Short communication

Structural and electrical properties of LiCoO$_2$ thin-film cathodes deposited on planar and trench structures by liquid-delivery metalorganic chemical vapour deposition

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Abstract

The electrochemical properties of annealed-LiCoO$_2$ cathodes deposited on planar and trench structures by liquid-delivery metalorganic chemical vapor deposition are investigated for various deposition temperatures and input Li:Co mole ratios. With the planar structure, the best crystallinity of the films is obtained at a deposition temperature of 450 °C and an input Li:Co mole ratio of 1.0. The deposition window for optimum initial discharge capacity and capacity retention is a deposition temperature of 450–500 °C and an input Li:Co mole ratio of 1.0, and an input Li:Co mole ratio of 1.0–1.2 at a deposition temperature of 450 °C. The initial discharge capacity and capacity retention of LiCoO$_2$ thin films deposited with an input Li:Co mole ratio of 1.2 at 450 °C are approximately 25 μAh/cm^2 μm and 77%, respectively. The initial discharge capacity of films deposited on a trench structure shows an increase of approximately 130% compared with that of films deposited on a planar structure with an input Li:Co mole ratio of 1.2. The rechargeabilities of films deposited in a trench structure are inferior to those in a planar structure because conformal growth in the trench structure is poor. Thus, a trench structure can improve the initial discharge capacity and capacity retention of lithium microbatteries.
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Keywords: LDMOCVD; LiCoO$_2$ thin films; Step-coverage; Trench-structure; Discharge-capacity; Pt collector

1. Introduction

With the development of electronic devices, thin-film solid-state batteries have received great attention because they can be completely integrated with microcircuits, such as microdevices, microsensors, and very-large-scale integration (VLSI) [1]. The operational acceptability of such integrated devices is contingent on the high specific energy and low power consumption of lithium-ion batteries [2–4]. Encouraged by this practical importance, the fabrication of thin-film cathodes has been the subject of much research in recent years. The three compounds that are of most interest are LiCoO$_2$, LiNiO$_2$ [5], and LiMn$_2$O$_4$ [6]. LiCoO$_2$ has been commercially used as positive electrodes (cathodes) in lithium-ion batteries during the past 10 years as it has high specific capacity, high operating cell voltage, and excellent rechargeability. Accordingly, the structural and physical properties of LiCoO$_2$ have been studied extensively [7–12].

Cathode films are usually prepared by electron beam evaporation [13,14], pulsed-laser ablation [15], sputtering [16,17], the sol–gel method [18], or chemical vapour deposition [19–21]. Although there are various reports of physical vapour deposition techniques, there are particular advantages to be gained by using a chemical vapour process to deposit thin films of these lithiated transition metal oxides. Chemical vapour deposition (CVD) techniques can easily prepare the desired high-temperature crystalline phases of LiCoO$_2$ at temperatures as low as 450 °C, and also offer advantages such as excellent control of stoichiometry and easy control of crystallinity, density and microstructure. CVD techniques also provide good step-coverage in trench structures and thereby can increase the cathode area per unit volume, as compared with planar deposition by physical vapour deposition techniques. The increase in cathode area which results from deposition in trench structures using CVD can enhance the discharge capacity of LiCoO$_2$ cathodes, as first reported by Cho and Yoon [22]. Nevertheless, the effect of annealing treatment on the electrical properties of LiCoO$_2$ cathodes has not been reported for planar and trench structures.

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In this study, LiCoO$_2$ cathode films are prepared on Pt/TiO$_2$/SiO$_2$/Si substrates with planar and trench structures using liquid-delivery metalorganic chemical vapour deposition (LDMOCVD) and then annealed at 700 °C for 30 min in an oxygen ambient. The initial discharge capacities and rechargeabilities of trench-cathode films are investigated for various input Li:Co mole ratios and compared with those of for a planar structure.

