



Epitaxial growth of (104)- and (018)-oriented LiCoO₂ films on MgO single crystals prepared by chemical vapor deposition

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ABSTRACT

The lithium cobaltate (LiCoO₂) films were deposited onto single-crystal magnesium oxide (MgO) substrates by metal organic chemical vapor deposition, and the in-plane orientation relationship, morphology and deposition rates were investigated. Hetero-epitaxial LiCoO₂ films oriented to (104) and (018) were obtained on (100) and (110) MgO substrates. The surface morphology of the (104) LiCoO₂ film showed diagonally arrayed rectangular facets, whereas the (018) LiCoO₂ film exhibited a roof-like structure extended unidirectionally to $\bar{1}10$ MgO. Twin structures formed with in-plane relationships of $[010]$ LiCoO₂ // $[0\bar{1}0]$ LiCoO₂ and $[42\bar{1}]$ LiCoO₂ // $[010]$ LiCoO₂ in the (104) LiCoO₂ film and with in-plane relationships of $[100]$ LiCoO₂ // $[100]$ LiCoO₂ in the (018) LiCoO₂ film. The deposition rates of the (104)- and (018)-oriented LiCoO₂ films were $10.8 \mu\text{m h}^{-1}$ and $8.8 \mu\text{m h}^{-1}$, respectively, which were almost 100 times greater than those reported for LiCoO₂ epitaxial films fabricated by pulsed laser deposition.

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1. Introduction

Films of lithium (Li) compounds have been extensively studied for the development of all-solid-state Li-ion batteries with high energy densities. Lithium cobaltate (LiCoO₂) has been widely used as a cathode because of its high capacity and excellent cycle stability. LiCoO₂ films have been fabricated using various deposition techniques, including pulsed laser deposition (PLD) [1–8], sputtering [7–11], and chemical vapor deposition (CVD) [12,13]. For all-solid-state batteries, the optimization of the solid/solid interface between an electrode and an electrolyte with high intercalation/deintercalation of Li⁺ ions in the cell is critical. LiCoO₂ assumes a rhombohedral layered rock-salt structure in which Li, cobalt (Co), and oxygen (O) atoms form a layer-by-layer structure in the direction of the *c*-axis. Li⁺ ions migrate along the Li layer, which results in anisotropic Li⁺ ion diffusion and intercalation/deintercalation [14]. Therefore, the electrochemical properties of LiCoO₂ films are expected to depend on the crystalline orientation; the (003) plane parallel to the substrate blocks the Li-ion current flow, whereas (003) inclined from the substrate enables the smooth migration of Li ions.

Non-(003)-oriented, e.g., (104)- and (110)-oriented, and randomly oriented LiCoO₂ films have been fabricated [1,5–10], although the (003) plane of a LiCoO₂ film is likely to grow parallel to the substrate because of the lower surface energy of the *c*-plane. Bouwman et al. prepared LiCoO₂ films with their (003) planes parallel to the substrate using PLD, and prepared (104)- and (110)-oriented films using RF sputtering [7,8]. They reported that only the surface of LiCoO₂ contributed to the

electrochemical intercalation process in the PLD film with a parallel alignment, whereas the RF films showed the full film capacity because of the accessible alignment of two-dimensional lithium diffusion planes to the electrolyte [7]. Xia and Lu reported that (104)-orientated LiCoO₂ films exhibited higher capacity on the first cycles and higher Li diffusivity compared to (003)-oriented films; however, they also reported that the (104)-orientated film showed faster capacity fade [1]. In contrast, Bates et al. reported no significant difference in the electrochemical properties between RF-sputtered LiCoO₂ films with an (003) orientation and those with (104) and (101) orientations [10]. Thus, previous results are neither consistent nor sufficient in number to obtain a clear understanding of the anisotropic nature of LiCoO₂ films.

