Preparation of Li–Co–O film by metal organic chemical vapor deposition

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LiCoO₂ films were prepared on polycrystalline Al₂O₃ substrates by metal organic chemical vapor deposition (MOCVD), and the effect of the Li to Co source vapor ratio ($R_{\text{Li/Co}}$) and substrate temperature (T_{sub}) on the phases, orientation, morphology, and deposition rates were investigated. At $R_{\text{Li/Co}} > 2.0$, Li₂CO₃, Li_xCo_{1–x}O, and a LiCoO₂–CoO solid solution were co-deposited with LiCoO₂, whereas Co₃O₄ was co-deposited with LiCoO₂ at $R_{\text{Li/Co}} < 0.7$. Single-phase LiCoO₂ films were obtained in the $R_{\text{Li/Co}}$ range of 0.7–2.0 at $T_{\text{sub}} > 873$ K. Rutherford backscattering spectrometry revealed that single-phase LiCoO₂ film had uniform and stoichiometric composition. The orientation of single-phase LiCoO₂ films changed from (003) to (104) and (012) with increasing T_{sub} at $R_{\text{Li/Co}} \sim 1.0$. LiCoO₂ film co-deposited with Co₃O₄ at $R_{\text{Li/Co}} = 0.4$ showed significant (101) orientation. The (003)-oriented LiCoO₂ had a flat surface with hexagonal faceted texture, whereas the (101)- and (104)-oriented LiCoO₂ had platelet grains in which the plate faces were tilted relative to the substrate surface. The highest deposition rate of single-phase LiCoO₂ film was 10–20 $\mu\text{m h}^{-1}$, which was 100 times greater than that reported in the literature.

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1. Introduction

Lithium cobaltate (LiCoO₂) cathode materials have exhibited high capacity and good reversibility in rechargeable Li ion batteries.¹⁾ Because of the excellent electrochemical properties, LiCoO₂ film has been extensively studied and fabricated for cathode film in all solid-state thin-film lithium-ion batteries for meeting the strict requirements of high power density and safety.²⁾ LiCoO₂ has a rock-salt structure (space group: $R\bar{3}m$), in which the anions and cations form layers perpendicular to the *c*-axis direction.³⁾ The charging/discharging of Li⁺ ions to and from the LiCoO₂ cathode takes place two-dimensionally in the Li layer between the anion layers along the *c*-plane.⁴⁾ Hence, the orientation and morphology of the LiCoO₂ films should be controlled for good transportations of Li⁺ ions at interfaces between a cathode and an electrolyte.

Fabrication of LiCoO₂ film has been reported by pulsed laser deposition (PLD),^{4)–6)} spray pyrolysis,^{7),8)} sputtering,^{9)–12)} chemical vapor deposition (CVD),^{13)–16)} and sol–gel synthesis.^{17),18)} In general, LiCoO₂ film is likely to grow in the *c*-axis direction because of the low surface energy of the (001) plane.^{12),19)} However, the intercalation/deintercalation of Li⁺ ions across the (001) plane of LiCoO₂ is rather difficult whereas that along the (001) plane can be easier. Therefore, non-(003) oriented LiCoO₂ films have been fabricated by using the PLD and sputtering methods. Bates and Hart prepared (101)- and (104)-oriented LiCoO₂ films by RF magnetron sputtering after annealing.^{10),12)} Xia reported that Li⁺ ion diffusivity in (104)-oriented LiCoO₂ film prepared by PLD was ten times faster than that in a (003)-oriented film.⁴⁾ Randomly oriented LiCoO₂ films prepared by PLD had better charge/discharge capacities than (003)-oriented films.²⁰⁾