2. Experimental

Thin films of platinum (100 Å thick) served as collectors and were prepared on trench-SiO$_2$/Si substrates by LDMOCVD using a Pt(EtCp)Me$_3$ (Pt(C$_5$H$_4$C$_2$H$_5$)(CH$_3$)$_3$) (Kojundo Chem. Lab. Co., Ltd.) precursor. TiO$_{2-x}$ thin layers were used to improve the adhesion between MOCVD-Pt and trench-SiO$_2$/Si substrates and were deposited by LDMOCVD using Ti(i-OPr)(TMHD)$_2$ [Ti(C$_3$H$_7$O)$_2$(C$_{11}$H$_{19}$O$_2$)$_2$] as a precursor. Thin-film LiCoO$_2$ cathodes were prepared by LDMOCVD using Li(TMHD) (TMHD: C$_{11}$H$_{19}$O$_2$) and Co(TMHD)$_3$ (STREM Chemicals, Inc.) as source materials for Li and Co, respectively. The organic precursors were dissolved in a solvent (tetrahydrofran, C$_4$H$_8$O, Sigma–Aldrich Chemical Co., Inc.) to form a source solution of 0.01 M Li(C$_{11}$H$_{19}$O$_2$) and Co(C$_{11}$H$_{19}$O$_2$). A solution of each precursor was mixed together and single-mixture solution at various concentrations were used for preparation of LiCoO$_2$ thin films.

The thin-film cathodes were deposited on planar and trench-CVD-Pt/TiO$_2$/SiO$_2$/Si substrates as a function of Li:Co input mole ratio at various temperatures using a single solution of 0.01 M. A schematic diagram of the LDMOCVD apparatus for LiCoO$_2$ cathode films has been given in an earlier study [21]. The apparatus consists of two main parts: a CVD reactor with a vacuum system, and a liquid source delivery system with a micro-syringe pump (KD Scientific Inc., KDS100) and vapourizer. The vapourizer is composed of a stainless-steel chamber, a stainless-steel mesh filter, a diaphragm vacuum gauge, and a heating system. A carrier gas containing the metalorganic source and oxidants was uniformly supplied to the substrate through a showerhead type nozzle with many holes. The temperature of the vapourizer was maintained at 260 °C during the deposition. When the single-mixture sources were pumped into the vapourizer at a flow rate of 0.4 ml per minute with a micro-syringe pump (KD Scientific Inc., KDS100), they evaporated immediately and were carried into the reactor with nitrogen carrier gas at 50 standard cc per minute (sccm). The typical deposition conditions of the Pt collector, the TiO$_2$ adhesion layer, and the LiCoO$_2$ cathode thin films are summarized in Table 1.

Film morphologies were examined by means of scanning electron microscopy (SEM, TOPCON DS-130C) and atomic force microscopy (AFM, PSI). X-ray diffraction (XRD, Rigaku D/MAX-RC) using Cu K radiation and a Ni filter was used to determine the crystal structure and preferred orientation of the films. The composition of films was qualitatively controlled by variation of the Li:Co mole ratio in the solution. For electrochemical measurements, the LiCoO$_2$ thin films were placed in an open beaker cell which contained 1 M LiClO$_4$ in propylene carbonate (PC) and lithium-foil counter and reference electrodes and was located inside an argon-filled glove box. Charge–discharge tests were performed with an EG&G electrochemical analysis system (model 273A). Discharge curves of the LiCoO$_2$ cathode films as a function of Li:Co composition were investigated at a constant current density of 100 μA cm^{-2} between 4.3 and 3.3 V at room temperature.

