||$SrTiO_3$ (110), and $LiCoO_2$ (104)||$SrTiO_3$ (100).

1. Introduction

Rechargeable lithium batteries are widely used in portable electronic devices and are anticipated to be installed in electric vehicles, smart grids, *etc.* [1,2]. Contrary to the large-size batteries for these applications, thin-film batteries [3–6], studies on which started in order to make up for the low ionic conductivity of solid electrolytes [7], are currently in demand for nonvolatile memories, microelectromechanical systems (MEMS), *etc.* Battery performance is always evaluated in terms of energy; for example, the quantity of energy that can be stored in a limited volume or weight. However, the performance expected from a limited footprint is more important in thin-film batteries. To store high quantities of energy within a limited footprint, the electrodes in thin-film batteries must be as thick as possible. However, increasing electrode thickness usually worsens battery performance [5] because ionic transport in a thick electrode predominantly determines the performance. Ionic transport is governed not only by ionic diffusion in the crystal framework but also by diffusion across grain boundaries. Therefore, the reduction of grain boundaries and the implementation of fast ionic conduction in active materials are necessary to achieve high performance in thin-film batteries.

Epitaxial growth is a promising technique for forming electrodes containing very few grain boundaries. However, epitaxial films are usually fabricated through vacuum processes, such as vacuum evaporation, radio frequency (RF) sputtering, and pulsed laser deposition (PLD). Although these methods have produced high-quality epitaxial films [8,9], they are not easy to be used in mass

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production because of the difficulty of making large-area films and their long deposition times and high cost. On the other hand, wet processes offer an alternative to vacuum processes that is low in cost and suitable for large-scale production.

Various transition metal oxides, including $LiCoO_2$ and $LiMn_2O_4$, have been successfully synthesized into thin films using wet processes [10–17]; however, most of the resulting films have been polycrystalline. The objective of this study is to develop a wet process for the epitaxial growth of battery materials. We selected $LiCoO_2$ as the battery material to be grown on sapphire (0001), $SrTiO_3$ (111), $SrTiO_3$ (110) and $SrTiO_3$ (100) substrates using the sol–gel method.

2. Experimental

2.1. Preparation of precursor solutions

A precursor solution was prepared from lithium acetate (CH_3COOLi, 99.99% in purity, Sigma Aldrich Ltd.) and cobalt (II) acetate tetrahydrate ($(CH_3COO)_2Co\cdot 4H_2O$, 99.0% in purity, Wako Pure Chemical Industries, Ltd.) as the Li and Co source, respectively. 1.1 g of CH_3COOLi and 4.0 g of $(CH_3COO)_2Co\cdot 4H_2O$ were dissolved in a mixed solvent of high-purity water (35.0 ml) and i-C_3H_7OH (10 ml), where the [Li]/[Co] ratio was 1.05 to compensate for possible lithium loss during heat treatment, and i-C_3H_7OH was mixed to improve the wettability of the solutions on the substrates during spin coating. Subsequently, 8.9 g of polyvinylpyrrolidone (PVP, average molecular weight of ~55,000, Sigma–Aldrich Ltd.) was added to the solution as a thickener. The prepared solution was red-brown in color and transparent. The solution was so stable that no precipitates were found even after several months of storage.

Part of the precursor solution was dried at 50 °C for 48 h into a dry gel and investigated by thermogravimetric and differential thermal analyses (TG-DTA) and powder X-ray diffraction (XRD). TG-DTA was carried out for the dry gel on a Rigaku TG-8120 analyzer in air at a heating rate of 1 $°C\ min^{-1}$. In addition, the dry gel was heated at various temperatures in the range of 300–800 °C for 5 h, and then the crystal structure was investigated by powder XRD performed on a Rigaku RINT-2000S diffractometer using graphite-monochromatized Cu-$K\alpha$ radiation.

Another precursor solution was prepared from nitrates in place of the acetates. 1 g of $LiNO_3$ (99.99% purity, Sigma Aldrich Ltd.) and 4.0 g of $Co(NO_3)_2\cdot 6H_2O$ (99.999% in purity, Sigma Aldrich Ltd.) were dissolved as the nitrates in a mixed solvent of 1 M HNO_3 (35.0 ml) and i-C_3H_7OH (10 ml), maintaining the [Li]/[Co] at 1.05 as in the above experimental conditions, and 8.9 g of PVP was added as a thickener.