The CVD technique allows the preparation of films at high deposition rates while controlling the morphology and orientation. The characteristics favor the fabrication of electrode films for high-capacity Li⁺ ion batteries.²¹⁾ Although Co₃O₄ films with preferred orientation have been fabricated using CVD,^{22)–24)} there are few reports regarding the control of the orientation of LiCoO₂ films by CVD. We reported (104)- and (018)-oriented LiCoO₂ films deposited on Al₂O₃ and MgO single crystals by CVD, in which the orientation of LiCoO₂ was dominated by the lattice matching to a plane of the single crystalline.^{25),26)} Here, the CVD conditions such as deposition temperature and supply rates of precursor vapors affect the film structure as well as the phase formation, which is another approach to fabricate LiCoO₂ films having a favorable orientation, irrespective of the crystal orientations of substrates. This study aims to prepare LiCoO₂ and its composite films orientated not only to (003) but also to non-(003) such as (104) and (101) on polycrystalline substrates. We prepared Li–Co–O films on polycrystalline Al₂O₃ substrates by CVD, and investigated the effect of the Li to Co source vapor ratio ($R_{\text{Li/Co}}$) and substrate temperatures (T_{sub}) on the phase formation, orientation, morphology and deposition rates of the Li–Co–O films.

2. Experimental

Li–Co–O films were prepared in a vertical cold-wall type CVD chamber shown in Fig. 1. Li(DPM) (dipivaloylmethanato-lithium) and Co(DPM)₃ (tri-dipivaloylmethanato-cobalt) were used as precursors. The vaporization temperature of Co(DPM)₃ was fixed at 465 K, whereas that of Li(DPM) ranged from 517–559 K. The $R_{\text{Li/Co}}$ ranged from 0.4–5.0. The Li- and Co-source vapors were carried to the CVD reactor by Ar gas. Oxygen gas was separately supplied by a double-tube nozzle and mixed with the Li and Co source vapors above the substrate. The total gas flow rate was fixed at $3.3 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. A polycrystalline Al₂O₃

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Fig. 1. Schematic of the CVD apparatus.

Table 1. Deposition conditions of Li-Co-O films

Vaporization temperature	
Li(dpm)	517–559 K
Co(dpm) ₃	465 K
Ar carrier gas flow rate	
for Li Li(dpm)	$0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
for Co(dpm) ₃	$0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Li to Co ratio ($R_{\text{Li/Co}}$)	0.4–5.0
O ₂ gas flow rate	$1.66 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Substrate	mirror-polished Al ₂ O ₃
Substrate temperature (T_{sub})	523–1223 K
Total pressure (P_{tot})	400 Pa
Distance between nozzle and substrate	5 mm
Deposition time	600–900 s

substrate (99.5% purity; 10 mm × 10 mm × 1 mm; Japan Fine Ceramics Co.) was set on a hot-stage, and T_{sub} were monitored by a thermocouple. Li-Co-O films were deposited at T_{sub} = 523–1223 K. The total pressure in the CVD chamber (P_{tot}) was fixed at 400 Pa. The experimental conditions are summarized in **Table 1**.

The phases and orientation of Li-Co-O films were analyzed by X-ray diffraction (θ -2 θ XRD, Rigaku RAD-2C). The compositional depth profiles of the Li-Co-O films was measured by Rutherford backscattering spectroscopy (RBS) using a 950 keV H⁺ beam obtained from a 1.7 MV tandem accelerator. The RBS spectra were evaluated by using the computer code SIMNRA 6.0²⁷⁾ where non-Rutherford cross sections were used for ⁷Li(p, p)⁷Li²⁸⁾ and ¹⁶O(p, p)¹⁶O.²⁹⁾ The surface and cross-sectional morphologies were observed by field emission-scanning electron microscopy (FE-SEM; JEOL, JSM-7500F). The deposition rate was calculated from the deposition time and thickness.

3. Results and discussion

Figure 2 depicts the effect of $R_{\text{Li/Co}}$ and T_{sub} on the XRD patterns of Li-Co-O films. At $R_{\text{Li/Co}}$ = 0.4, spinel Co₃O₄ co-deposited with LiCoO₂ [Fig. 2(a)]. Single-phase LiCoO₂ films were obtained at $R_{\text{Li/Co}}$ = 0.9 and 1.2 [Figs. 2(b) and 2(c)]. At $R_{\text{Li/Co}}$ = 3.9 [Fig. 2(d)], LiCoO₂ and Li₂CO₃ were identified whereas the reflection peaks of CoO at 38.8, 42.7, and 62.0° had shifted to higher angles than those of the powder pattern of CoO (JCPDS card No. 48-1719). It is known that Li and CoO can form Li_xCo_{1-x}O solid solutions with the rock-salt struc-

Fig. 2. Effect of $R_{\text{Li/Co}}$ and T_{sub} on the XRD patterns of Li-Co-O films; (a) $R_{\text{Li/Co}}$ = 0.4 and T_{sub} = 923 K, (b) $R_{\text{Li/Co}}$ = 0.9 and T_{sub} = 923 K, (c) $R_{\text{Li/Co}}$ = 1.2 and T_{sub} = 1123 K and (d) $R_{\text{Li/Co}}$ = 3.9 and T_{sub} = 923 K.

