Orientation control of LiCoO₂ epitaxial thin films on metal substrates

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Abstract

We demonstrate the deposition of $\text{LiCoO}_2(11-20)$ epitaxial thin films on chemically etched $\text{Pt}(110)$ substrates, and compare their electrochemical properties with those of $\text{LiCoO}_2(10-14)$ epitaxial thin films on sputter-annealed $\text{Pt}(110)$ reconstructed substrates. Cyclic voltammogram measurements of $\text{LiCoO}_2(11-20)$ epitaxial films exhibit stable charge and discharge operations, despite the application of a compressive strain on the films.

Keywords

Epitaxial films; Lithium ion batteries; LiCoO_2 ; Crystal orientation

1. Introduction

The fabrication of high-quality epitaxial thin films of Li-battery materials is one of the key issues in the investigation of the physical and chemical properties of battery operations and in the improvement of battery performance. Epitaxial growth techniques provide avenues for investigating interfaces in a controlled manner. The control of crystal orientation and area enables quantitative studies that cannot be performed using particle systems.

LiCoO_2 (LCO) with a layered-rhombohedral $\alpha\text{-NaFeO}_2$ structure is of particular interest in battery materials. It has been widely used as a cathode material for commercially available lithium batteries, and is a promising cathode material for all-solid-state lithium batteries [1]. Epitaxial thin films with controlled crystal orientations can be achieved by selecting the low-index planes of the substrate surface [2,3,4]. We have deposited flat $\text{LCO}(0001)$ films (the notation of crystal planes is based on a hexagonal setting) on step-and-terrace $\text{Al}_2\text{O}_3(0001)$ substrates [5], and confirmed their high crystal quality by directly observing Li atoms using transmission electron microscopy (TEM) [6]. Although crystal-orientation control techniques have been established for insulating and electrochemically inactive substrates, few researchers have addressed crystal-orientation control on *metal* substrates and their impact on electrochemical properties.

Preparing epitaxial films on metal substrates allows us to investigate in detail the electrochemical properties of the films [7]. We have successfully controlled the crystal orientation of LCO on $\text{Pt}(110)\text{-(}2\times 1\text{)}$ reconstructed substrate surfaces, and reported on battery operations using liquid and solid electrolytes [8]. The reconstructed $\text{Pt}(110)$ surface consists of alternately arrayed $\{111\}$ nanofacets, exhibiting what is called a

“missing row” zigzag structure. On the reconstructed Pt(110) surface, we observed the growth of LCO(10-14) epitaxial films, which have CoO_2 layers tilted by 52° with respect to the surface normal. In the layered structure of LCO, Li ions have a predominant two-dimensional diffusion along the CoO_2 layers, and it is unlikely that the Li ions can penetrate through a CoO_2 layer to an adjacent layer. This implies that the (10-14)- and (11-20)-oriented LCO epitaxial films are suitable for smooth Li-ion conduction along a direction perpendicular to the LCO films, in contrast to the (0001)-oriented case. Hence, a comparison of the electrochemical properties of LCO(11-20), (10-14), and (0001) films would illustrate the dependence of ion conductivity and electrochemical stability on orientation [2,3,9]. However, there has been no report on the growth of LCO(11-20) epitaxial films on metal surfaces. Furthermore, the electrochemical properties of LCO(11-20) on metal substrates have not been reported on.

In this study, we investigate the effects of substrate surface treatments on the growth of LCO films and report on the epitaxial growth of LCO(11-20) films. We deposited LCO thin films on Pt(110) substrates etched with aqua regia, and found that the substrate surface treatment has a significant influence on the growth orientation of LCO films. Furthermore, the films exhibited different charge/discharge characteristics depending on the orientation, that is, the LCO(11-20) and (10-14) orientations.

2. Experimental

We employed Pt(110) single crystals as substrates, and prepared the substrate surfaces using two methods. One involved a Pt(110) surface etched with aqua regia for 5 min. The other involved a reconstructed Pt(110)- 2×1 surface prepared by extensive

sputtering-annealing cycles in ultrahigh vacuum [10]. Thin films of LCO were deposited on the Pt(110) substrates via pulsed laser deposition [5,8]. A Li-rich target, $\text{Li}_{1.2}\text{CoO}_2$, was used to compensate for the loss of Li during deposition. A KrF excimer laser (wavelength: 248 nm) was used to irradiate the target at a repetition rate of 5 Hz. The fluence at the target was 1.0 J/cm^2 . During the deposition process, the partial pressure of oxygen was 1×10^{-6} Torr, and the substrate was kept at room temperature.

The as-grown samples were epitaxial films, but Li and Co cations were randomly distributed along the c-axis, as discussed by Wang *et al.* [11] and Bouwman *et al.* [12]. Hence, the as-grown films were subsequently annealed at 650°C in air to obtain a layered-rhombohedral $\alpha\text{-NaFeO}_2$ LCO phase [5]. The LCO films were typically 100-nm thick. The crystal structures of the films were characterized using X-ray diffraction (XRD) (D8 Discover, Bruker) and TEM (JEM-2100HC, JEOL Ltd.) [6]. Cyclic voltammetry (CV) measurements were conducted using 1 M of LiClO_4 in ethylene carbonate/diethyl carbonate (1:1 by volume) as the electrolyte, with Li metal foils as anodes. The CV measurements were made at a scan rate of 0.1 mV/s.