Hetero-epitaxial growth is a powerful method to fabricate films oriented to a specific plane and direction on single crystals. Epitaxial LiCoO₂ films with well-defined structures and orientations provide a promising pathway to study the anisotropic nature of LiCoO₂ and the underlying mechanisms of electrochemical responses. Tsuruhama et al. and Ohnishi and Takada fabricated epitaxial (003)-oriented LiCoO₂ films on Al₂O₃ single crystals using PLD [14,15]. Hirayama et al. fabricated epitaxial (003)-, (104)-, and (101)-oriented LiCoO₂ films on SrTiO₃ single crystals [16]. They reported that (101)-oriented LiCoO₂ films exhibited good reversibility, whereas (003)-oriented LiCoO₂ films showed limited capacity. Although epitaxially oriented LiCoO₂ films can be fabricated by PLD, the deposition rate is slow, at most 18 Å min^{-1} [15]. A deposition technique with a high deposition rate is advantageous in practical applications of LiCoO₂ films. CVD allows the fabrication of films with various oriented textures at high deposition rates [17]. Barreca et al. demonstrated the fabrication of cobalt oxide anode films with various nanostructures and oriented textures using CVD [18–22]. However, few studies

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on the control of the orientation and on the deposition rate for LiCoO₂ films using CVD have been reported [13,23]. Because single-crystal MgO has commercially available three distinct types, i.e., (100), (110) and (111) MgO, single-crystal MgO is valuable in studying the epitaxial growth of LiCoO₂ films. In the present study, the LiCoO₂ films were prepared on single-crystal MgO substrates by metal organic CVD, and the orientation, morphology and deposition rates were investigated.

2. Experimental

LiCoO₂ films were prepared using a vertical cold-wall-type CVD chamber. Dipivaloylmethanato-lithium (Li(DPM)) and tri-dipivaloylmethanato-cobalt (Co(DPM)₃), which showed stable vaporization behavior, were used as precursors. The precursors were vaporized at 535 K and 465 K, respectively, by electrical furnaces. The source vapor ratio of Li(DPM) to Co(DPM)₃ was approximately 1.0. The precursor vapors were carried to the CVD reaction chamber by argon gas at a flow rate of $0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. Oxygen gas was separately carried through a double tube nozzle at a flow rate of $1.66 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and was mixed with the Li and Co vapors above a substrate. The CVD chamber was maintained at a total pressure of 400 Pa. MgO single crystals with (100), (110), and (111) orientations were used as substrates (Dalian Keri Optoelectronic Technology, 99.9% purity, $10 \times 10 \times 0.5 \text{ mm}^3$); they were placed on a hot stage and heated at 923 K during deposition. The deposition temperature was monitored with a thermocouple beneath the substrate. The deposition time was 900 s.

X-ray diffraction (θ – 2θ XRD, Rigaku RAD-2C) was used to examine the phases and orientations of the LiCoO₂ films. The in-plane orientation relationship of the LiCoO₂ film was analyzed by XRD pole-figures (Rigaku, Ultima IV). The surface and cross-sectional morphologies were observed using a field-emission scanning electron microscope (FE-SEM; JEOL, JSM-7500F). The deposition rates were calculated from the deposition time and thickness. The crystal structures were drawn using the VESTA software package [24].

3. Results and discussion

The XRD patterns of LiCoO₂ films deposited on MgO single crystals are shown in Fig. 1. The LiCoO₂ films prepared on (100), (110), and (111) MgO exhibited strong (104)-, (018)-, and (003)-preferred orientations, respectively. The lattice mismatches between (104) LiCoO₂ and (200) MgO, (018) LiCoO₂ and (220) MgO, and (003) LiCoO₂ and (111) MgO were 4.98%, 4.39%, and 3.80%, respectively. These small mismatches and the strong orientation suggested the hetero-epitaxial growth of LiCoO₂ films on the MgO single-crystal substrates. The (003) LiCoO₂ epitaxial films were fabricated by PLD using (111) MgO and (0001) Al₂O₃ [14,15]. Although (104)-, (018)-, and (003)-oriented LiCoO₂ films have been fabricated on Al₂O₃ single crystals by CVD [23], the (104) and (018) LiCoO₂ films were not fully oriented and showed inhomogeneous grain growth.

