

Solid-Liquid Phase Epitaxy of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Thin Film

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Abstract. Thin film of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, a candidate material of anode for next generation Li-ion battery, was heteroepitaxially grown on SrTiO_3 single crystal by the solid-liquid phase epitaxy method: Amorphous Li-Ti-O thin film, which was deposited by pulsed laser deposition at room temperature and was covered with LiNO_3 molten salt, was heated at 600 °C. Then it was washed with distilled water. The product was polycrystalline epitaxial $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film, which was composed of rather small crystallites (~20 nm), with an epitaxial relationship of $(001)[100]\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel (001)[100]\text{SrTiO}_3$.

Introduction

Recently, all-solid-state Li-ion batteries (LIBs) have received much attention because the nonflammable nature can improve the safety of LIBs [1]. The key for realization of the all-solid-state LIBs is to clarify the ion transport mechanism at the interface between solid electrode and electrolyte [2]. However, it is very difficult to investigate the transport mechanism of Li ion with the powders or ceramics. Single crystal and/or single crystalline film of solid electrode and electrolyte with atomically flat surface is essentially important to produce the ideal interfaces, but the fabrication of single crystalline film of Li-containing oxide is extremely difficult by a conventional vapor phase epitaxy method because the re-vaporization of Li occurs during film growth due to its extremely high vapor pressure. For example, in order to supplement the lost Li during the film growth by pulsed laser deposition (PLD) at high temperature, the Li-rich (Li was additionally added) target was selected, but the composition of Li was very difficult to control [3,4].

Here, we have proposed novel solid-liquid phase epitaxial growth method for the

fabrication of Li-containing oxide thin films. The key point of our method is that the surface of the film is covered with the Li molten salt during annealing at high temperature to prevent re-evaporation of Li-species from the film. In the present study, we fabricated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [5] thin film, which is most promising anode materials for the next generation LIBs [6].

Experimental

Figure 1 schematically illustrates the solid-liquid phase epitaxy procedure for the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ epitaxial films. Amorphous Li-Ti-O films were deposited at room temperature (RT) on (001) SrTiO_3 single crystal substrates by PLD with KrF excimer laser pulse ($\lambda=248$ nm, 20 ns, 10 Hz, ~ 3 J cm^{-2} pulse $^{-1}$) using a dense $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ceramic as the target. The resultant film was covered with LiNO_3 powder, and was heated at 600 °C for 30 min in air in an Al_2O_3 crucible using electric furnace. During the heating process, the LiNO_3 powder melted due to the low melting point of 261 °C and entirely covered the Li-Ti-O film at 600 °C. Then the film was naturally cooled down to RT in the furnace. The annealed film was washed by distilled water since the film surface was covered with the remaining LiNO_3 film.

Crystalline phase and orientation were analyzed by high-resolution X-ray diffraction (HR-XRD, ATX-G, $\text{CuK}\alpha_1$, Rigaku Co.) and a conventional transmission electron microscope (TEM, JEM-2010HC, JEOL Ltd.) and an atomic-resolution scanning transmission electron microscope (STEM, JEM-ARM200F, JEOL Ltd.). Surface morphology of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ epitaxial film was observed by a scanning probe microscopy (SPM, Nanocute, Hitachi High-Tech Science Co.).



Fig. 1: Solid-liquid phase epitaxy of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film. Step 1: Amorphous Li-Ti-O films were deposited at RT on (001) SrTiO_3 single crystal substrates by PLD using a dense $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ceramic as the target. Step 2: The resultant film was heated at 600 °C for 30 min in air with LiNO_3 powder, which melted during the heating process, in an Al_2O_3 crucible using electric furnace. Then the film was naturally cooled down to room temperature in the furnace. Step 3: The resultant film was washed by distilled water since the film surface was covered with remaining LiNO_3 film.

Results and discussion

Figure 2 summarizes the XRD patterns of the resultant films. Only intense diffraction peaks of 00/ SrTiO_3 can be observed in the out-of-plane XRD pattern of as-deposited Li-Ti-O film [Fig. 2(a)], indicating that the as-deposited film was amorphous. After this amorphous film was annealed at 600 °C in air, 004 TiO_2 diffraction peak was observed though $\text{Li}_4\text{Ti}_5\text{O}_{12}$

diffraction peak could not be seen in the out-of-plane XRD pattern [Fig. 2(b)], suggesting re-vaporization of Li occurred.

In contrast, an intense diffraction peak of 004 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was observed after the film was heated with LiNO_3 molten salt at 600 °C [Fig. 2(c)]. At this stage, the actual re-vaporization temperature of Li in Li-Ti-O film has not been examined yet, the LiNO_3 , which melted at low melting point of 261 °C and entirely covered the film, successfully suppressed the re-vaporization of Li and enabled the crystallization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase.

The estimated crystallite size was ~23 nm, which was ~1/7 of the film thickness (150 nm). The full width at half maximum (FWHM)

value of the out-of-plane rocking curve for 004 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ diffraction is ~2° [Fig. 2(d)]. The epitaxial orientation was investigated by in-plane XRD measurement [Fig. 2(e)]. Only intense diffraction peak of 400 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was observed with $h00$ SrTiO_3 . The ϕ scan of 400 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ diffraction [Fig. 2(e) inset] shows four-fold rotational symmetry every 90° originating from the cubic symmetry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice. These results prove the heteroepitaxial growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film on SrTiO_3 substrate with an epitaxial relationship of $(001)[100]\text{Li}_4\text{Ti}_5\text{O}_{12}|| (001)[100]\text{SrTiO}_3$.