3. Results and discussion

Fig. 1(a) and (b) show the X-ray diffraction patterns and the variation of full-width half maximum (FWHM) of LiCoO$_2$ thin films (input Li:Co mole ratio: 1.0) annealed at 700 °C for 30 min in O$_2$ after deposition at each temperature. Annealed samples have a preferred orientation of

Table 1
Deposition conditions of TiO$_2$ adhesion layer, Pt collector, and LiCoO$_2$ cathode by liquid-delivery metalorganic chemical vapour deposition

Deposition parameters	TiO$_2$ adhesion layer	Platinum collector	LiCoO$_2$ cathode
Deposition temperature	450 °C	350 °C	350–550 °C
Deposition pressure	1 T	700 mT	2 T
Precursor	Ti(i-OPr)(TMHD[a])$_2$	Pt(EtCp)Me$_3$[b]	Li(TMHD)Co(TMHD)$_3$
Solvent	Tetrahydrofuran	Tetrahydrofuran	Tetrahydrofuran
Vaporizer temperature	240 °C	130 °C	260 °C
Concentration of precursor	0.05 mol/l	0.05 mol/l	0.01 mol/l
Input mole ratio	–	–	0.6–1.4 (Li:Co)
N$_2$ gas flow rate	150 sccm	100 sccm	50 sccm
O$_2$ gas flow rate	100 sccm	150 sccm	100 sccm
Substrate	Planar and trench SiO$_2$/Si	Planar and trench TiO$_2$/SiO$_2$/Si	Planar and trench Pt/TiO$_2$/SiO$_2$/Si
Annealing	–	–	700 °C, 30 min, O$_2$

[a] TMHD: C$_{11}$H$_{19}$O$_2$.
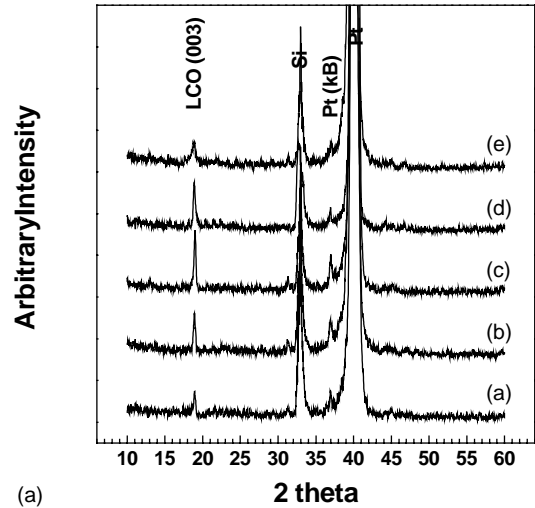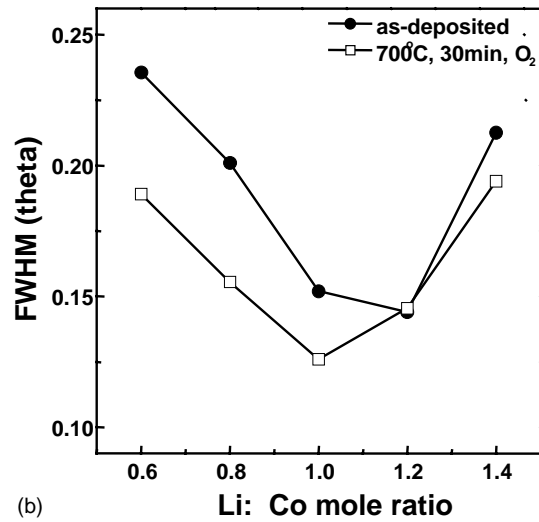[b] Pt(EtCp)Me$_3$: Pt(C$_5$H$_4$C$_2$H$_5$)(CH$_3$)$_3$.
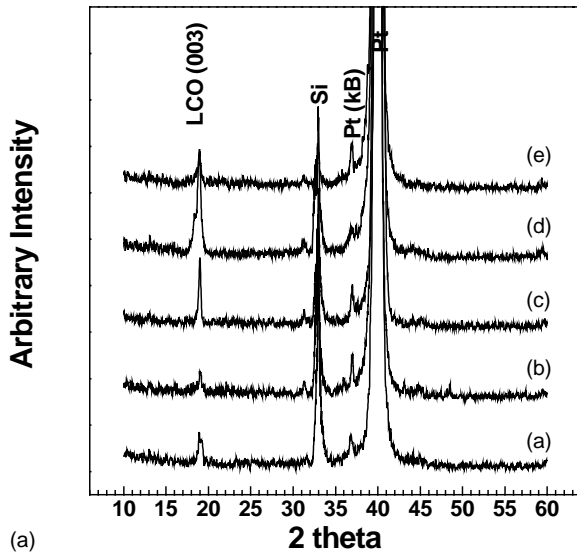
(a)
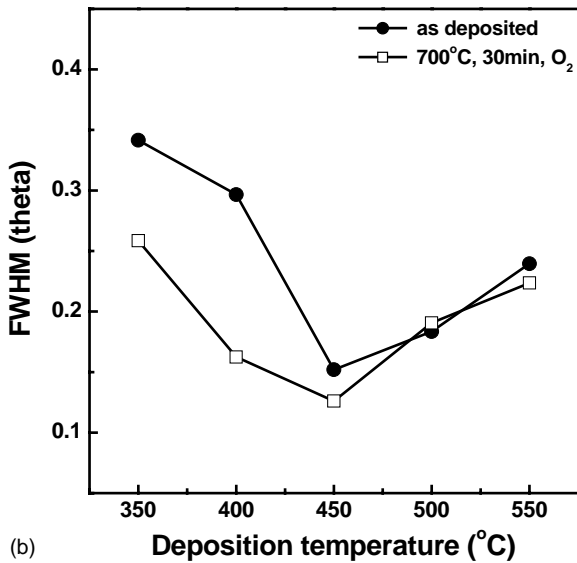
(b)