The pole-figure pattern for the (003) reflection of the (104) LiCoO₂ film and that for the (110) reflection of the (100) MgO substrate is shown in Fig. 2. The four reflection spots at an elevation angle (α) of 45° in the pole-figure pattern for (100) MgO are consistent with the four-fold symmetry relationship attributed to the {110} planes with a complementary angle of 45° to (100) MgO. At $\alpha = 35^\circ$ and an azimuth angle (β) inclined at 45° from these reflection spots, four (003) reflection spots were observed in the (104) LiCoO₂ film. These pole-figure reflections indicated that the (104) LiCoO₂ grains were aligned in fourfold directions, as described in Fig. 3(a), where the (104)-oriented LiCoO₂ unit cells are shown on the (100) MgO plane. The in-plane epitaxial growth relationship between the (104) LiCoO₂ film and the (100) MgO substrate is described in Fig. 3(b), i.e., (104) LiCoO₂ // (100) MgO (100) and [010] LiCoO₂ // [011] MgO. The fourfold symmetry of the Mg and O atomic alignment on the (100) plane resulted in the epitaxial growth of (104) LiCoO₂ in a fourfold direction.

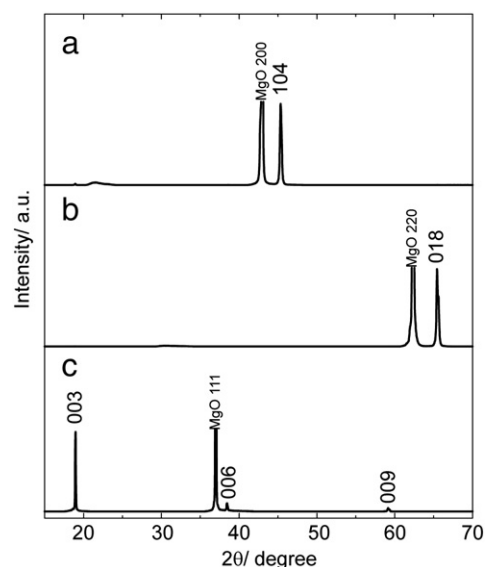


Fig. 1. XRD patterns of LiCoO₂ films deposited on (100), (110) and (111) MgO substrates.

The surface morphology of the (104) LiCoO₂ epitaxial film deposited on the (100) MgO substrate is shown in Fig. 4. Rectangular facets were diagonally arrayed in the azimuthal [010] and [001] directions of the MgO substrate. The diagonal alignment comprises the (104) LiCoO₂ grains with a fourfold epitaxial relationship between (104) LiCoO₂ and (100) MgO, as shown in Fig. 3(a). The cross-sectional morphology of the (104) LiCoO₂ film, where the cross-sectional surface of the MgO