The surface morphology of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ epitaxial film was observed by SPM (Fig. 3). Rather smooth surface (root mean square roughness, $R_{\text{rms}} \sim 5$ nm) with grain structure (grain size 100 – 200 nm) was seen in the whole area. The magnified image shows that every grain consisted of very small (~20 nm) crystallites, indicating polycrystalline nature of the film.

In order to further clarify the microstructure of the resultant film, TEM/STEM analyses were carried out (Fig. 4). The plan view TEM bright field image shows that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film is composed of the small grains with the diameter of ~50 nm [Fig. 4(a)]. In addition, the grain boundaries could be clearly observed [inset of Fig. 4(a)], indicating that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film is polycrystalline. In the STEM bright field image, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice (ab plane) is

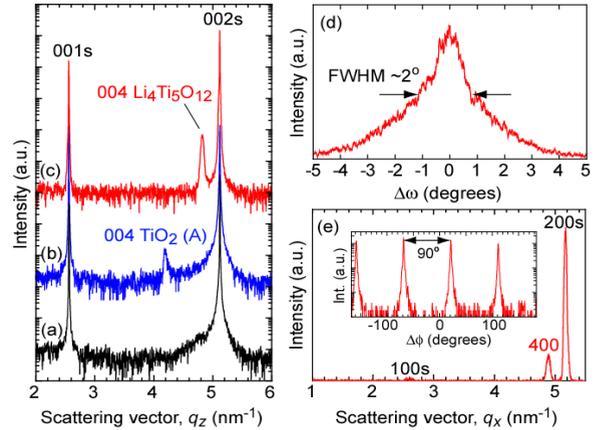


Fig. 2: Out-of-plane XRD patterns of the Li-Ti-O films [(a) as-deposited, (b) heated at 600°C without LiNO_3 , (c) heated at 600°C with LiNO_3 (solid-liquid phase epitaxy)]. (d) X-ray rocking curve of the 004 $\text{Li}_4\text{Ti}_5\text{O}_{12}$. FWHM value was ~2 degrees. (e) In-plane XRD pattern of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film grown by solid-liquid phase epitaxy.

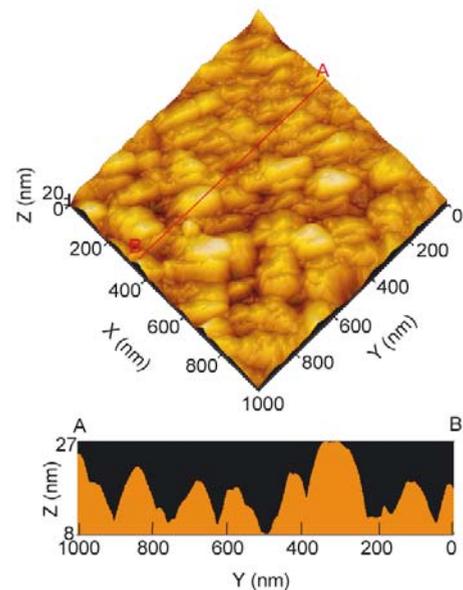


Fig. 3: Topographic SPM image of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ epitaxial film grown by the solid-liquid phase epitaxy.

clearly seen [Fig. 4(b)]. However, rather broad spots are seen in the electron diffraction pattern [Fig. 4(c)], indicating large twisting of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grains. These results are consistent with the results of XRD patterns.

Summary

We have demonstrated the solid-liquid phase epitaxy of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film as an example. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film was successfully obtained by our solid-liquid phase epitaxy method using LiNO_3 molten salt though re-vaporization of Li species occurred when the film was heated without LiNO_3 molten salt. The resultant film was composed of rather small crystallites (~20 nm) with an epitaxial relationship of $(001)[100]\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel (001)[100]\text{SrTiO}_3$.

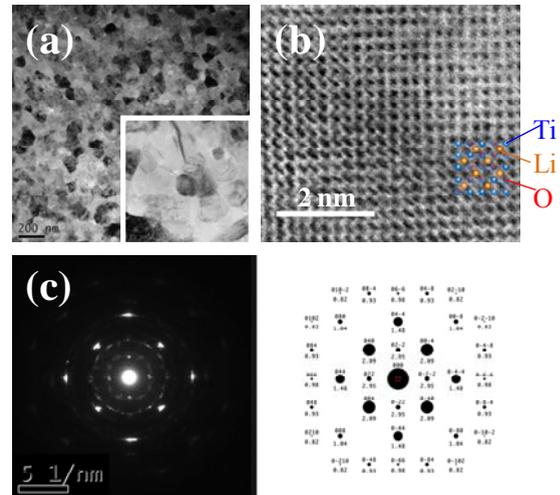


Fig. 4: TEM/STEM analyses of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ epitaxial film grown by the solid-liquid phase epitaxy. (a) Plan view TEM bright field image. The inset shows a magnified view. (b) STEM bright field image of [100]-oriented $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grain. (c) Electron diffraction pattern of [100]-oriented $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Right shows the simulation of (c).

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