Epitaxial thin film synthesis of layered rocksalt high-entropy oxide Li*M*O_2 (*M*=1/6Cr, 1/6Mn, 1/6Fe, 1/6Co, 1/6Ni, and 1/6Cu)

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1. Introduction

Recently, the synthesis of high-entropy oxide (HEO) materials has intrigued much attention. The interaction among various metal cations in HEOs gives rise to unexpected superior performances, for instance, in energy storage devices [1]. Currently, a variety of HEOs have been developed in bulk systems; HEOs in the cubic system, such as rock salt [1], fluorite [4], and perovskite [5], have been reported. However, HEOs with anisotropic crystal structures have been paid little attention yet. In addition, the synthesis of HEO epitaxial thin films is still in the early stages of research [2,3]. Accordingly, in this study, we focused on synthesizing HEO epitaxial thin films with a layered rock-salt structure, Li*M*O_2, containing six transition metals (*M*: Cr, Mn, Fe, Co, Ni, and Cu) in equiatomic ratios. Furthermore, we investigated battery performances by fabricating thin-film type all-solid-state Li batteries using the HEO epitaxial thin films as a positive electrode.

2. Experiments

HEO epitaxial thin films were synthesized on an Al_2O_3 (0001) single crystal substrate using a pulsed laser deposition technique. A KrF excimer laser (wavelength: 248 nm, pulse duration: ~20 ns, repetition frequency: 5 Hz, spot size: 0.019 cm^2, and fluence: 1.05 J cm^{-2}) was used to ablate a polycrystalline target of $Li_{1.2}Cr_{1/6}Mn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}O_x$. The substrate temperature (T_s) during the thin film growth was varied in the range of 500–800°C. An oxygen pressure was set as 1×10^{-3} Torr for the thin film growths. X-ray diffraction (XRD) measurement was performed to investigate the crystal structure and orientation for the synthesized HEO thin films.

3. Results

Figure 1 shows the out-of-plane XRD patterns of HEO thin films grown at a variety of T_s. Diffraction peaks are indexed as the layered rock-salt structure. The XRD patterns of all the HEO thin films exhibited 003 and 006 reflections, indicating (001) orientation for the HEO thin films. On the other hand, these 003 and 006 reflections showed different peak intensities among the samples. Figure 2 shows the intensity ratios of 003 and 006, I_{003}/I_{006}, which is a measure of the crystallinity of a layered rock-salt structure [6,7]. The HEO thin film grown at 600 °C exhibited the highest value of I_{003}/I_{006}, indicating the best quality of the (001)-oriented thin films. In conclusion, we succeeded in synthesizing the $LiCr_{1/6}Mn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}O_2$ (001) epitaxial thin film. We will report on the detailed characterization of the thin films and battery operation.

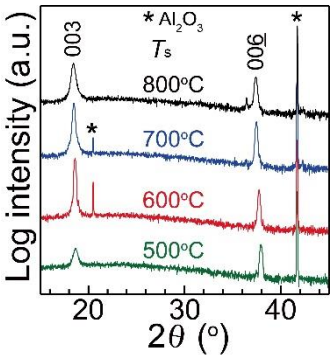

Figure 1. Out-of-plane XRD patterns for the thin films grown at a variety of substrate temperatures (T_s).

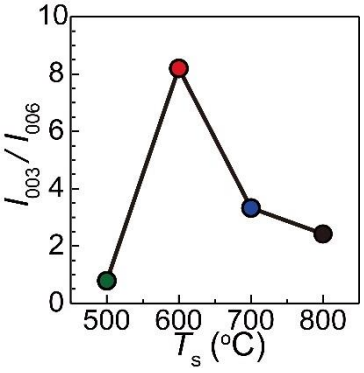

Figure 2. X-ray diffraction intensity ratios of I_{003}/I_{006} for the thin films.

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