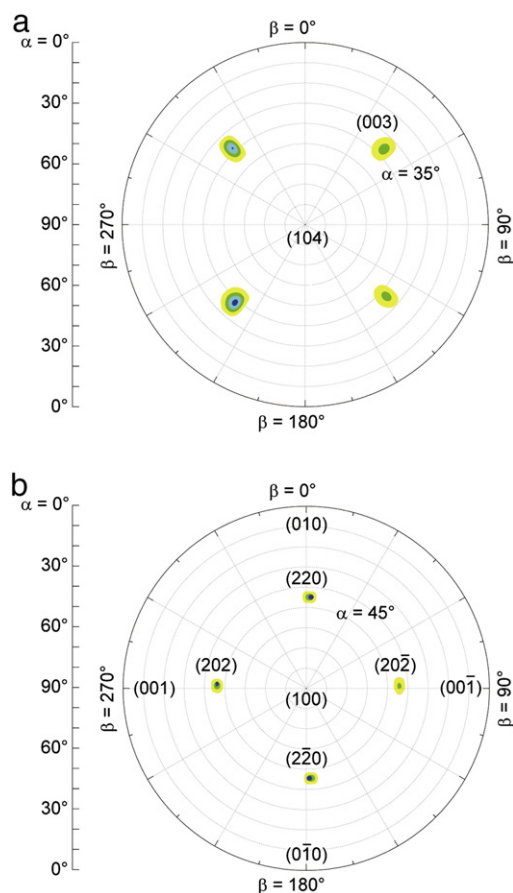


Fig. 2. Pole figure diffraction pattern of the (003) reflection of LiCoO₂ film, and that of the (220) reflection of the (100) MgO substrate.

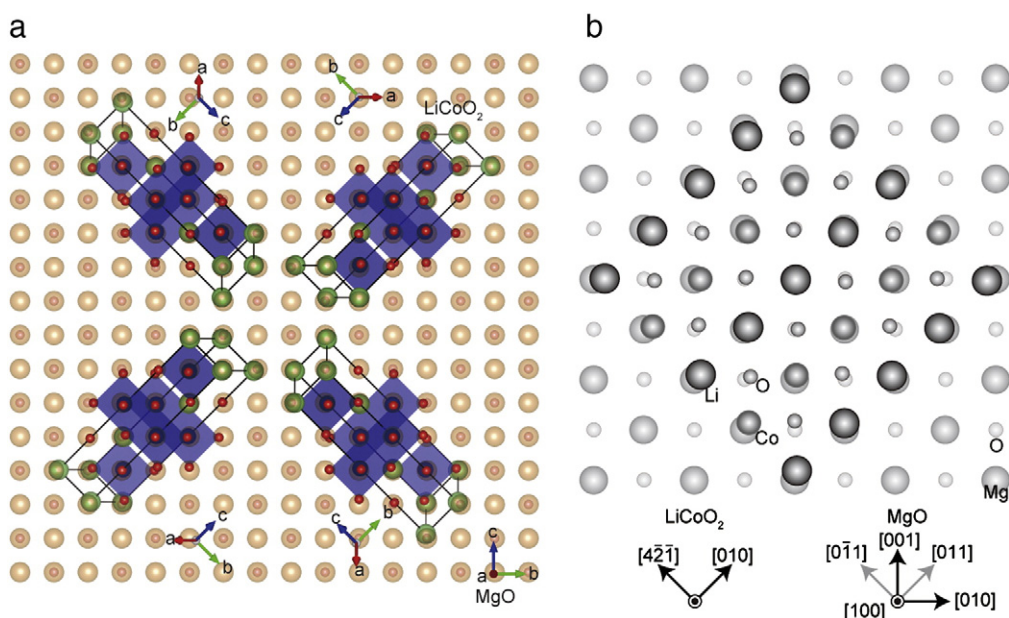


Fig. 3. Schematic illustration of crystal structure of LiCoO₂ deposited on (100) MgO; unit cells of (104) LiCoO₂ in the four directions based on the pole figure diffraction pattern (a), and the relationship between an atomic layer of the (104) LiCoO₂ plane and that of (100) MgO plane (b).

substrate is the (011) plane, is shown in Fig. 5(a). Striations could be attributed to the layered structure of LiCoO₂. The typical angles between the striations were 75° and 120°, as indicated by the square in Fig. 5(a). Among the (104) LiCoO₂ grains in the fourfold directions, two (104) LiCoO₂ grains with in-plane orientation relationships of [010] LiCoO₂ // [01̄0] LiCoO₂ and [42̄1] LiCoO₂ // [010] LiCoO₂ can form twin structures, as shown in Fig. 5(b) and (c). At the twin grain boundaries, atomic strings in the *c*-plane of the LiCoO₂ layered structure intersect at 75° and 120°, and these angles are consistent with the striation angles in the cross-sectional morphology, as shown in Fig. 5(a). The growth of these twin structures with combinations of the fourfold (104) LiCoO₂ grains resulted in the diagonally aligned surface morphology shown in

