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Preparation of cubic and tetragonal $Li_7La_3Zr_2O_{12}$ film by metal organic chemical vapor deposition

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ABSTRACT

$Li_7La_3Zr_2O_{12}$ films were prepared on polycrystalline Al_2O_3 by metal organic chemical vapor deposition. The effect of deposition temperature (T_{sub}) on the phase formation, morphology and deposition rates was investigated. Tetragonal $Li_7La_3Zr_2O_{12}$ film formed at $T_{sub} = 1023$–1173 K. The morphology changed from small-sized granular, polygonally faceted granular to flat and smooth surface with increasing T_{sub}. Cubic $Li_7La_3Zr_2O_{12}$ film with fine granular surface was deposited at $T_{sub} = 1173$–1223 K. The deposition rates of the cubic and tetragonal $Li_7La_3Zr_2O_{12}$ films were approximately 20 μm h^{-1}, which were one to two orders of magnitude greater than those of $Li_7La_3Zr_2O_{12}$ films by pulsed laser deposition.

1. Introduction

All-solid-state lithium-ion batteries have attracted much attention owing to strong safety requirements. Solid-state electrolyte films with high ionic conductivity are necessary for miniaturizing electronic devices; hence, Li-ion-conducting solid electrolytes require high ion conductivity and electrochemical stability against the Li metal anode. Sulfide compounds, such as $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ and Li_2S–P_2S_5 glass, with Li-ion conductivity greater than 10^{-3} S cm^{-1} have been developed as electrolytes [1–4]. Oxide electrolytes, on the other hand, offer high chemical stability in air. Li-β alumina [5], perovskite-type $Li_{0.5}La_{0.5}TiO_3$ [6], and glass-ceramic $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ [7] exhibit high lithium-ion conductivity of 10^{-3}–10^{-4} S cm^{-1} at room temperature. The Li-ion conductivity of these compounds is applicable for all-solid-state batteries; however, the Li metal anode would reduce the oxide electrolytes [8]. Among oxide electrolytes, garnet-type Li compounds, such as $Li_5La_3M_2O_{12}$ (M = Nb, Ta, Hf) and $Li_6ALa_2M_2O_{12}$ (A = Ca, Sr, Ba; M = Nb, Ta) [9–11], exhibit Li-ion conduction and good stability in contact with Li metal, e.g., $Li_6BaLa_2Ta_2O_{12}$ shows the highest Li-ion conductivity of 4×10^{-5} S cm^{-1}. However, such conductivities are insufficient for high power density solid state batteries [12].

Murugan et al. have reported garnet-type $Li_7La_3Zr_2O_{12}$. This compound has a high conductivity of 3×10^{-4} S cm^{-1} and a wide potential window [8,13,14]. They fabricated cubic $Li_7La_3Zr_2O_{12}$ by solid-state reaction at 1503 K. The structure of cubic $Li_7La_3Zr_2O_{12}$, with a space group of $Ia\bar{3}d$ (no. 230) and a lattice parameter of 1.29827(4) nm, was determined by single-crystal X-ray diffraction [15]. Awaka et al. synthesized tetragonal $Li_7La_3Zr_2O_{12}$ by solid-state reaction at 1253 K and reported a space group of $I4_1/acd$ (no. 142) [16]. It is known that the Li-ion conductivity of cubic $Li_7La_3Zr_2O_{12}$ is two orders of magnitude higher than that of the tetragonal phase at room temperature.

$Li_7La_3Zr_2O_{12}$ bulk forms have been fabricated by solid-state reaction and sol–gel process [8,12–20]. However, there are few publications regarding $Li_7La_3Zr_2O_{12}$ films [21,22]. Tan and Tiwawi fabricated $Li_7La_3Zr_2O_{12}$ film on $SrTiO_3$ (100) and sapphire (0001) single crystals by pulsed laser deposition (PLD) and subsequent post-annealing [21], whereas Kim et al. reported the epitaxial growth of $Li_7La_3Zr_2O_{12}$ films on garnet $Gd_3Gd_5O_{12}$ single crystals by PLD [22]. Metal-organic chemical vapor deposition (MOCVD) is a versatile technique for fabricating films at high deposition rates and moderate vacuum conditions (several hundred Pa to even atmospheric pressure). Moreover, the morphology and phase formation of the thin films is well controlled, and thus, it is well suited for producing the wide-ranging designs of all-solid-state thin-film batteries. We have fabricated $LiCoO_2$ cathode films with highly orientated textures on polycrystalline and single-crystal substrates by MOCVD at high deposition rates [23–25]. To date, there are no reports on the fabrication of $Li_7La_3Zr_2O_{12}$ films on poly-crystalline substrates and on the formation of the tetragonal phase. In this study, cubic and tetragonal $Li_7La_3Zr_2O_{12}$ films were prepared on poly-crystalline Al_2O_3 by MOCVD, and the effect of deposition temperature (T_{sub}) on the phase formation, morphology and deposition rates was investigated.