Fig. 3. Effect of $R_{\text{Li/Co}}$ and T_{sub} on phases of Li-Co-O films.

ture.^{3),21),30)} Therefore, the reflection peaks of CoO were denoted as those of Li_xCo_{1-x}O in Fig. 2(d). The x value in Li_xCo_{1-x}O was 0 < x < 0.2. In Li-Co-O films, the x value of Li_xCo_{1-x}O was estimated at 0.085–0.15 from the lattice parameter of Li_xCo_{1-x}O.³⁾ The effects of $R_{\text{Li/Co}}$ and T_{sub} on the phase formation of Li-Co-O films are shown in **Fig. 3**. At $R_{\text{Li/Co}}$ > 2.1 and T_{sub} = 923 K, a mixture of LiCoO₂, Li₂CO₃, and Li_xCo_{1-x}O was obtained, whereas no Li₂CO₃ was identified at T_{sub} > 1023 K. Since Li₂CO₃ is unstable and decomposes at 923 K, the Li₂O

Fig. 4. RBS spectrum of 950 keV protons incident on the LiCoO₂ film prepared at $R_{\text{Li/Co}} = 0.9$ and $T_{\text{sub}} = 923$ K. The solid line is the simulation for the LiCoO₂ film on Al₂O₃ substrate using SIMNRA code.

phase must have formed at $R_{\text{Li/Co}} > 2.0$, and reacted with CO₂ gas during the cooling process or after being exposed to air. Li₂CO₃ formation due to air exposure was reported in Li₂ZrO₃ and Li₂TiO₃.³¹⁾ At $R_{\text{Li/Co}} < 0.5$ and $T_{\text{sub}} > 923$ K, Co₃O₄ co-deposited with LiCoO₂. At $T_{\text{sub}} = 823$ K, a mixture of Co₃O₄, Li_xCo_{1-x}O and LiCoO₂ was deposited irrespective of $R_{\text{Li/Co}}$. A single-phase LiCoO₂ film was obtained in the $R_{\text{Li/Co}}$ range from 0.5–2.0 at $T_{\text{sub}} > 923$ K. **Figure 4** depicts the backscattering spectrum of the LiCoO₂ film prepared at $R_{\text{Li/Co}} = 0.9$. The backscattering yielded edges at 580, 780, and 940 keV that corresponded to those of protons backscattered from Li, O, and Co atoms at the surface of the LiCoO₂ film, respectively. The solid line is from the simulation of a stoichiometric LiCoO₂ film, in which plural scattering is included.²⁷⁾ The simulated areal density of LiCoO₂ was 2.77×10^{23} atoms m⁻² and was converted to a thickness of 2.22 μm assuming a density of LiCoO₂ of 5.06 Mg m⁻³. The experimental backscattering spectrum agreed well with the simulation, indicating that the LiCoO₂ film had a uniform stoichiometric composition throughout the thickness. Since the source vapors, i.e., Li(DPM) and Co(DPM)₃, contain hydrocarbon ligands, the presence of C impurities in LiCoO₂ films is possible; however no increase in the backscattering yield of C was identified in the spectrum. Therefore, we inferred that the LiCoO₂ film contained almost no C impurities.