Fig. 1. (a) X-ray diffraction patterns of LiCoO$_2$ thin films deposited at (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C. (b) FWHM of LiCoO$_2$ thin films as a function of deposition temperature (input Li:Co mole ratio: 1.0, samples annealed at 700 °C for 30 min in O$_2$).

(a)

(b)

Fig. 2. (a) X-ray diffraction patterns of LiCoO$_2$ thin films deposited with input Li:Co mole ratio of (a) 0.6, (b) 0.8, (c) 1.0, (d) 1.2, and (e) 1.4. (b) FWHM of LiCoO$_2$ thin films as a function of input Li:Co mole ratio (samples annealed at 700 °C for 30 min in O$_2$ after deposition at 450 °C).

(0 0 3) and the intensity of the (0 0 3) main peak increases with increasing deposition temperature and decreases at 550 °C, see Fig. 1(a). The crystallinity of the films can be identified from the FWHM of the (0 0 3) peak for various deposition temperatures, as shown in Fig. 1(b). Samples deposited at 450 °C and annealed at 700 °C display the lowest FWHM value. Films deposited at 450 °C have the greatest crystallinity. Fig. 2(a) and (b) present X-ray diffraction patterns and the variation of FWHM of LiCoO$_2$ thin films annealed at 700 °C for 30 min in O$_2$ after deposition at 450 °C as a function of input Li:Co mole ratio. As shown in Fig. 2(a), the peak intensity of the (0 0 3) plane increases with increasing input Li:Co mole ratio up to 1.0, but slightly decreases at ratios above 1.0. These results sug-

gest that the Li concentration in LiCoO$_2$ thin films plays an important role in the crystallinity of the films. As shown in Fig. 2(b), the FWHM of the (0 0 3) plane of LiCoO$_2$ films deposited with an input Li:Co mole ratio of 1.0 shows the lowest value in films annealed at 700 °C, which results in the highest crystallinity.

