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 (Rli/Co) and substrate temperature (Tsub) on the phases, orientation, morphology, and deposition rates were investigated. At Rli/Co > 2.0, Li2O, LiCoO2, Li3O2, and a LiCoO2–CoO solid solution were co-deposited with LiCoO2, whereas CoO2 was co-deposited with LiCoO2 at Rli/Co < 0.7. Single-phase LiCoO2 films were obtained in the Rli/Co range of 0.7–2.0 at Tsub > 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 Tsub at Rli/Co~ 1.0. LiCoO2 film co-deposited with Co3O4 at Rli/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 μm 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.11 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.22 LiCoO2 has a rock-salt structure (space group: R3m), in which the anions and cations form layers perpendicular to the c-axis direction.5 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.2 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),4,5 spray pyrolysis,7,8 sputtering,9,10 chemical vapor deposition (CVD),11,12 and sol–gel synthesis.16,17 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-(001) 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.9,12 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.6 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 oriented 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 (Rli/Co) and substrate temperatures (Tsub) 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 463 K, whereas that of Li(DPM) ranged from 517–559 K. The Rli/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 × 10−3 m3 s−1. A polycrystalline Al2O3,

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sured by Rutherford backscattering spectroscopy (RBS) using a...

The total pressure in the CVD chamber ($P_{\text{tot}}$) was 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–2θ 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 $^7$Li(p, p)$^7$Li28) 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 $R_{\text{Li}/\text{Co}}$ and $T_{\text{sub}}$ on the XRD patterns of Li-Co-O films. At $R_{\text{Li}/\text{Co}} = 0.4$, spinel Co$_3$O$_4$ co-deposited with LiCoO$_2$ [Fig. 2(a)]. Single-phase LiCoO$_2$ films were obtained at $R_{\text{Li}/\text{Co}} = 0.9$ and 1.2 [Figs. 2(b) and 2(c)]. At $R_{\text{Li}/\text{Co}} = 3.9$ [Fig. 2(d)], LiCoO$_2$ and Li$_2$CO$_3$ 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$_x$Co$_{1-x}$O solid solutions with the rock-salt structure.31,21,30) Therefore, the reflection peaks of CoO were denoted as those of Li$_x$Co$_{1-x}$O in Fig. 2(d). The $x$ value in Li$_x$Co$_{1-x}$O was 0 < $x$ < 0.2. In Li-Co-O films, the $x$ value of Li$_x$Co$_{1-x}$O was estimated at 0.085–0.15 from the lattice parameter of Li$_x$Co$_{1-x}$O.31 The effects of $R_{\text{Li}/\text{Co}}$ and $T_{\text{sub}}$ on the phase formation of Li-Co-O films are shown in **Figure 3**. At $R_{\text{Li}/\text{Co}} > 2.1$ and $T_{\text{sub}} = 923$ K, a mixture of LiCoO$_2$, Li$_2$CO$_3$, and Li$_x$Co$_{1-x}$O was obtained, whereas no Li$_2$CO$_3$ was identified at $T_{\text{sub}} > 1023$ K. Since Li$_2$CO$_3$ is unstable and decomposes at 923 K, the Li$_2$
phase must have formed at $R_{Li/Co} > 2.0$, and reacted with CO$_2$ gas during the cooling process or after being exposed to air. Li$_2$CO$_3$ formation due to air exposure was reported in Li$_2$ZrO$_3$ and Li$_2$TiO$_3$. At $R_{Li/Co} < 0.5$ and $T_{sub} > 923$ K, Co$_3$O$_4$ co-deposited with LiCoO$_2$. At $T_{sub} = 823$ K, a mixture of Co$_3$O$_4$, Li$_2$CoO$_3$, and LiCoO$_2$ was deposited irrespective of $R_{Li/Co}$. A single-phase LiCoO$_2$ film was obtained in the $R_{Li/Co}$ range from 0.5–2.0 at $T_{sub} > 923$ K. Figure 4 depicts the backscattering spectrum of the LiCoO$_2$ film prepared at $R_{Li/Co} = 0.9$. The backscattering yielded edges at 580, 780, and 940 keV that correspond to those of protons backscattered from Li, O, and Co atoms at the surface of the LiCoO$_2$ film, respectively. The solid line is from the simulation of a stoichiometric LiCoO$_2$ in which plural scattering is included. The simulated areal density of single-phase LiCoO$_2$ films could be evaluated by the Harris texture coefficient ($TC$) using Eq. 1:

$$TC(hkl) = N \sum \frac{I_{0}(hkl)I_{m}(hkl)}{I_{0}(hkl)}$$

where $I_{0}(hkl)$ and $I_{m}(hkl)$ 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 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 orientations $[TC(003), TC(104) and TC(012)]$ of single-phase LiCoO$_2$ films at $R_{Li/Co} \sim 1.0$, and on $TC(101)$ of LiCoO$_2$ for LiCoO$_2$–Co$_3$O$_4$ composite films at $R_{Li/Co} = 0.4$.

Figure 6 depicts the typical surface morphology of (003)- and (104)-oriented LiCoO$_2$ films, and that of (101)-oriented LiCoO$_2$ film containing Co$_3$O$_4$. Flat surface with hexagonal facets, which would reflect $c$-planes in the rhombohedral LiCoO$_2$ lattice, were observed in the (003)-oriented film at $R_{Li/Co} = 1.0$ and $T_{sub} = 923$ K (a). Rounded platelet grains were grown in the (104)-oriented LiCoO$_2$ film at $R_{Li/Co} = 1.2$ and $T_{sub} = 1123$ K (b). Elongated platelets with a thickness of several tens nm were observed on (101)-oriented LiCoO$_2$ film containing Co$_3$O$_4$ prepared at $R_{Li/Co} = 0.4$ and $T_{sub} = 923$ K (c). The lowest surface energy of the (003) plane forming the layer-stacking structure of LiCoO$_2$, the rounded and elongated platelet facets [Figs. 6(b) and 6(c)] could be (003) LiCoO$_2$ 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 Yoon in an Arrhenius format. Li–Co–O films were single-phase LiCoO$_2$ at $T_{sub} > 923$ K, a mixture of Li$_2$CoO$_3$–Co$_3$O$_4$, and LiCoO$_2$ at $T_{sub} = 823–873$ K, and CoO at $T_{sub} < 773$ 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
we found that the preferred orientation of LiCoO₂ changed from (003) to (104) at $T_{\text{sub}} = 923$ K in their work. The temperature range of LiCoO₂ formation was limited by mass transfer (diffusion) in the gas phase and deposition rates became almost constant or slightly decreased at high temperatures. In the high deposition rates at $T_{\text{sub}} > 900$ K, LiCoO₂ co-deposited with Co₃O₄ 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 changed from (003) to (104) with increasing $T_{\text{sub}}$.

4. Conclusions

We prepared single-phase LiCoO₂ and its composite films with CoO and Li₂CoO₂ on polycrystalline Al₂O₃ substrates by metal organic CVD. At $R_{\text{LiCoO}_2} > 2.0$ and $T_{\text{lab}} > 900$ K, LiCoO₂ and Li₂CoO₂ were co-deposited with LiCoO₂ whereas the composite of LiCoO₂ and CoO was deposited at $R_{\text{LiCoO}_2} < 0.7$. Single-phase LiCoO₂ films having uniform stoichiometric composition in the growth direction without C impurities were obtained in the $R_{\text{LiCoO}_2}$ 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 $T_{\text{sub}}$. The LiCoO₂ co-deposited with CoO prepared at $R_{\text{LiCoO}_2} = 0.4$ 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 CoO was characterized by elongated platelets tilted relative to the substrate surface, reflecting the layered crystal structure of LiCoO₂.

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