2. Experimental

Li–La–Zr–O films were prepared in the vertical cold-wall type CVD chamber shown in Fig. 1. Li(DPM) (dipivaloylmethanato-

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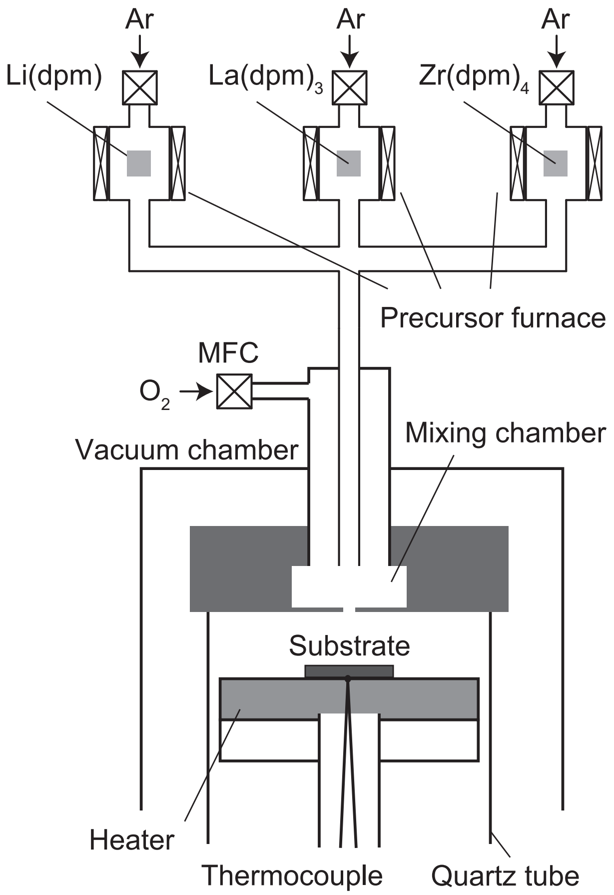

Fig. 1. Schematic of a cold wall type CVD apparatus.

lithium), La(DPM)$_3$ (tri-dipivaloylmethanato-lanthanum) and Zr(DPM)$_4$ (tetrakis-dipivaloylmethanato-zirconium) were used as precursors. The vaporization temperatures of Li(DPM), La(DPM)$_3$ and Zr(DPM)$_4$ were 555–560, 517–519 and 517–519 K, respectively. The molar ratios of the Zr source vapor to Li ($R_{Li/Zr}$) and Zr to La ($R_{La/Zr}$) were 4.0 and 1.0, respectively. The source vapor was carried into the CVD reactor by Ar gas. Oxygen gas was separately supplied via a double-tube nozzle and mixed with the source vapor above the substrate. The total gas flow rate was fixed at 4.0×10^{-6} m^3 s^{-1}. A polycrystalline Al$_2$O$_3$ substrate (99.5% purity; 10 mm × 10 mm × 1 mm; Japan Fine Ceramics Co.) was used as a substrate. The Al$_2$O$_3$ substrate was set on a hot stage, and T_{sub} was monitored with a thermocouple. Li–La–Zr–O films were deposited at T_{sub} = 923–1273 K. The total pressure in the CVD chamber (P_{tot}) was fixed at 400 Pa. The experimental conditions are summarized in Table 1.

Table 1
Deposition conditions of Li–La–Zr–O films.