The rms roughness of LiCoO$_2$ thin films deposited at various temperatures (with Li:Co = 1.0) and as a function of input Li:Co mole ratio at 450 °C is shown in Fig. 3(a) and (b), respectively. The surface roughness increases slightly with increasing deposition temperature up to 450 °C, but increases abruptly above 450 °C, see Fig. 3(a). The roughness of annealed samples deposited at each temperature increases in a similar manner to that of as-deposited samples. The abrupt increase of rms roughness of films deposited above 450 °C may be due to a transition from a surface reaction to a gas-phase transport mechanism. The variation of
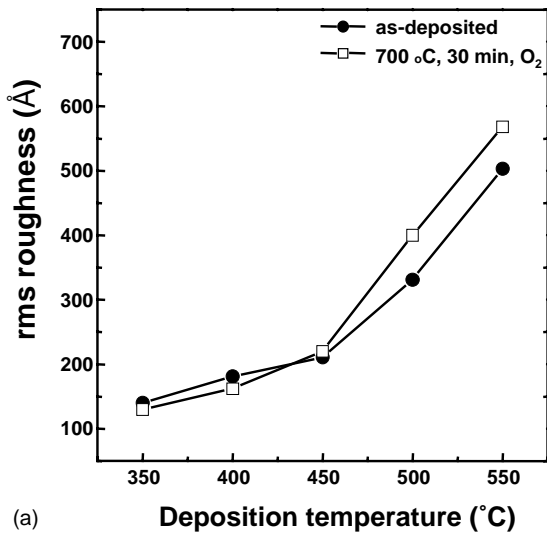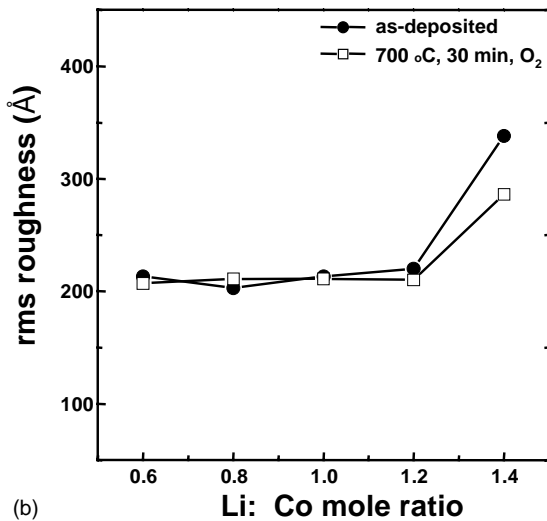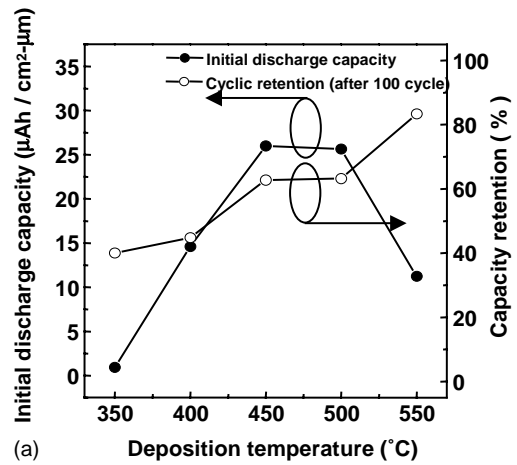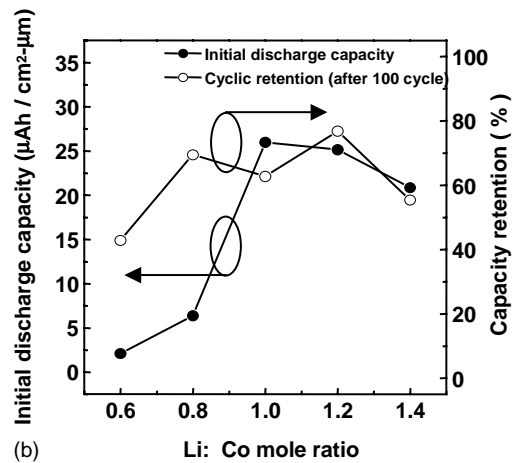
Fig. 3. Variation of rms roughness of LiCoO$_2$ thin films deposited at (a) various temperatures (with Li:Co = 1.0) and (b) as a function of input Li:Co mole ratio at 450 °C.

