



Short communication

Lattice orientation control of lithium cobalt oxide cathode film for all-solid-state thin film batteries

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HIGHLIGHTS

- ▶ Lithium cobalt oxide thin film cathodes for the all-solid-state thin film batteries.
- ▶ The enhancement of ionic and electrical conductivities by controlling the lattice orientation.
- ▶ The improved rate performance of the cathode films with the controlled grain growth.

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ABSTRACT

For the application to all-solid-state thin film batteries, LiCoO₂ thin films are deposited by RF-sputtering with controlling the lattice orientations to maximize lithium-ion diffusivity in film textures. The nano-sized crystalline grains grow up with the (003) preferred orientation parallel to the substrates at room temperature due to the lowest surface energy of this atomic plane. However, because the surface energy difference of atomic planes of LiCoO₂ reduces with increasing substrate temperature, the influence of surface energy becomes weaker at high temperature. The LiCoO₂ thin films with the (110) preferred orientation are obtained at higher temperatures by dominant influence from the lowest the volume strain energy of this orientation. To take advance of this orientation effect in full cell, the influences of the metallic current collector layer on the structural properties of sputtered cathode are investigated. It turns out that the Li₂O buffer layers between the cathode films and the metallic current collector layers can suppress the formation of lithium-deficient phase, Co₃O₄, and the growth of (003) plane by reducing the lattice match between of LiCoO₂ plane and Al(111) plane. The LiCoO₂ films with the controlled orientation show enhanced rate performance owing to improved interfacial resistance and lithium-ion conductivity.

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1. Introduction

Needs for miniaturized electronic device have created demands on the development of all-solid-state thin film batteries [1,2]. This type of battery is suitable as a power source in medical diagnosis devices, drug delivery devices, active RF cards, miniature transmitters, personal data assistant systems and micro electro mechanical systems (MEMS) devices [3–5]. The micro battery cell is usually less than 10 μm in total thickness and aims for integration with microelectronic devices. Since the first epoch-making report on practical thin film battery was announced in 1982 from Hitachi Corporation, intensive efforts have been made to obtain high performance electrode and electrolyte materials for thin film

batteries [6]. However, in spite of numerous research efforts, the real challenge still resides in finding appropriate thin film materials to satisfy the requirements imposed by of the electronic devices in terms of specific capacity, cycle life, reliability, and safety.

A lithium-ion battery contains an electrolyte, an anode, and a cathode. Electrolyte provides the separation of ionic transport and electronic transport, and electrodes act as a source or a reservoir of lithium ions. The electrode carries out the reversible electrochemical lithium insertion–extraction reaction during battery cycling. Thus, cathode system must provide the mobility of both lithium ions and electrons. However, many electrochemically active materials do not provide enough electronic conduction, so it is necessary to add supplementary electronic conducting materials such as carbon black. For example, olivine-type structure materials of LiMPO₄ (M = 3⁺ cation) have intrinsic disadvantages such as low electronic conductivity lower than 10^{−9} S cm^{−1} and the low lithium-ion diffusivity preventing the realization of its theoretical

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capacity [7,8]. These drawbacks prevent it from being applied as a thin film cathode for all-solid-state thin film batteries since thin film cathode cannot contain additives such as conductive agents or binders. The electrochemical performance of cathode films should be maximized by fully utilizing their intrinsic properties.

Therefore, it is a natural consequence that LiCoO_2 thin films have received considerable attention as a cathode for thin film batteries due to their high electronic conductivity [9]. LiCoO_2 has hexagonal layered crystal structure, consisting of the rhombohedron constructed by cobalt and lithium alternately occupying octahedral sites between adjacent close-packed planes of oxygen [10–12]. It exhibits alternating Co^{3+} and Li^+ planes in ABCABC stacking arrangement, with lithium ions in octahedral sites between O–Co–O sheets. Lithium-ion diffusion occurs via vacancy hopping mechanism within the lithium plane. Electrical properties of this layered structure will be strongly dependent on the crystal orientation due to its anisotropic crystal structure. Thus, in case of layered LiCoO_2 in all-solid-state thin film batteries, lithium-ion mobility and electrochemical reaction with the solid electrolyte and the current collector can be improved by minimizing the interfacial resistance of cathode layers through controlling growth orientation. Bouwman et al. [13] reported that the vertical alignment of (110) plane to the substrates is favorable for fast lithium-ion diffusion in the structures, while the lithium diffusivity of the thin films with (003) plane aligned horizontally to substrate is lower by a few orders of magnitude. Also, Dudney and Jang [14] reported the influence of cathode film thickness on the discharge properties of the thin film batteries. The crystallographic planes with (003) preferred orientation was grown horizontally to the substrate in the early stage of growth, while the grains with (101) and (104) planes parallel to the substrate were grown in the later stage for the films thicker than about $\sim 1 \mu\text{m}$.