3. Results and discussions

First, we discuss the growth of LCO on the Pt(110) substrates chemically etched with aqua regia. The out-of-plane XRD pattern of the LCO film grown on the chemically etched Pt(110) substrate shows an LCO 11-20 peak (Fig. 1(a)). The in-plane XRD pattern (Fig. 1(b)) shows LCO 0003, 0006, and 0009 peaks, in addition to a Pt 111 peak. The ϕ -scans obtained at $\psi = 90^\circ$ ($\psi = 0^\circ$ is the surface normal) show that the LCO 0003 and Pt 111 peaks appear at the same ϕ angles. These results indicate that (11-20)-oriented epitaxial films were grown on the etched Pt(110) substrates, and the

in-plane epitaxial relationship can be described as $[0003]_{\text{LCO}} (11-20)_{\text{LCO}} // [111]_{\text{Pt}} (110)_{\text{Pt}}$. In this orientation, the c-axis and the CoO_2 layers in LCO are parallel and perpendicular to the $\text{Pt}(110)$ surface, respectively, as illustrated in the inset of Fig. 1(a).

In addition to the $\text{LCO}(11-20)$ phase, we found a minor secondary phase with a different crystal orientation. As shown in Fig. 2(a), a θ - 2θ scan obtained at $\psi = 35^\circ$ exhibits LCO 0003 and 0006 peaks in addition to a Pt 111 peak. This result indicates the epitaxial growth of $\text{LCO}(01-18)$, which has a (0001) plane tilted by 35° with respect to the $\text{Pt}(110)$ surface normal (inset of Fig. 2(a)). An identical secondary phase was also observed on the large $\{111\}$ nanofacets formed on the reconstructed $\text{Pt}(110) 2 \times 1$ surface [8], but the volume fraction was much smaller than that on the chemically etched substrate, as confirmed from the XRD peak intensity. Hence we speculate that, owing to the surface roughness of the etched $\text{Pt}(110)$ substrate, the (111) facet of Pt is exposed on the topmost surface. Considering the epitaxial relationship between the $[0003]_{\text{LCO}}$ and $(111)_{\text{Pt}}$, we expect the growth of $\text{LCO}(0001)$ film on this (111) facet. Indeed, exposure of the $\text{Pt}(111)$ facets on the chemically etched $\text{Pt}(110)$ substrate surface is suggested from surface morphology measurements.

An atomic force microscopy (AFM) image of an etched Pt surface shows large surface roughness of $R_a = 29.1$ nm (Fig. 3(a)), which is in contrast to the smaller value observed on the reconstructed $\text{Pt}(110)$ surface ($R_a \approx 0.93$ nm) (Fig. 3(b)). **The surface roughness increases with increasing etching time. When the surface roughness R_a was 18.3 nm prepared by chemically-etching for 3 min, a mixture of $\text{LCO}(11-20)$ and $(10-14)$ phases was grown (not shown here). This implies that the orientation of LCO films depends on the surface roughness of Pt substrate.**

Cross-sectional TEM observation reveals microscopic feature of the LCO films (Fig.

3(c)). The film surface is rough, which agrees with Fig. 3(a) and the thickness is approximately 100 nm as we aimed. The thickness is nearly constant throughout the film. We noticed that film surface morphology is quite similar to substrate surface one. This suggests that substrate surface roughness is a cause of film surface roughness. An electron diffraction pattern taken from the interface region confirms that the LCO film epitaxially grows on the Pt substrate (Fig. 3(d)). The patterns include two sets of hexagonal patterns: One is from Pt observed along [111] direction and the other one is from LCO observed along [0001] direction. This shows that [111] of Pt is parallel to [0001] of LCO in the in-plane direction, which agrees with the in-plane XRD profile in Fig. 1(b). On the other hand, top spots in both of the hexagonal patterns indicate (110) of Pt and (11-20) of LCO. This is again consistent with the out-of-plane XRD profile in Fig. 1(a).

Finally, we examined the electrochemical properties of the epitaxial LCO(11-20) film and compared them with those of the LCO(10-14) film. Figure 4(a) shows the CV curves of an electrochemical cell consisting of the LCO(11-20) film, a liquid electrolyte, and a Li anode. The peaks observed in the charge and discharge cycles correspond to the extraction and insertion of Li ions in LCO, respectively. The appearance of those peaks at 3.94 (C1), 3.97 (C1'), 4.08 (C2), and 4.18 V (C3) in the charging process (and at 3.89 (D1'), 4.06 (D2), and 4.16 V (D3) in the discharging process) is a typical feature observed in the CV curves of polycrystalline bulks and films [13,14,15,16]. The C1' peak is also observed in Fig. 4(b), and the peak current at 3.85 V (D1') in the discharge process decreases to about half of C1' in the charging one. This implies that the D1' peak in Fig.4(a) is much smaller than D1, resulting in the double (C1 and C1') and single peaks (D1) in the charging and discharging processes, respectively. Furthermore,