Fig. 4. Variation of initial discharge capacity and capacity retention after 100 cycles as a function of (a) deposition temperature and (b) an input Li:Co mole ratio at deposition temperature of 450 °C (samples annealed at 700 °C for 30 min in oxygen atmosphere).

surface roughness versus input Li:Co mole ratio at a deposition temperature of 450 °C maintains a constant value of approximately 20 Å up to Li:Co = 1.2, and then increases rapidly (Fig. 3(b)). The latter feature may be due to an increase of lithium incorporation in LiCoO$_2$ films. The variation of initial discharge capacity and capacity retention after 100 cycles as a function of deposition temperature and input Li:Co mole ratio (at a deposition temperature of 450 °C) is shown in Fig. 4(a) and (b), respectively. The deposition window which gives optimum initial discharge capacity and capacity retention is at a deposition temperature of 450–500 °C for an input Li:Co mole ratio of 1.0. The discharge capacity and capacity retention is approximately 25 μAh/cm^2 μm and 63%, respectively. In terms of the input Li:Co mole ratio, the window for optimum initial discharge capacity and capacity retention is at a ratio of approximately 1.0–1.2 at a deposition temperature of 450 °C. The initial discharge capacity

and capacity retention of LiCoO$_2$ thin films deposited with an input Li:Co mole ratio of 1.2 are about 25 μAh/cm^2 μm and 77%, respectively.

A trench structure with an aspect ratio of 1.0 (4 × 4 μm) was used to increase the initial discharge capacity of LiCoO$_2$ thin films. The surface area in the trench structure is 154% greater than that of the planar structure when both structures have the apparent surface area. The step-coverage of Pt/TiO$_2$ deposited on to a SiO$_2$/Si trench structure by LD-MOCVD and LiCoO$_2$ deposited on to a Pt/TiO$_2$ collector is shown in Fig. 5(a) and (b), respectively. An interfacial layer of TiO$_2$ (thickness 10 Å) improves the adhesion between the Pt collector and the SiO$_2$/Si trench. The step-coverages of Pt/TiO$_2$ deposited on SiO$_2$/Si and LiCoO$_2$ on Pt are 65 and 60%, respectively. The variation of the initial discharge capacity of films deposited on both planar and trench structures as a function of input Li:Co mole ratio at 450 °C is given in Fig. 6. The films deposited on both structures at 450 °C were annealed at 700 °C for 30 min in an oxygen atmosphere. The initial discharge capacity of films deposited
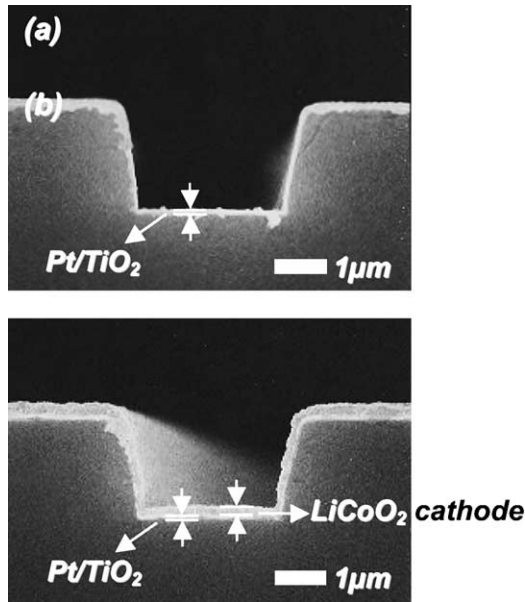
Fig. 5. Step-coverage of (a) Pt/TiO_2 deposited on SiO_2/Si trench structure and (b) $LiCoO_2$ deposited on Pt/TiO_2 collector by LDMOCVD.

on the trench structure shows an increase of approximately 130% compared with that of films on the planar structure for an input Li:Co mole ratio of 1.2.