A significantly high (003) reflection peak was observed in the LiCoO₂ film prepared at $R_{\text{Li/Co}} \sim 1.0$ and $T_{\text{sub}} = 923$ K [Fig. 2(b)], whereas the (104) reflection was prominent at $T_{\text{sub}} = 1123$ K [Fig. 2(c)]. The LiCoO₂ film containing Co₃O₄ prepared at $R_{\text{Li/Co}} = 0.4$ had a prominent (101) peak [Fig. 2(a)]. The orientation can be evaluated by the Harris texture coefficient (TC) using Eq. 1.³²⁾

$$TC(hkl) = N \frac{I_m(hkl)/I_0(hkl)}{\sum I_m(hkl)/I_0(hkl)} \quad (1)$$

where $I_m(hkl)$ and $I_0(hkl)$ is the intensity from the (hkl) plane, by measurement, and the powder pattern, respectively. (003), (101), (012), (104), and (018) peaks were used in the calculation ($N = 5$). $TC(hkl)$ values range between 0 and N , depending on the orientation of the (hkl) plane. The TC of a non-oriented plane

Fig. 5. Effect of T_{sub} on orientations [$TC(003)$, $TC(104)$ and $TC(012)$] of single-phase LiCoO₂ films at $R_{\text{Li/Co}} \sim 1.0$, and on $TC(101)$ of LiCoO₂ for LiCoO₂–Co₃O₄ composite films at $R_{\text{Li/Co}} = 0.4$.

is 1.0. If the $TC(hkl)$ is more than 1.0, the film can be defined as being partially oriented relative to the (hkl) plane. **Figure 5** depicts the effect of T_{sub} on $TC(003)$, $TC(104)$ and $TC(012)$ of the LiCoO₂ films prepared at $R_{\text{Li/Co}} \sim 1.0$, and on $TC(101)$ of the LiCoO₂ film containing Co₃O₄ prepared at $R_{\text{Li/Co}} = 0.4$. The $TC(003)$ of LiCoO₂ films prepared at $T_{\text{sub}} = 823$ to 1073 K was 2.5 to 4, indicating a significant (003) orientation. At $T_{\text{sub}} = 1123$ –1173 K, the LiCoO₂ films were oriented to (104) as the $TC(104)$ was 2–2.5 and $TC(003)$ was lower than 1. The $TC(012)$ reached 2.5 in the single-phase LiCoO₂ film prepared at $T_{\text{sub}} = 1223$ K. The $TC(101)$ of the LiCoO₂ film containing Co₃O₄ prepared at $R_{\text{Li/Co}} = 0.4$ and $T_{\text{sub}} = 923$ K reached 2.9.

Figure 6 depicts the typical surface morphology of (003)- and (104)-oriented LiCoO₂ films, and that of (101)-oriented LiCoO₂ film containing Co₃O₄. Flat surface with hexagonal facets, which would reflect c -planes in the rhombohedral LiCoO₂ lattice, were observed in the (003)-oriented film at $R_{\text{Li/Co}} = 1.0$ and $T_{\text{sub}} = 923$ K (a). Rounded platelet grains were grown in the (104)-oriented LiCoO₂ film at $R_{\text{Li/Co}} = 1.2$ and $T_{\text{sub}} = 1123$ K (b). Elongated platelets with a thickness of several tens nm were observed (101)-oriented LiCoO₂ film containing Co₃O₄ prepared at $R_{\text{Li/Co}} = 0.4$ and $T_{\text{sub}} = 923$ K (c). Given the lowest surface energy of the (003) plane forming the layer-stacking structure of LiCoO₂, the rounded and elongated platelet facets [Figs. 6(b) and 6(c)] could be (003) LiCoO₂ planes tilted at 55 and 79° relative to the (104) and (101) planes. Further micro-structural analysis using a transmission electron microscope are still required to determine the detail textures.

Figure 7 depicts the effect of T_{sub} on the deposition rates of Li–Co–O films compared with that reported by Cho and Yoon¹³⁾ in a Arrhenius format. Li–Co–O films were single-phase LiCoO₂ at $T_{\text{sub}} > 923$ K, a mixture of Li_xCo_{1-x}O, Co₃O₄, and LiCoO₂ at $T_{\text{sub}} = 823$ –873 K, and CoO at $T_{\text{sub}} < 773$ K. The deposition rate linearly increased with increasing T_{sub} below 773 K with activation energy of 34 kJ mol⁻¹. The Arrhenius relationship between T_{sub} and deposition rates implies that the film growth could be controlled by surface reaction forming CoO at T_{sub} below 773 K. Although there are no literature data on the activation energy of CoO formation on the substrate surface by

Fig. 6. Surface morphology of LiCoO₂ films prepared at $R_{\text{Li/Co}} \sim 1.0$ and $T_{\text{sub}} = 923$ (a) and 1123 K (b), and that of LiCoO₂ films containing Co₃O₄ at $R_{\text{Li/Co}} = 0.4$, and $T_{\text{sub}} = 923$ K (c).

