Oriented growth and electrical property of LiAl_5O_8 film by laser chemical vapor deposition

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LiAl_5O_8 films were prepared by laser chemical vapor deposition, and the effect of the deposition temperature (T_{dep}) on the orientation, microstructure, and deposition rate was investigated. In the T_{dep} range of 980–1040 K, highly (110)-oriented LiAl_5O_8 film comprising flake-like grains elongated to [110] with flatter face of (111) formed at the maximum deposition rate of $70 \mu\text{m h}^{-1}$. Above $T_{\text{dep}} = 1050 \text{ K}$, dense LiAl_5O_8 films slightly oriented to (100) were deposited with faceted columnar grains of pyramidal and terrace shapes. The electrical properties of the LiAl_5O_8 films were examined using AC impedance spectroscopy. The complex plane plots of the dense LiAl_5O_8 film consisted of a semicircle associated with the bulk response and an inclined spike, suggesting the ionic conduction in the LiAl_5O_8 film.

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1. Introduction

LiAl_5O_8 is a stable phase in the Al_2O_3 – Li_2O pseudo-binary system. LiAl_5O_8 is a promising material for catalysts and supports, and is a host material for rare-earth-free oxide phosphors.^{1)–8)} The crystal structure of LiAl_5O_8 is an inverse spinel with cubic lattice,⁷⁾ which has similarities to the spinel of the γ - Al_2O_3 catalyst.⁸⁾ Li_5AlO_4 is known as a Li-ionic conductor in the Al_2O_3 – Li_2O system,⁹⁾ whereas the Li-ion conduction of LiAl_5O_8 has not been defined.

It is difficult to synthesize LiAl_5O_8 using the conventional solid–solid reaction route because of the high vapor pressure of Li_2O and the chemical inertness of Al_2O_3 powder.^{2),10),11)} Although LiAl_5O_8 has been fabricated via melt-solidification^{2),7)} and wet chemical processing,⁵⁾ the precise composition of LiAl_5O_8 could be hardly controlled. LiAl_5O_8 films were synthesized by a sol–gel method, and a transparent $\text{Fe}^{3+}/\text{Co}^{2+}$ -doped LiAl_5O_8 film exhibited fluorescence.¹²⁾ It is of importance to control the crystal orientation of LiAl_5O_8 film for catalytic supports, because microstructures of catalytic materials could be affected by surface orientations of supports.¹³⁾

Chemical vapor deposition (CVD) is a versatile technique used to synthesize films with a variety of microstructures and oriented textures.^{14)–16)} As LiAl_5O_8 contains the highly volatile Li element, the precise control of the compositions and phases by vapor deposition is difficult because of the significant loss of Li-precursor vapor at high temperature. Laser CVD is a suitable method to synthesize materials containing volatile elements, because the irradiation of the high-power laser can activate precursors and chemical reactions locally at the substrate surface, avoiding the loss of volatile precursors.^{17),18)} Ito et al. reported the synthesis of highly oriented Al_2O_3 films with a variety of oriented textures controlled by the deposition parameters in laser CVD, such as deposition temperatures and pressures.¹⁹⁾

We have demonstrated the synthesis of Li–Al–O films by laser CVD.²⁰⁾ This study investigated the effect of the deposition temperature (T_{dep}) on the preferred orientation, microstructure, deposition rate (R_{dep}) and electrical properties of LiAl_5O_8 films and reported the ionic conduction of LiAl_5O_8 films.

