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Influences of high deposition rate on $LiCoO_2$ epitaxial films prepared by pulsed laser deposition

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ABSTRACT

This study exhibits influence of deposition rate on $LiCoO_2$ epitaxial films prepared by pulsed laser deposition. High deposition rates tend to destabilize trivalent Co, resulting in formation of an oxygen-deficient phase with a rock-salt structure as an impurity in the deposited films. Because the oxygen-deficient phase originates from incomplete oxidation, post-annealing in air eliminates the impurity phase. Moreover, since it also improves the crystallinity of the film, the post-annealing enhances the electrode performance of the $LiCoO_2$ films.

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1. Introduction

Thin-film lithium batteries [1–3] are key components in today's portable electronics and the micro-devices such as MEMS and drug delivery systems. One of the objectives in the development of thin-film batteries is to increase the areal capacity in order to store a high energy within the limited footprint. Although new concepts such as 3D solid-state batteries [4] were proposed for this purpose, the battery structures look very complicated to assemble. A simple way to increase the areal capacity is, of course, increasing the electrode thickness; however, it lowers the rate capability [5]. Because one of the dominant factors that govern the rate capability is grain boundary resistance, a promising approach to enhance the rate capability is growing the active materials into epitaxial films without grain boundaries.

We are focusing this study on epitaxial growth of $LiCoO_2$ by pulsed laser deposition (PLD). Although deviation from the target composition in the deposited film is relatively small in PLD, the film compositions are surely affected by various factors [6,7]. Our previous studies on the $LiCoO_2$ films have also revealed that composition control is very important to obtain high-quality films, which can be accomplished through adjusting the laser energy density (fluence), chamber pressure as well as the target composition. For example, $LiCoO_2$ films with high crystallinity and purity are obtained from a stoichiometric $LiCoO_2$ target under low fluence for congruent ablation and low pressure satisfying molecular beam epitaxy (MBE) condition [8], while such $LiCoO_2$ films are deposited from Li-enriched targets at higher fluence and pressure [9]. Based on the higher deposition rate in the latter, this study aims at further increasing the deposition rate in order to prepare thick $LiCoO_2$ film electrodes. It has revealed influences of the high deposition rate on the film quality and the electrode properties.

2. Experimental

2.1. Film deposition

PLD system used in this study is almost the same as that in our previous one [10] except for an excimer laser employed for high rate deposition. The KrF excimer laser (COMPex Pro 50, COHERENT, Inc.) was used in this study, because it is operatable at a higher repetition rate of 50 Hz. The laser fluence and laser repetition rate were set at 0.65 J cm^{-2} and 40 Hz, unless otherwise noted, which are higher compared with that in our previous study in order to achieve the higher deposition rate. Laser spot size on the target was 0.031 cm^2 in this study, which is smaller than in our previous ones in order to achieve the higher fluence for the higher deposition rate. On the other hand, the small spot sizes widen the plume divergence, resulting in composition deviation to lithium deficiency, as demonstrated in Refs. [8] and [9]. Therefore, a sintered pellet with a Li-enriched composition of $Li_{1.2}CoO_{2+\delta}$ (20 mm

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in diameter and 5 mm in thickness, TOSHIMA Manufacturing Co., Ltd.) was used as the target.

$LiCoO_2$ films were deposited on 0.5 wt.% Nb-doped $SrTiO_3$ (100) substrates (Nb:$SrTiO_3$, 10 mm in diameter and 0.5 mm in thickness, SHINKOSHA Co., Ltd.). Because the Nb-doping adds the metallic conduction to the substrates, the substrates act as current collectors in the electrochemical measurement. In addition, $LiCoO_2$ epitaxial thin film is (104)-oriented on the $SrTiO_3$ (100) plane [10,11], which is regarded as preferable orientation for the lithium intercalation/deintercalation during charge/discharge operation. Oxygen pressure in the chamber (P_{O2}) and substrate temperature (T_{sub}) were varied from 0.01 to 0.1 Pa and from 600 to 800 °C, respectively. The incident angle of the excimer laser on the target surface was 30°, and the target–substrate distance was set at 58 mm. Part of the deposited films were post-annealed at 700 °C for 5 h in air.

2.2. Characterization of the films

Crystal phases in the deposited films were investigated by out-of-plane X-ray diffraction (XRD) measurement on a diffractometer (SmartLab, Rigaku Corp.) equipped with a rotating cupper target. The films were also characterized by Raman spectroscopy. The Raman spectra were collected in a backward micro-configuration using 514.5 nm line from an Ar^+ laser on a subtractive triple spectrometer (T64000, Jobin-Yvon/Atago Bussan). Film thickness was measured using a surface profiler (Dektak 150, Veeco Instruments Inc.).

Electrode properties of the films were investigated in solid-state electrochemical cells by using $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ (*thio*-LISICON [12]) as the solid electrolyte. Because interfacial resistance between $LiCoO_2$ and sulfide solid electrolytes is too high to investigate the electrode properties, the surface of the $LiCoO_2$ films must be coated with an oxide-based solid electrolyte that reduces the interfacial resistance [13]. In this study, Li_3PO_4 was employed as the oxide-based solid electrolyte, because a Li_3PO_4 thin film formed on film surface of $LiCoO_2$ was reported to reduce the interfacial resistance to be low enough for the electrochemical measurement [14]. The 50 nm-thick film of Li_3PO_4 was formed by PLD as reported in the reference before the cell assembly. In–Li alloy was selected as counter electrode. This alloy was prepared by attaching a small piece of lithium foil of 2 mg to an indium foil of 60 mg. The Li_3PO_4-coated $LiCoO_2$ film on Nb:$SrTiO_3$ (100) substrate and the In–Li alloy were attached to each side of *thio*-LISICON layer (150 mg). They were pressed together at around 500 MPa to form a three-layered pellet with a 10 mm diameter.