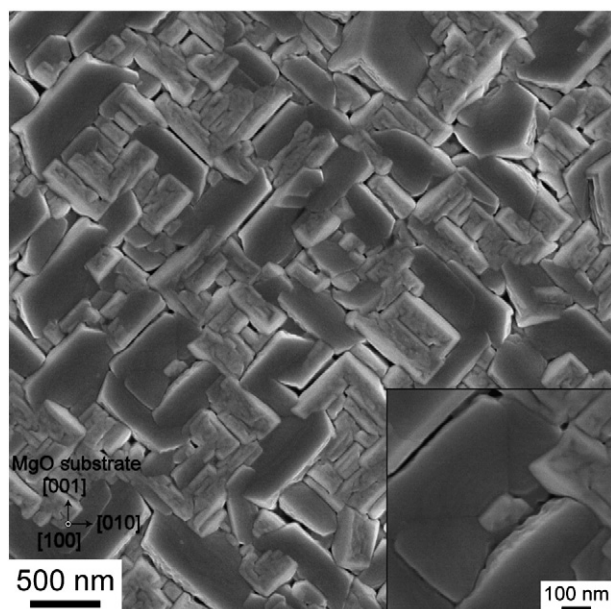


Fig. 4. Surface morphology of (104) LiCoO₂ films deposited on a (100) MgO substrate.

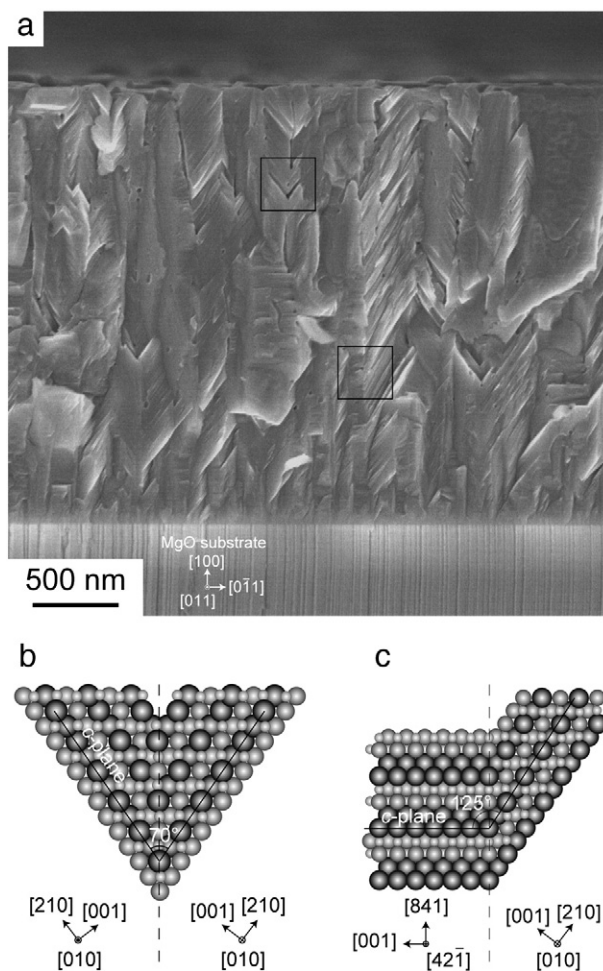


Fig. 5. (a): Cross-sectional morphology of (104) LiCoO₂ films deposited on a (100) MgO substrate, (b) and (c): Schematic illustrations of twin structures of the (104) LiCoO₂ grains.

Fig. 4. The deposition rate of the (104) LiCoO_2 film was $10.8 \mu\text{m h}^{-1}$ at 923 K. This deposition rate is 100 times greater than the $0.108 \mu\text{m h}^{-1}$ ($18 \text{ \AA min}^{-1}$) rate reported for PLD [15].