Fig. 7. Effect of T_{sub} on the deposition rate of Li-Co-O film.

CVD, the activation energy for the growth of Co₃O₄ was reported between 82 and 101 kJ mol⁻¹.³³⁻³⁵ The growth of a mixture of CoO and Co₃O₄ was reported to decrease the apparent activation energy to 47–58 kJ mol⁻¹.³⁶ Hence, the activation energy for the formation of single-phase CoO is expected to be lower than Co₃O₄, which is consistent with the present value of 34 kJ mol⁻¹. In the high T_{sub} region ($T_{\text{sub}} > 800$ K) in which LiCoO₂ formed, the deposition rates became almost constant or slightly decreased (Fig. 7). It is commonly understood that chemical reactions are fast enough at high temperatures and the deposition rates are limited by mass transfer (diffusion) in the gas phase and depended less on temperature.³⁷ Homogeneous reactions in the gas phase would be also attributed to the slight decrease in the deposition rates at $T_{\text{sub}} > 900$ K.³⁸ The deposition rate for single-phase LiCoO₂ at $T_{\text{sub}} > 923$ K was approximately 10–20 μm h⁻¹ which is 100 times higher than that reported by Cho and Yoon.¹³ These authors prepared (003)-oriented LiCoO₂ films and regarded the limiting factor in LiCoO₂ formation as mass transfer in the gas phase since the deposition rate did not depend on the deposition temperature (activation energy: 14 kJ mol⁻¹). While the temperature range of LiCoO₂ formation in their work was from 573–723 K, which is lower than that in the present study, we found that the preferred orientation of LiCoO₂ changed from (003) to (104) at $T_{\text{sub}} \sim 1100$ K (Fig. 5). The difference in the deposition rate and temperature range for LiCoO₂ formation

between the present study and the report of Cho and Yoon could be caused by the CVD regime, i.e., precursors, delivery system of the precursors to substrates and deposition pressure. Note that Li(TMHD), (TMHD: C₁₁H₁₉O₂, 2,2,6,6-tetramethyl-3,5-heptanedionate), and Co(TMHD)₃ were dissolved in an organic solvent and evaporated using a vaporizer, and the deposition pressure was at 133 Pa in their work.¹³

4. Conclusions

We prepared single-phase LiCoO₂ and its composite films with Co₃O₄ and Li_xCo_{1-x}O on polycrystalline Al₂O₃ substrates by metal organic CVD. At $R_{\text{Li/Co}} > 2.0$ and $T_{\text{sub}} > 900$ K, Li₂CO₃ and Li_xCo_{1-x}O were co-deposited with LiCoO₂, whereas the composite of LiCoO₂ and Co₃O₄ was deposited at $R_{\text{Li/Co}} < 0.7$. Single-phase LiCoO₂ films having uniform stoichiometric composition in the growth direction without C impurities were obtained in the $R_{\text{Li/Co}}$ range of 0.7–2.0 at $T_{\text{sub}} > 900$ K. The orientation of single-phase LiCoO₂ films changed from (003) to (104) and to (012) with increasing T_{sub} . The LiCoO₂ co-deposited with Co₃O₄ prepared at $R_{\text{Li/Co}} = 0.4$ showed (101) orientation. The (003)-oriented LiCoO₂ had a flat surface with hexagonal faceted texture, whereas rounded platelet grains were observed in the (104)-oriented LiCoO₂ film. The texture of (101)-oriented LiCoO₂ co-deposited with Co₃O₄ was characterized by elongated platelets tilted relative to the substrate surface, reflecting the layered crystal structure of LiCoO₂. The deposition rate for single-phase LiCoO₂ was 10–20 μm h⁻¹, which was hundred times more than the value reported in the literature.

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