The $LiCoO_2$ film was charged and discharged at room temperature using potentio-galvanostats (VSP, Bio-Logic SAS, and PS-08, Toho Technical Research Co., Ltd.). Because the electrode potential of In–Li alloy counter electrode is 0.62 V *vs.* Li^+/Li, the upper cutoff voltage was set at 3.58 V to charge the $LiCoO_2$ to 4.2 V *vs.* Li^+/Li. Since the $LiCoO_2$ is expected to be charged up to $Li_{0.5}CoO_2$ at the potential [15], 1 C rate in this paper is defined as 137 mA g^{-1}. The films were charged at 0.01 C to the cutoff voltage and then discharged down to 2.62 V *vs.* Li^+/Li at various rates. The film weights to calculate the specific capacities were estimated from the film thickness and the theoretical density of 5.0 g cm^{-3}. It should be noted that the cell voltage is presented by adding 0.62 V, which is the electrode potential of the In–Li alloy *versus* Li metal, to the measured voltage in order to show the voltage as if Li metal were used as the counter electrode.

3. Results and discussion

3.1. Influences of deposition rate on the $LiCoO_2$ films

The deposition rate has attained *ca.* 1.2 Å s^{-1} under this condition with higher fluence and laser repetition rate, which is 31 times higher than that in our previous study [10]. Fig. 1a shows out-of-plane XRD patterns of the films deposited under fast deposition conditions, where P_{O2} was kept at 0.1 Pa, while T_{sub} varies from 600 to 800 °C. Because epitaxial $LiCoO_2$ films exhibit (104) orientation on $SrTiO_3$ (100) substrates, 104 reflections appear in the patterns from the films. Increasing T_{sub} increases the diffraction intensity, as indicated in Fig. 1b, which is attributable to the enhanced crystallinity by the increasing T_{sub}. On the other hand, the increasing T_{sub} to 750 °C gives another reflection around $2\theta = 43°$ ($d = 2.1$ Å), which suggests inclusion of an impurity phase in the films. The reflection is denoted by "rock-salt $LiCoO_{2-\delta}$ 200" in the figure for the reason discussed later.

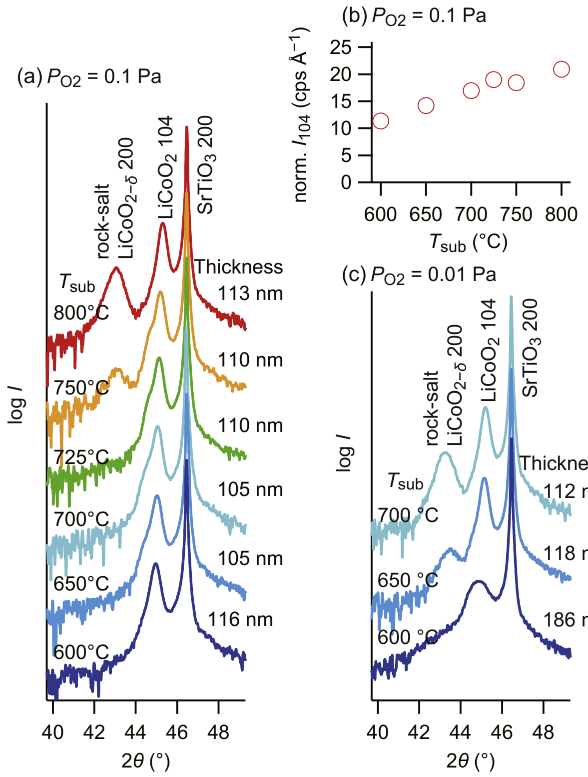

Fig. 1. Out-of-plane XRD patterns of the $LiCoO_2$ films grown under various T_{sub} and P_{O2} = 0.1 Pa (a), and 0.01 Pa (c). The vertical axes indicate the intensity in logarithmic scale (log I). Intensities of the $LiCoO_2$ 104 diffractions in (a) are normalized by the film thickness (norm. I_{104}) and plotted against T_{sub} in (b) in linear scale. Thickness of the films is indicated near the respective patterns.

Fig. 2 demonstrate electrode properties of these films. It is clear from the figure that the increasing T_{sub} from 600 to 750 °C improves the electrode performance; that is, the film deposited at $T_{sub} = 600$ °C delivers only a small discharge capacity of 37 mAh g^{-1} even at a low rate of 0.01 C, while increasing T_{sub} to 750 °C has increased it to 91 mAh g^{-1}. Discharge capacity at the 2 C-rate also increases from 10 to 40 mAh g^{-1} in this T_{sub} range. On the other hand, increasing T_{sub} to 800 °C worsens the electrode performance to the contrary.

The coincidence between the results from the XRD and electrochemical-measurement suggests two factors that govern the electrode performance of the $LiCoO_2$ films: one is the crystallinity, and the other is the presence of the impurity phase that gives a reflection at $d \approx 2.10$ Å. That is, the increasing T_{sub} up to 725–750 °C that enhances the crystallinity improves the electrode performance, while the further increasing T_{sub} that gives rise to the appearance of the impurity phase worsen it. Because the highest discharge capacity is only 91 mAh g^{-1} even at the low rate discharge of 0.01 C, higher electrode performance is expected to be achieved through eliminating the impurity phases as well as enhancing the crystallinity. However, higher T_{sub} for further enhancing the crystallinity increases the amount of the impurity phase, as shown in Fig. 1. Therefore, it is necessary to elucidate the origin of the impurity phase in order to break out of the dilemma.

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