2. Experimental

LiAl_5O_8 films were prepared by laser CVD. A continuous wave diode laser (InGaAlAs, wavelength: 808 nm) was employed with a laser power output ranging from 60 to 200 W and an irradiation spot size of 15 mm in diameter. An AlN substrate (10 mm × 10 mm × 1 mm) was placed on a hot stage pre-heated to 873 K. T_{dep} was measured using a thermocouple beneath the substrate. A schematic diagram and description of the deposition procedure are presented elsewhere.²⁰⁾ The vaporization temperatures of the $\text{Al}(\text{acac})_3$ (acac: acetylacetonate) and $\text{Li}(\text{dpm})$ (dpm: dipivaloylmethanate) precursors were 443 and 493 K, respectively, at which the vaporized ratio of Li/Al precursors ($R_{\text{Li/Al}}$) was 0.3. The precursor vapors and O_2 gas were separately introduced into the CVD chamber through a double-tube nozzle. The flow rates of the Ar carrier gas for each precursor and O_2 gas were 8.3×10^{-7} and $1.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, respectively. The temperature of all the gas lines was maintained at 553 K to prevent the condensation of the precursor during the transport. The total chamber pressure was maintained at 200 Pa, and the deposition time was maintained at 600 s.

The deposition rate was calculated from the thickness increase of the films as a function of the deposition time. The crystalline phase of the Li–Al–O films was examined by X-ray diffraction (XRD; Cu-K α , RAD-C, Rigaku, Japan). The degree of orientation on the (*hkl*) reflection was calculated using the Harris texture coefficient (*TC*):²¹⁾

$$TC(hkl) = N \frac{I_m(hkl)/I_0(hkl)}{\sum I_m(hkl)/I_0(hkl)} \quad (1)$$

where $I_m(hkl)$ and $I_0(hkl)$ are the intensities from the (*hkl*) plane,

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by measurement, and from the powder pattern (JCPDS #87-1278), respectively. The (210), (220), (222), (400), (422), and (511) reflections of LiAl_5O_8 were used for the calculation ($N = 6$). The microstructure was examined using scanning electron microscopy (SEM; S-3100H, Hitachi, Japan) and transmission electron microscopy (TEM, EM-002B, TOPCON, Japan). Crystal structure illustrations were produced using VESTA software.²²⁾

The electrical properties were investigated using an AC impedance analyzer (a model SI-1260 impedance/gain-phase analyzer coupled with a model SI-1286 electrochemical interface and a model 1296 dielectric interface, Solartron Analytical Co., Farnborough, UK) in the frequency range of 1–10⁶ Hz in the temperature range of 773–1173 K. A Pt layer with a thickness of 200 nm was deposited as a lower electrode on an AlN substrate using D.C. sputtering at 1073 K for 900 s. The LiAl_5O_8 film was deposited on the Pt/AlN substrate. An Au upper electrode was prepared on the LiAl_5O_8 film using Au paste heated at 1073 K in air for 7.2 ks. The measurement cell was maintained at the testing temperature for at least 1.8 ks to stabilize the specimens.

3. Results and discussion

Figure 1 presents the XRD patterns of the LiAl_5O_8 films prepared at $T_{\text{dep}} = 1013$ K (a) and 1164 K (b). At $T_{\text{dep}} = 1013$ K [Fig. 1(a)], the (220) and (440) reflection peaks at 32.0 and at 66.9°, respectively, were significantly high, whereas the (311) reflection at 37.7° was the strongest in the powder reference pattern (JCPDF#87-1278). This indicated that the LiAl_5O_8 film was grown with preferred (110)-orientation. At $T_{\text{dep}} = 1164$ K [Fig. 1(b)], the (400) reflection at 45.9° exhibited high intensity, compared with the (220) and (440) reflection peaks, although definite peaks from various indexed planes, e.g., (210), (211), (222) and (511), were identified. Because the (440) reflection peak was the second strongest in the powder reference, the LiAl_5O_8 film was slightly oriented to (100).

Figure 2 depicts the effect of T_{dep} on $TC(220)$ and $TC(400)$ of the LiAl_5O_8 films. At T_{dep} below 1050 K, $TC(220)$ exhibited high values in the range of 2.8–3.9, whereas $TC(400)$ was lower than 1.0. With increasing T_{dep} , $TC(220)$ decreased at approximately $T_{\text{dep}} = 1050$ K whereas $TC(400)$ increased to 2.0. Thus, the LiAl_5O_8 films exhibited a preferred orientation to (110) at low

temperatures ($T_{\text{dep}} < 1050$ K), whereas slightly (100)-oriented LiAl_5O_8 films were grown at high temperatures ($T_{\text{dep}} > 1050$ K).

