



Orientation control of LiCoO₂ epitaxial thin films on metal substrates



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ARTICLE INFO

Article history:

Received 26 June 2015

Received in revised form 25 December 2015

Accepted 11 January 2016

Available online 21 January 2016

Keywords:

Epitaxial films

Lithium ion batteries

LiCoO₂

Crystal orientation

ABSTRACT

We demonstrate the deposition of LiCoO₂(11–20) epitaxial thin films on chemically etched Pt(110) substrates, and compare their electrochemical properties with those of LiCoO₂(10–14) epitaxial thin films on sputter-annealed Pt(110) reconstructed substrates. Cyclic voltammogram measurements of LiCoO₂(11–20) epitaxial films exhibit stable charge and discharge operations, despite the application of a compressive strain on the films.

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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.

LiCoO₂ (LCO) with a layered-rhombohedral α -NaFeO₂ 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 LCO(0001) films (the notation of crystal planes is based on a hexagonal setting) on step-and-terrace Al₂O₃(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 Pt(110)-(2 × 1) reconstructed substrate surfaces, and reported on battery operations using liquid and solid electrolytes [8]. The reconstructed 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 CoO₂ 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 CoO₂ layers, and it is unlikely that the Li ions can penetrate through a CoO₂ 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.

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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 α - 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 Pt(110) surface, respectively, as illustrated in the inset of Fig. 1(a).

In addition to the 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 LCO(01–18), which has a (0001) plane tilted by 35° with respect to the 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 Pt(110) 2×1 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 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 LCO(0001) film on this (111) facet. Indeed, exposure of the Pt(111) facets on the chemically etched 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 $R_a = 29.1 \text{ nm}$ (Fig. 3(a)), which is in contrast to the smaller value observed on the reconstructed Pt(110) surface ($R_a \approx 0.93 \text{ nm}$) (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 LCO(11–20) and (10–14) phases was grown (not shown here). This

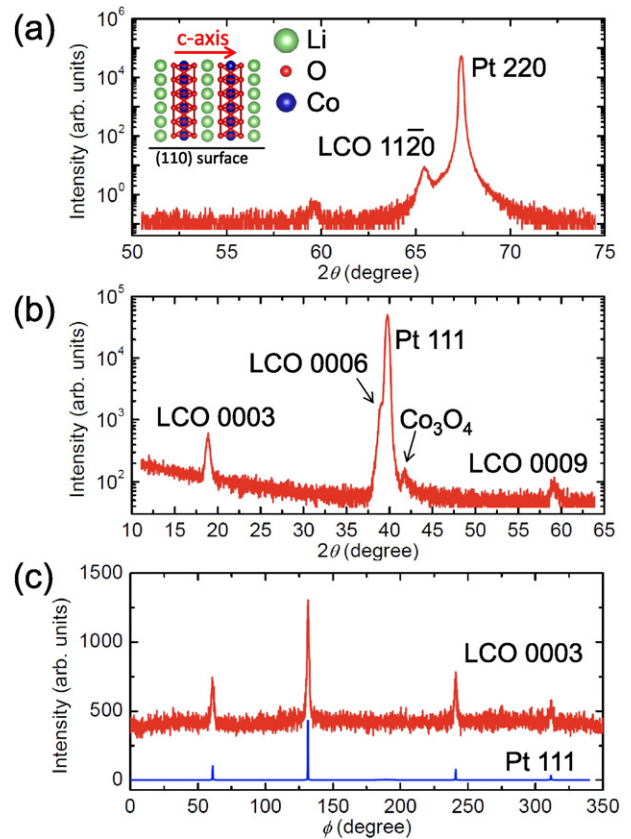


Fig. 1. (a) Out-of-plane and (b) in-plane XRD patterns of LiCoO_2 thin films on a Pt(110) substrate etched with aqua regia. The inset of (a) shows the crystal alignment of CoO_2 layers and Pt substrates. (c) The ϕ -scans of LCO 0003 and Pt 111 diffractions obtained at $\psi = 90^\circ$.

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

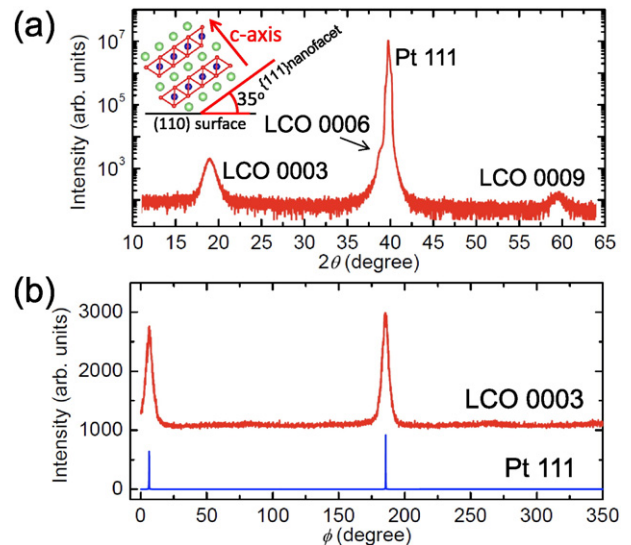


Fig. 2. XRD patterns of LCO thin films on a Pt(110) substrate etched with aqua regia. The inset shows the crystal alignment of CoO_2 layers and the Pt substrate. (a) A θ - 2θ scan obtained at $\psi = 35^\circ$. (b) The ϕ -scans of LCO 0003 and Pt 111 diffractions obtained at $\psi = 35^\circ$.

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