The rechargeabilities of trench-$LiCoO_2$ thin films deposited at 450 °C with a various input Li:Co mole ratios are presented in Fig. 7. The films deposited with an input Li:Co mole ratio of 1.2 display good rechargeabilities up to 100 cycles. By contrast, the rechargeabilties (∼30%) of films with a trench structure are inferior to those (∼77%) with a planar structure because conformal growth in the trench structure is poor, as shown in Fig. 5(b). First of all,
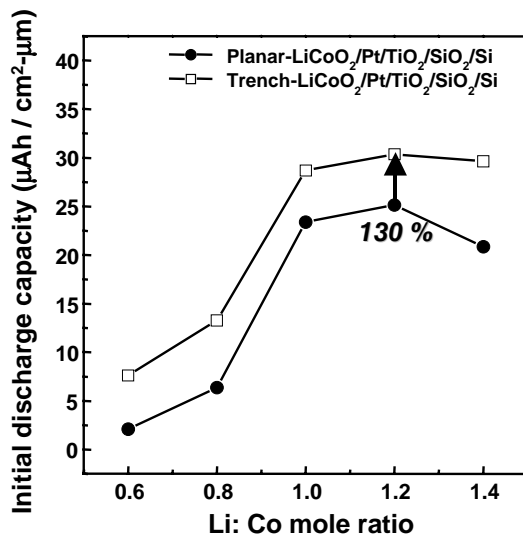

Fig. 6. Variation of initial discharge capacity of films deposited on both planar and trench structures as function of input Li:Co mole ratio at 450 °C (samples annealed at 700 °C for 30 min in oxygen atmosphere).
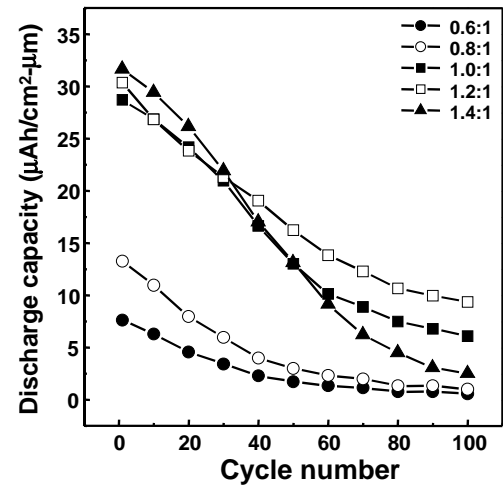

Fig. 7. Rechargeabilities of trench-$LeCoO_2$ thin films deposited at 450 °C with various input Li:Co mole ratios (samples annealed at 700 °C for 30 min in oxygen atmosphere).

the rechargeability in films with a trench structure depends on the improvement of the step-coverage as well as of an increase in crystallinity. Step-coverage in a trench-structure can be improved by controlling the deposition parameters such as deposition temperature, input Li:Co mole ratio, and system pressure.

4. Conclusions

The structural and electrical properties of $LiCoO_2$ cathodes deposited on planar and trench structures by LD-MOCVD have been investigated for various deposition temperatures and input Li:Co mole ratios. The best crystallinity of the films is obtained at a deposition temperature of 450 °C and an input Li:Co mole ratio of 1.0. The deposition window which gives optimum initial discharge capacity and capacity retention is a deposition temperature of 450–500 °C for an input Li:Co mole ratio of 1.0, and an input Li:Co mole ratio of 1.0–1.2 at a deposition temperature of 450 °C. The initial discharge capacity and capacity retention of $LiCoO_2$ thin films deposited with an input Li:Co mole ratio of 1.2 at 450 °C are approximately 25 $\mu Ah/cm^2$ μm and 77%, respectively. The initial discharge capacity of films deposited on a trench structure shows an increase of approximately 130% compared with that for films deposited on a planar structure with an input Li:Co mole ratio of 1.2. The rechargeabilities of films with a trench structure are inferior to those of films with a planar structure because conformal growth in the trench structure is poor.

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