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Electrochemical Properties of $Li_4Ti_5O_{12}$ and $LiTi_2O_4$ Epitaxial Thin Films

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Abstract

We fabricated $Li_4Ti_5O_{12}$(111) and $LiTi_2O_4$(111) epitaxial thin films by using pulsed laser deposition. By annealing the LiT_2O_4 epitaxial films at 750°C under oxygen partial pressure of 1×10^{-3} Torr, the films transformed to high crystallinity $Li_4Ti_5O_{12}$ epitaxial thin films with a rocking curve full width at half-maximum of 0.057°. However, the high crystallinity $Li_4Ti_5O_{12}$ films showed poor electrochemical performance compared to that of the as-grown ones. These results indicate that oxygen partial pressure during annealing treatments strongly influences crystal structures and electrochemical properties of lithium titanate battery materials.

1. Introduction

$Li_4Ti_5O_{12}$ has shown great promise as lithium ion battery anode materials because they have stable battery operation. The most characteristic feature of $Li_4Ti_5O_{12}$ is negligible volume expansion and contraction during insertion and extraction of Li ion. The synthesis of the films is important because they are useful for battery applications in the field of micromachine, basic research for understanding of battery mechanism.

Pulsed laser deposition (PLD) is a powerful deposition technique for the synthesis of high-quality oxide thin films [1]. Recently, epitaxial thin films of electrode materials such as $LiCoO_2$ [2-5], $Li_4Ti_5O_{12}$ [6], and $LiMn_2O_4$ [7], have been reported. In our previous work, we showed synthesis of $LiTi_2O_4$ and $Li_4Ti_5O_{12}$ epitaxial thin films from a single $Li_4Ti_5O_{12}$ target by varying the oxygen partial pressure P_{O2}. However, the as-grown $Li_4Ti_5O_{12}$ has a wider rocking curve full width at half-maximum (FWHM) compared to that of $LiTi_2O_4$.

In this study, we report the fabrication of lithium titanate (LTO) epitaxial thin films using PLD. We successfully improved crystallinity of $Li_4Ti_5O_{12}$ through the post-deposition annealing of $LiTi_2O_4$. We further examined electrochemical properties of $Li_4Ti_5O_{12}$ and $LiTi_2O_4$ films by charge and discharge battery operation.

2. Experimental

Lithium titanate (LTO) thin films were deposited by using PLD on $MgAl_2O_4$ (111) and Nb-doped $SrTiO_3$(001) substrates. A polycrystalline $Li_4Ti_5O_{12}$ target (Toshima Manufacturing) was used for the deposition. A KrF excimer laser (wavelength: 248 nm) was used for the deposition with a repetition rate of 5Hz and a fluence of 0.6 J/cm^2. The P_{O2} was varied from 1×10^{-6} to 1×10^{-3} Torr, and the substrate temperature during deposition was kept at 800°C. The LTO films were typically 200 nm thick. The crystal structures of the films were characterized with an x-ray diffractometer (NEW D8 Discover, Bruker). The electrochemical properties of epitaxial LTO films were examined with 2032 coin type Li cells using Li metal foils as anode. The electrolyte used was EC (ethylene carbonate)-DEC (diethyl carbonate) with a molar ratio of 3:7 as a solvent and supporting electrolyte of 1M $LiPF_6$. The cut-off voltages in charge and discharge measurements were 0.8 and 2.5 V, and the current was set at 1.2 □A (approximately 0.33C).

3. Results and discussions

Figure 1 shows the out-of-plane XRD patterns of $Li_4Ti_5O_{12}$ thin films deposited in different conditions. For comparison, the result of $LiTi_2O_4$ is also shown. The as-grown $Li_4Ti_5O_{12}$ was obtained at high P_{O2} of 1×10^{-3} Torr, while $LiTi_2O_4$ was at low P_{O2} of 1×10^{-6} Torr [6]. In the as-grown $Li_4Ti_5O_{12}$ and $LiTi_2O_4$, we found (111), (222), (333) and (444) peaks from $Li_4Ti_5O_{12}$ and $LiTi_2O_4$, respectively, in addition to peaks from the $MgAl_2O_4$ substrate, indicating the epitaxial growth of LTO although in–plane XRD results were not shown here. In addition, a small peak from rutile TiO_2 was observed as a shoulder in the right side of (222) peak from $MgAl_2O_4$ substrate in the as-grown $Li_4Ti_5O_{12}$. A closer look of Fig. 1 indicates a shift of (444) peaks of $LiTi_2O_4$ to a lower 2θ angle compared to that of as-grown $Li_4Ti_5O_{12}$, as shown in Fig. 1. Furthermore, we could clearly see a remarkable difference in crystallinity by comparing FWHM values between the two films. The FWHM values of the XRD rocking curve of the LTO(111) peaks were 0.17° and 0.044° for the as-grown $Li_4Ti_5O_{12}$ and $LiTi_2O_4$, respectively.