The microstructure of the (110)-oriented LiAl_5O_8 film prepared at $T_{\text{dep}} = 1013$ K is shown in **Fig. 3**. The surface SEM image [Fig. 3(a)] reveals flake-like grains with the sizes of several

Fig. 2. Effect of T_{dep} on $TC(220)$ and $TC(400)$ of LiAl_5O_8 films.

Fig. 1. XRD patterns of LiAl_5O_8 films prepared at $T_{\text{dep}} = 1013$ K (a) and 1164 K (b). A reference powder pattern of LiAl_5O_8 (JCPDF#87-1278) is also included at the bottom.

Fig. 3. Microstructures of LiAl_5O_8 films at $T_{\text{dep}} = 1013$ K: surface (a) and cross-sectional (b) SEM images, a cross-sectional bright field TEM image (c) and electron diffraction pattern (d) of a flake-like grain. The crystal texture of a flake-like grain is also illustrated in (e) and (f).

Fig. 4. Surface (a) and cross-sectional (b) SEM images of LiAl_5O_8 films at $T_{\text{dep}} = 1164 \text{ K}$. The textures of pyramidal and terrace facets are illustrated in (c–e).

micrometers. The flake-like grains were perpendicular to the substrate surface, as observed in the SEM image in the cross-sectional image [Fig. 3(b)]. The TEM bright-field image [Fig. 3(c)] and electron diffraction pattern [Fig. 3(d)] of a flake-like grain revealed that the thin flatter face was (111) and the top thin surface corresponded to (110). Hence, the oriented texture of the flake-like grain can be described as illustrated in Fig. 3(e). The crystal structure of LiAl_5O_8 is an inverse spinel with a cubic lattice (space group: $P4332$, lattice constant: $a = 7.908 \text{ nm}$);⁷⁾ Li atoms and half of the Al atoms form six-coordinated octahedra (LiO_6 and AlO_6) sharing their edges and the other Al atoms form four-coordinated tetrahedra (AlO_4) sharing corners of the octahedral. Here, strings consisting of edge-sharing LiO_6 and AlO_6 octahedra are extended to [110] [dotted lines in Fig. 3(e)], where the shared edges are parallel to (110) as indicated by the solid lines in Fig. 3(e). Figure 3(f) illustrates the crystal structure in the direction parallel to [110], corresponding to the top view of a flake-like grain. Strings of LiO_6 and AlO_6 octahedra are aligned along the (111) plane, forming a layered structure. Next to the layer, another layer consisting of strings of LiO_6 and AlO_6 octahedra and AlO_4 tetrahedra is placed. These two types of layers are alternatively stacked in the direction perpendicular to (111). At low $T_{\text{dep}} < 1050 \text{ K}$, the crystal growth rate in the direction of [111] could be slow, whereas the strings of edge-sharing LiO_6 and AlO_6 octahedra to [110] were preferably extended, resulting in (110)-oriented texture with flake-like grains.

Figure 4 depicts SEM images of the surface and cross section of the LiAl_5O_8 film at $T_{\text{dep}} = 1164 \text{ K}$. The surface morphology comprising of faceted grains with the sizes of approximately $1 \mu\text{m}$ with a dense columnar cross section. The typical facets had pyramidal and terrace shapes, as indicated by (c) and (d) in Fig. 4(a). Because the film at $T_{\text{dep}} = 1164 \text{ K}$ was slightly oriented to (100) (as indicated in Figs. 1 and 2), the pyramidal facets could consist of (120) planes, as illustrated in Fig. 4(c), whereas the terrace facets were flanked with (120) planes and the (100) plane placed on the top in Figs. 4(d) and 4(e).

