Preparation of well-oriented Li$_4$Ti$_5$O$_{12}$ single crystal films from TiO$_2$ wafers.

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1. Introduction

Spinel-type lithium titanium oxide (Li$_4$Ti$_5$O$_{12}$, LTO) is one of the promising materials for negative electrodes of Li-ion batteries, due to its superior electrochemical properties. To investigate its unique feature, fine crystal and electronic structures should be studied in detail by spectroscopic, imaging and theoretical methods. However, it is difficult to perform such studies with actual materials, due to the lack of well-defined LTO crystal samples. Such samples are highly needed for ideal experiments, which put theoretical studies on a firm basis. Previously, we prepared a Li$_4$Ti$_5$O$_{12}$ (111) single crystal film from a TiO$_2$ (111) wafer so as to perform surface imaging[1]. In the present study, we tried to prepare the well-oriented Li$_4$Ti$_5$O$_{12}$ single crystal films and discuss the growth mechanism of the Li$_4$Ti$_5$O$_{12}$ single crystal.

2. Experimental

Commercial rutile TiO$_2$ wafers (SHINKOSHA, co, ltd.) of (110), (001) and (111) orientations with the size of 2×2×0.5 mm$^3$ in each pieces were calcined with 2~3 mg of LiOH.H$_2$O in a 99.5%-Al$_2$O$_3$ crucible. After heated 1173K for 15 hours, Li$_4$Ti$_5$O$_{12}$ films of about 20 μm thickness were formed on the TiO$_2$ wafer.

3. Results and discussion

Figs. 1(a), (b) and (c) show the photographs of surfaces of Li$_4$Ti$_5$O$_{12}$ films prepared from TiO$_2$(110), (001) and (111), respectively. Some micro facets observed in all the films pass through the cracks, which indicates that the crystallinity of the films was not influenced by the cracks. The Li$_4$Ti$_5$O$_{12}$ films on TiO$_2$(110) and (111) have uniform features, while the film on TiO$_2$(001) shows two types of micro facets, indicating the existence of two types of crystalline domains. Fig. 2 shows the XRD spectra of each prepared film. All the strong sharp peaks in each film correspond to those of the Li$_4$Ti$_5$O$_{12}$ (Fd-3m, a = 8.358 Å) structure with highly-oriented single crystalline features. The Li$_4$Ti$_5$O$_{12}$ films show the following growth orientations: TiO$_2$(110) vs. Li$_4$Ti$_5$O$_{12}$(001), TiO$_2$(001) vs. Li$_4$Ti$_5$O$_{12}$(110), and TiO$_2$(111) vs. Li$_4$Ti$_5$O$_{12}$(111). This characteristic growth relation should be explained as crystal models as shown in Fig. 3. The inter-plane distances for TiO$_2$(001) and Li$_4$Ti$_5$O$_{12}$(220) are 2.97 Å and 2.96 Å, which are almost the same. Therefore, the Li$_4$Ti$_5$O$_{12}$(220) planes should be grown parallel to the TiO$_2$(001) planes, which should correspond to the XRD result of the overlap of the Li$_4$Ti$_5$O$_{12}$(440) diffraction line with the TiO$_2$(002) angle. Note that TiO$_2$(001) and Li$_4$Ti$_5$O$_{12}$(110) have 4 and 2 order of rotation symmetry, which should lead to the two types of crystal grains with different in-plane directions grown on the TiO$_2$(001) wafer in equal probability as shown in Fig. 1(b). Considering the crystal symmetry, we could understand the Li$_4$Ti$_5$O$_{12}$(001) growth from the TiO$_2$(110) wafer, as...
shown in Figs. 3(a) and (b), and this relation is summarized in Fig. 3(c). The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystal growth in the $<001>$ direction should be accompanied by about 28% lattice expansion from the TiO$_2$ lattice, and thus the $\text{Li}_4\text{Ti}_5\text{O}_{12}(111)$ plane would be oriented with the TiO$_2$(111) plane.

References

Fig. 1 Photographs of surfaces of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples that prepared from (a) TiO$_2$(110), (b) TiO$_2$(001) and (c) TiO$_2$(111). Magnified photos were shown as inset in each images.

Fig. 2 XRD spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ films that prepared from TiO$_2$(110), TiO$_2$(001) and TiO$_2$(111) wafers. Each spectra were shown as blue, green and red solid lines respectively.

Fig. 3 Crystal structure of (a) spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) rutile TiO$_2$ rendered by VESTA$^{[2]}$. (c) Overlapping view from TiO$_2$ $<110>$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ $<111>$. Unit of plane distance numbers were Å.