Vaporization temperature	
Li(dpm)	555–560 K
La(dpm)$_3$	517–519 K
Zr(dpm)$_4$	517–519 K
Ar carrier gas flow rate	
For Li Li(dpm)	0.67×10^{-6} m^3 s^{-1}
For La(dpm)$_3$	0.67×10^{-6} m^3 s^{-1}
For Zr(dpm)$_4$	0.67×10^{-6} m^3 s^{-1}
O$_2$ gas flow rate	1.33×10^{-6} m^3 s^{-1}
Substrate	Mirror-polished Al$_2$O$_3$ Sintered SrRuO$_3$
Substrate temperature (T_{sub})	923–1273 K
Total pressure (P_{tot})	400 Pa
Deposition time	900 s

The phases and orientation of Li–La–Zr–O films were analyzed by X-ray diffraction with Cu Kα radiation (θ–2θ XRD; RAD-2C, Rigaku). The surface and cross-sectional morphologies were observed by scanning electron microscopy (SEM; S3100-H, Hitachi) at 10 kV acceleration voltage. The chemical state and composition were examined by X-ray photoelectron spectroscopy (XPS; AXIS ultra, Kratos) with Al K*a* radiation operated at 15 kV and 10 mA with the analyzing area of 110 μm in diameter. The surface of the film was sputtered by Ar$^+$ at 4 keV for 2.7 ks with the sputtering rate of 0.115 nm s^{-1} to remove carbonate formed on the top surface of the films due to exposure to air after the deposition. The deposition rate was calculated from the deposition time and thickness.

3. Results and discussion

Fig. 2 shows the effect of T_{sub} on the XRD patterns of Li–La–Zr–O films. La$_2$Zr$_2$O$_7$ film with the pyrochlore structure formed at T_{sub} = 973 K, as shown in Fig. 2(a). This film showed a strong (222) peak. The crystal structure of La$_2$Zr$_2$O$_7$ belongs to the pyrochlore type, comprising six-coordinated Zr ions and eight-coordinated La ions that forms a network of corner-shared octahedra of ZrO$_6$ with the dodecahedra of LaO$_8$ filling the interspaces [26]. The (111) plane forms a network of chains of edge-sharing ZrO$_6$ and LaO$_8$ alternately aligned in the direction to $\left\langle 1\bar{1}0 \right\rangle$. As T_{sub} increased to 1073 K (Fig. 2(b)), tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ formed, which was a Li-containing oxide having the La/Zr

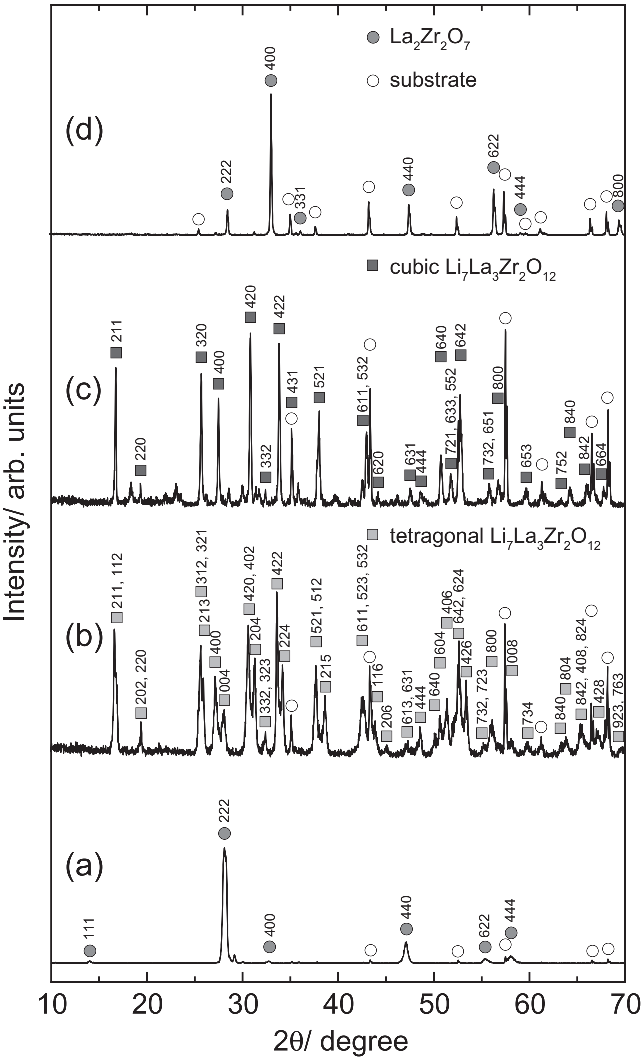

Fig. 2. XRD patterns of Li–La–Zr–O films at T_{sub} = 973 (a), 1073 (b), 1223 (c) and 1273 K (d).