The pole-figure patterns for the (003) reflection of the (018) LiCoO_2 film and for the (200) reflection of the (110) MgO substrate are shown in Fig. 6. The twofold symmetry relationship in (110) MgO was attributed to the {100} planes with a complementary angle of 45° to (110) MgO, as shown in Fig. 6(a). The pole-figure pattern for the (003) reflection of the (018) LiCoO_2 film showed twofold symmetry at $\alpha = 54^\circ$, as shown in Fig. 6(b). The azimuth-angle deviation between the (018) LiCoO_2 film and (110) MgO indicated the in-plane orientation relationships of (018) $\text{LiCoO}_2 // (110) \text{MgO}$ and $[100] \text{LiCoO}_2 // [\bar{1}10] \text{MgO}$.

The surface morphology of the (018) LiCoO_2 film showed a unidirectionally arrayed roof-like faceted structure, as shown in Fig. 7(a). The azimuth orientation of the (110) MgO substrate determined by the XRD pole-figure indicates that these facets extended along MgO $[\bar{1}10]$. The cross-sectional SEM image of the (018) LiCoO_2 film, where the cross-sectional surface of the MgO substrate is the $(\bar{1}10)$ plane, is shown in Fig. 7(b). The cross section is notched by striations that reflect the layered structure of LiCoO_2 . Given the twofold epitaxial relationship of (018) LiCoO_2 on (110) MgO, (018) LiCoO_2 grains with two in-plane orientation relationships of $[100] \text{LiCoO}_2 // [\bar{1}10] \text{MgO}$ and $[\bar{1}00] \text{LiCoO}_2 // [\bar{1}10] \text{MgO}$ exist, which can form the twin structure described in Fig. 7(c). The atomic strings in the c -plane of the LiCoO_2 layered structure intersect at 108° at the grain boundary of the twin structure. This angle was in agreement with that of the notched striations observed in the cross section of the (018) LiCoO_2 film. The growth of the twofold twin structure, accompanied by layer-stacking of c -planes, resulted in

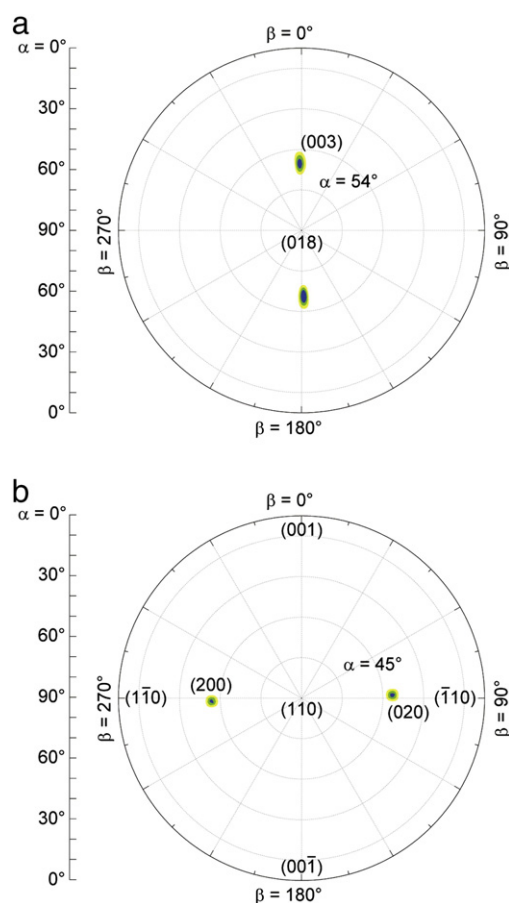


Fig. 6. Pole figure diffraction pattern of the (003) reflection of LiCoO_2 film, and that of the (200) reflection of the (110) MgO substrate.