we confirmed stable charging and discharging processes in the LCO(11-20) film, where the characteristics did not degrade even after the third cycle. In contrast, the LCO(10-14) film exhibits apparent degradation on cycling (Fig. 4(b)), which was also observed in the LCO(10-14) film on a Au(110) substrate [8]. Hiramama *et al.* carried out in-plane XRD of LiMn_2O_4 epitaxial films using synchrotron x-rays, and found small lattice change during charge-discharge operations. They concluded that the lattice change in the epitaxial films grown on single-crystal substrates was restricted during battery operations [17]. The same behaviors were also observed for epitaxial films, such as Li_2RuO_3 [18] and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [19]. Furthermore, Ichitsubo *et al.* reported that the discharge capacity of Sn electrodes was only about 1% of the ideal value of Sn when the samples are under mechanical strain [20]. In the case of LCO(11-20), therefore, it is reasonable to assume that c-lattice expansion and contraction is having an impact on charge/discharge cycles, and thus we expected that fast degradation would take place during Li insertion and extraction reactions [21]. When the film is in a charged state, the c-lattice should undergo a lattice expansion of ~2% [22], as a result of Li extraction from the film. The volume change might be hindered in the LCO(11-20) films, as the c-axis in LCO(11-20) is parallel to the surface. The film, however, does not exhibit a significant difference between the second and third cycles, strongly suggesting that the film possesses good electrochemical properties under compressive strain [2,9]. The voltage dependence of c-lattice in the epitaxial LCO films is still unknown. Further work of these systems is needed to show the effects of lattice strain in epitaxial films on the electrochemical properties.

4. Conclusions

We successfully fabricated epitaxial $\text{LiCoO}_2(11-20)$ thin films on $\text{Pt}(110)$ single-crystal substrates etched with aqua regia. The crystal orientation of the epitaxial films was tuned by controlling the surface morphology of the substrate. Furthermore, we confirmed stable and repeatable charge/discharge characteristics, even though the film is compressed.

Acknowledgments

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Figure captions

Fig. 1. (a) Out-of-plane and (b) in-plane XRD patterns of LiCoO_2 thin films on a Pt(110) substrate etched with aqua regia. The inset of (a) shows the crystal alignment of CoO_2 layers and Pt substrates. (c) The ϕ -scans of LCO 0003 and Pt 111 diffractions obtained at $\psi = 90^\circ$.

Fig. 2. XRD patterns of LCO thin films on a Pt(110) substrate etched with aqua regia. The inset shows the crystal alignment of CoO_2 layers and the Pt substrate. (a) A θ - 2θ scan obtained at $\psi = 35^\circ$. (b) The ϕ -scans of LCO 0003 and Pt 111 diffractions obtained at $\psi = 35^\circ$.

Fig. 3. AFM images of (a) etched and (b) reconstructed Pt(110) surfaces. The insets show photos of the Pt(110) substrates after the surface treatments. The chemically etched Pt(110) surface becomes lusterless after the etching treatments. (c) A TEM image of LCO on etched Pt(110). (d) An electron diffraction pattern taken from the region including LCO and Pt substrate. Electron incident axis is parallel to [111] of Pt substrate and [0001] and LCO. Sets of white and yellow arrows indicate the diffraction spots from Pt and LCO, respectively.

Fig. 4. Cyclic voltammograms of $\text{LiCoO}_2/\text{Pt}(110)$: (a) LCO(11-20) film on etched Pt(110) and (b) LCO(10-14) film on reconstructed Pt(110).

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Fig. 1 XRD patterns of LiCoO₂ thin films on a Pt(110) substrate etched with royal water. The inset shows a crystal alignment of CoO₂ layers and Pt substrates. (a) Out-of-plane (b) In-plane (c) ϕ -scan of LiCoO₂ 0003 and Pt 111 diffractions obtained at $\psi = 90^\circ$.

Fig. 2 XRD patterns of LiCoO_2 thin films on a $\text{Pt}(110)$ substrate etched with royal water. The inset shows the crystal alignment of CoO_2 layers and substrate. (a) θ - 2θ scan obtained at $\psi = 35^\circ$. (b) ϕ -scans of LiCoO_2 0003 and Pt 111 diffractions obtained at $\psi = 35^\circ$.

(a) chemically-etched
Pt(110) substrate

(b) reconstructed
Pt(110) substrate

Fig. 3. AFM images of (a) etched and (b) reconstructed Pt(110) surfaces. The insets show photos of the Pt(110) substrates after the surface treatments. The chemically etched Pt(110) surface becomes lusterless after the etching treatments. (c) A TEM image of LCO on etched Pt(110). (d) An electron diffraction pattern taken from the region including LCO and Pt substrate. Electron incident axis is parallel to $[111]$ of Pt substrate and $[0001]$ and LCO. Sets of white and yellow arrows indicate the diffraction spots from Pt and LCO, respectively.

Fig. 4 Cyclic voltammogram of LiCoO₂/Pt(110). (a) LCO(11-20) film on etched Pt(110). (b) LCO(10-14) film on reconstructed Pt(110).