2.2. Film preparation

The precursor solutions were spin-coated on sapphire (0001) substrates at 4500 rpm for 60 s. Dimensions of the sapphire substrate were $10 \times 10 \times 0.5\ mm^3$. In this work, we applied a two-step heat treatment to the spin-coated films. The first step involved heating the spin-coated films on a hotplate at 200, 300, 400, and 500 °C for 20 min at a heating rate of 10 $°C\ min^{-1}$. Subsequently, the films were heated in an electric furnace at 600–800 °C for 1–20 h at a heating rate of 1 $°C\ min^{-1}$. The synthesized films were approximately 100 nm in thickness, as measured using a surface profiler (Dektak150, Veeco).

The precursor solutions obtained from the nitrates as well as the acetates were used in the above film growth on sapphire substrates. In addition, $LiCoO_2$ films were also prepared on single-crystal $SrTiO_3$ (100), (110), and (111) substrates with dimensions of $7.5 \times 7.5 \times 0.5\ mm^3$ from the nitrate solution.

2.3. Characterization of the films

The crystal structures and orientations of the films were investigated by X-ray diffraction, including pole figure measurements. A Rigaku RINT-2000S diffractometer was used for the out-of-plane measurement, and a Rigaku SmartLab was used for the in-plane and pole figure measurements.

Scanning electron microscope (SEM) images of the films were taken on JEOL JSM-7000F operated at accelerating voltage of 5 kV. A film/substrate interface was observed on a transmission electron microscope (JEOL ARM-200F). A $LiCoO_2$ film grown on a $SrTiO_3$ (100) substrate was used for the observation. The TEM sample was prepared by focused ion beam (FIB, JEOL JEM-9320-FIB) after carbon deposition on the film surface as a protective layer. The TEM observation was performed at the accelerating voltage of 200 kV.

Electrode properties of a $LiCoO_2$ film were investigated in a solid electrolyte by the same procedure as reported in ref. 18. The $LiCoO_2$ film was grown on a 0.5 wt% Nb-doped $SrTiO_3$ (100) substrate, because the substrate must have electronic conduction in order to act as a current collector in the electrochemical measurement. Thickness of the film was 50 nm, and the dimensions of the substrate were 10 mm in diameter and 0.5 mm in thickness. A 10-nm-thick Li_3PO_4 film was formed on the surface of the $LiCoO_2$ film by PLD as a buffer layer. The Li_3PO_4-coated film was used as the working electrode in the solid-state cell, and the solid electrolyte and the counter electrode were $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ and In–Li alloy, respectively. Because the electrode potential of the In–Li alloy is 0.62 V *vs.* Li^+/Li, the cell was charged up to 3.58 V at 0.02 C in order to charge the film at 4.2 V *vs.* Li^+/Li, and then discharged down to 2.0 V at various discharge rates, where 1 C was defined as 137 $mAh\ g^{-1}$, and the film weight was estimated from the film thickness.

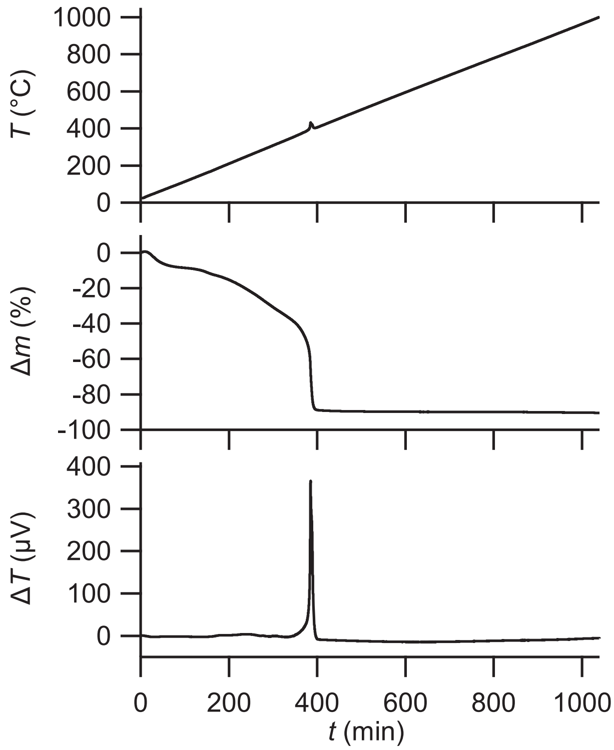

Fig. 1. TG–DTA curves of the residual powder obtained by drying the precursor solution at 50 °C for 48 h. Temperature (T), weight change (Δm), and temperature difference (ΔT) measured as thermo electromotive force are indicated as a function of measurement time (t).