However, in either study, homogeneous and stable microstructures with the desirable crystallographic orientation have not been achieved. Therefore, we investigated the method to control the lattice orientation of LiCoO_2 films to improve intercalation characteristics of all-solid-state battery. The structural alteration by various growth conditions was also investigated, and the effects of this microstructure control on electrochemical performance were studied.

2. Experimental

The lithium cobalt oxide thin films were deposited onto silicon substrates by radio-frequency magnetron sputtering. Silicon substrates were washed by HF, ethanol, and distilled water and dried thoroughly. A 2-inch commercial target (LTS, USA) was used, and it was bonded onto copper plates. LiCoO_2 sputtering was carried out under working pressure of 5×10^{-3} Torr with 90% Argon (5 N pure) – 10% oxygen (5 N pure) mixed gas. The RF power used for cathode deposition was 150 W, and the distance between the substrate and the target was 10 cm. The substrate holder was rotated to obtain homogeneous films. LiCoO_2 thin films show deposition rate of about $5\text{--}6.7 \text{ nm min}^{-1}$, and the thickness of the samples deposited for 60 min was about 300–400 nm. The targets were pre-sputtered for 30 min under the same conditions in order to eliminate impurities. The as-deposited LiCoO_2 thin films were annealed at 500°C for 2 h in air.

For the investigation of the metallic current collector effect, the aluminum metal was sputtered with thickness of $\sim 20 \text{ nm}$ on silicon wafers. Also, $\text{Li}_2\text{O}/\text{Al}/\text{Si}$ substrates were prepared by depositing Li_2O for 10 min on the Al current collector film to control the influence of the metallic layer. The crystallographic orientation of cathode thin films was characterized by X-ray diffraction using a Rigaku Ultima IV with $\text{Cu-K}\alpha$ radiation. The surface and cross-

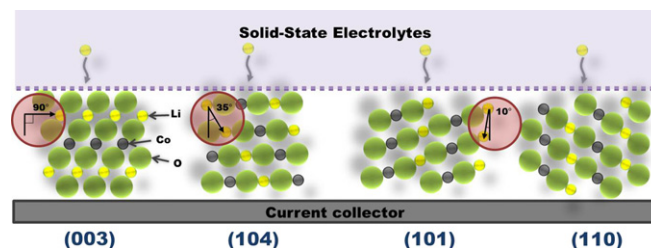


Fig. 1. Lithium-ion diffusion and intercalation pathway in LiCoO_2 thin film layers oriented to various lattice planes.

sectional morphology of thin films were observed by scanning electron microscopy (Hitachi S-4800, Japan). Electron-transparent samples for transmission electron microscopy investigations were prepared by using the combination of Focused Ion Beam (FIB) and scanning electron microscopy system (SMI-8300, Japan).

To evaluate the electrochemical properties, the 2032 coin-type half-cells were used. The cells were made up of lithium foils as a counter and reference electrode, a LiCoO_2 cathode thin films deposited with an active area of $\sim 1 \text{ cm}^2$ and a thickness of $\sim 500 \text{ nm}$ as a working electrode, and 1 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 vol%) as electrolyte. The cells were electrochemically cycled over the voltage range of 3.3 and 4.1 V by applying the various current densities of 20–640 $\mu\text{A cm}^{-2}$ at room temperature.

3. Results and discussion

Fig. 1 illustrates the intercalation pathways of lithium ions through various lattice planes of LiCoO_2 layers. The intercalation pathway for (003) plane is horizontal to substrate surface, while that of (110) plane is almost vertical to substrate surface. The angle between lithium-ion pathway and lattice planes is decreased from (003) to (110) plane. It is expected that LiCoO_2 films with different orientations should exhibit different diffusion kinetics. Takahashi et al. [15,16] demonstrated that the electrical resistance of (110) plane of LiCoO_2 structure is about two-orders of magnitude smaller than (003) plane. Generally, in the deposition of the anisotropic structures, the formation of the specific lattice plane can be explained by the minimization of the structural energy at a given condition. Bates et al. [17] have shown that the crystalline lattice

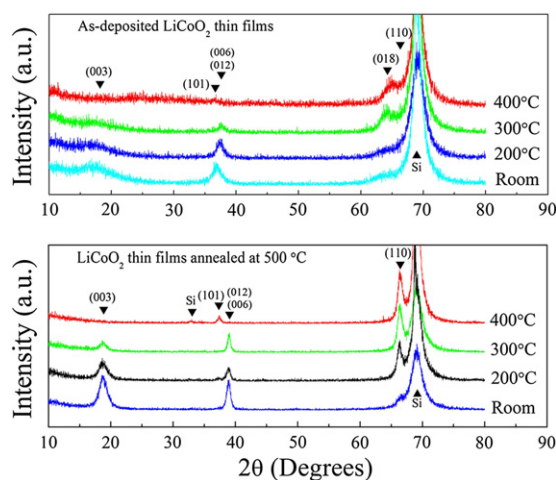


Fig. 2. X-ray diffraction patterns of the as-deposited and annealed lithium cobalt oxide thin films deposited at various substrate temperatures.

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