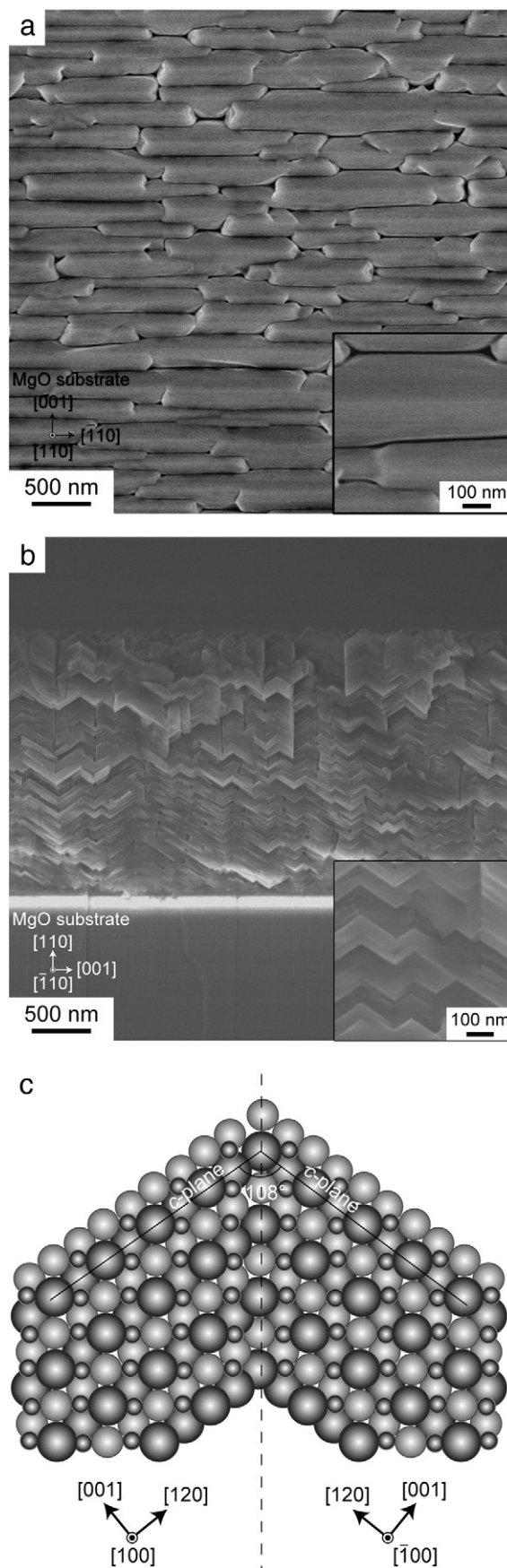


Fig. 7. Surface (a) and cross-sectional (b) morphologies of (018) LiCoO_2 films deposited on a (110) MgO substrate, and the schematic illustration of twin structure of (018) LiCoO_2 grains (c).

the roof-like texture observed on the surface in Fig. 7(a). The deposition rate of the (018) LiCoO₂ film was 8.8 μm h⁻¹.

4. Conclusions

We fabricated hetero-epitaxial (104) and (018) LiCoO₂ films on (100) and (110) MgO single crystals by CVD at high deposition rates and clarified the epitaxial relationship between film-growth and oriented textures. The epitaxial in-plane orientation relationships of the (104) LiCoO₂ films on (100) MgO and of the (018) LiCoO₂ films on (110) MgO were [010] LiCoO₂ // [011] MgO and [100] LiCoO₂ // $\bar{1}$ [10] MgO, respectively. The orientation relationships and microstructural observations revealed that the faceted surface morphologies and cross-sectional striations of (104) and (018) LiCoO₂ films were due to the growth of twin structures; the twins that comprised fourfold (104) LiCoO₂ grains formed the diagonally arrayed rectangle facets and those of twofold (018) LiCoO₂ resulted in roof-like structures. The deposition rates of (104)- and (018)-oriented films were 10.8 μm h⁻¹ and 8.8 μm h⁻¹, which were almost 100 times greater than those reported for LiCoO₂ epitaxial films fabricated by PLD. These LiCoO₂ films with well-defined structures fabricated at a high deposition rate enable investigations that will provide greater understanding of the mechanisms of electrochemical properties and of the industrial fabrication process.

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