Considering that the as-grown $Li_4Ti_5O_{12}$ was obtained at high P_{O2} during the deposition, we speculated that high-crystallinity $Li_4Ti_5O_{12}$ could be obtained by post-deposition annealing of high-quality $LiTi_2O_4$. Hence, we annealed a $LiTi_2O_4$ film at 750°C to obtain high quality $Li_4Ti_5O_{12}$ and found that $Li_4Ti_5O_{12}$ was formed at higher P_{O2} than 1×10^{-3} Torr, as shown in Fig. 1. Furthermore, the post-deposition-annealed $Li_4Ti_5O_{12}$ obtained at P_{O2} of 1×10^{-3} Torr showed high crystallinity single phase with FWHM of 0.056°.

The growth of $Li_4Ti_5O_{12}$ was also confirmed by electrochemical properties. In charge and discharge curves of Figure 2, we can clearly see the plateaus at 1.59 V, and good reproducibility. These plateaus are characteristic to $Li_4Ti_5O_{12}$ and indicate the formation of $Li_4Ti_5O_{12}$ [8,9]. Here we compare the electrochemical properties of the as-grown and post-deposition-annealed $Li_4Ti_5O_{12}$. The charge curves for the as-grown $Li_4Ti_5O_{12}$ shows are very flat plateau at 1.59 V in the capacity range between 20 and 160 mAh/g, and the charge capacity was about 250 mAh/g and does not change with cycle. In contrast, the capacity range for the post-annealed $Li_4Ti_5O_{12}$ was between 20 and 100 mAh/g in the first charge, and decreased with cycle. These results indicate that the post-deposition-annealed $Li_4Ti_5O_{12}$ shows poor electrochemical properties in spite of its good crystallinity.

3. Conclusions

We fabricated $Li_4Ti_5O_{12}$ epitaxial thin films by using PLD. The charge and discharge curves of the as-grown $Li_4Ti_5O_{12}$ show plateaus at 1.59 V, and the capacity was 250 mAh/g, which were consistent with the previous powder data. Furthermore, we obtained high-quality $Li_4Ti_5O_{12}$ by annealing the as-grown one at oxygen partial pressure of 1×10^{-3} Torr, but the charge and discharge curves show poor electrochemical properties in spite of its good crystallinity. These results indicate that oxygen partial pressure during annealing treatments strongly influences crystal structures and electrochemical properties of lithium titanate battery materials.

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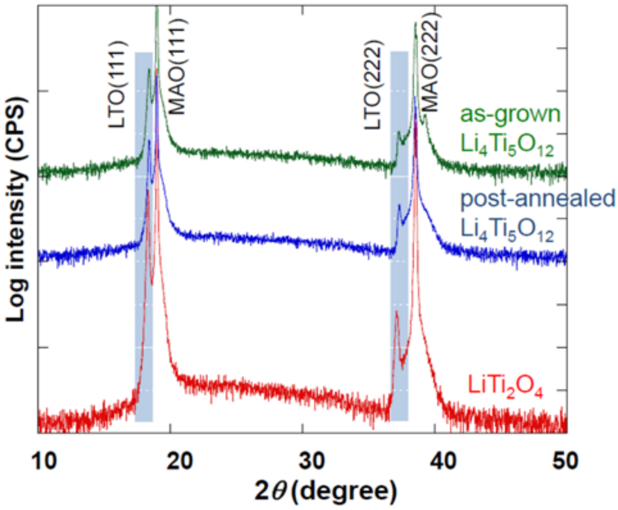

Fig. 1. XRD patterns from $Li_4Ti_5O_{12}$ and $LiTi_2O_4$ epitaxial films.

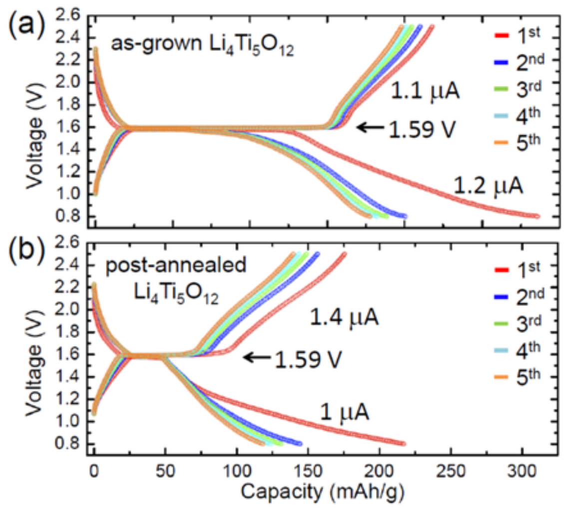

Fig. 2. The charge and discharge curves of (a) as-grown and (b) post-deposition annealed $Li_4Ti_5O_{12}$ epitaxial films.