Figure 5 summarizes the deposition rate of the LiAl_5O_8 films in the Arrhenius format. At $T_{\text{dep}} < 1050 \text{ K}$, the deposition rate increased with an increase in T_{dep} and reached a maximum value

Fig. 5. Effect of T_{dep} on the deposition rate in Arrhenius format.

Fig. 6. Complex plane plots at 873 K (a) and 1073 K (b) for the LiAl_5O_8 film prepared at $T_{\text{dep}} = 1164 \text{ K}$. The insets present the corresponding plots for high magnitudes and low frequencies.

of $70 \mu\text{m h}^{-1}$ at 1013 K . Here, the film exhibited the preferred (110) orientation with flake-like grains. As T_{dep} further increased above 1050 K , the deposition rate decreased, and slightly (100)-oriented LiAl_5O_8 films were deposited with a dense faceted morphology.

At $T_{\text{dep}} < 1050 \text{ K}$, preferential growth of LiAl_5O_8 with (110) orientation occurred with flake-like grains, for which it was difficult to perform impedance spectroscopy. However, dense LiAl_5O_8 films formed at $T_{\text{dep}} > 1050 \text{ K}$. **Figure 7** depicts the complex impedance plots at 873 K (a) and 1073 K (b) for the dense LiAl_5O_8 film prepared at $T_{\text{dep}} = 1164 \text{ K}$. The complex plane plots at 873 K [Fig. 6(a)] consisted of a semicircle con-

Fig. 7. Spectroscopic plots of Z'' and M'' at 873 K for the LiAl₅O₈ film prepared at $T_{\text{dep}} = 1164$ K.

verging to the original point at high frequency and an inclined spike at low frequency. The inclined spike extended straight-forward to high Z' and Z'' [Fig. 6(a), inset]. Figure 7 shows a spectroscopic spectra of Z'' and M'' of the dense LiAl₅O₈ film. The M'' spectrum had a single relaxation peak at 3×10^4 Hz, whereas the Z'' spectrum consisted of a relaxation peak at 3×10^4 Hz and low-frequency dispersion. Assuming the paired Z'' and M'' peaks at 3×10^4 Hz were the Debye peaks associated with a parallel RC element, the magnitudes of Z''_{max} and M''_{max} at the peak maxima are given by Eqs. (2) and (3).²³⁾

$$Z''_{\text{max}} = \frac{R}{2} \quad (2)$$

$$M''_{\text{max}} = \frac{\varepsilon_0}{2C} \quad (3)$$

Here, ε_0 is the permittivity of free space, 8.854×10^{-14} F cm⁻¹. The capacitance (C) associated with the M'' relaxation peak at 3×10^4 Hz in Fig. 7 was calculated to be 9.6×10^{-13} F cm⁻¹, which was a typical value for the bulk capacitance.^{24),25)} This relaxation with paired Z'' and M'' peaks yielded the semicircular impedance response in the complex plane plots in Fig. 6; hence, the semicircle was interpreted as a bulk response of the LiAl₅O₈ film, expressed as a single parallel RC element. As the temperature increased to 1073 K, the magnitude of the semicircle decreased because of a decrease in the bulk resistance of the LiAl₅O₈ film as observed in Fig. 6(b). In the low-frequency range ($>10^3$ Hz), the dispersion of the Z'' spectroscopic plot (Fig. 7) yielded the strong inclined spike in the complex plane plots (Fig. 6, insets). This strong spike could be attributed to electrode polarization. The electrode polarization is associated with the blocking of charge transport at the interface of the electrode–bulk LiAl₅O₈ film. The spike was inclined at approximately 45°, which is commonly referred to as the infinite Warburg impedance of a parabolic diffusion process for ionic charge carriers.²⁶⁾ Thereby, the inclined spike (Fig. 6) associated with low-frequency dispersion in the Z'' spectroscopic plot could suggest ionic conduction in the LiAl₅O₈ film.

Figure 8 shows the effect of temperature on the electrical conductivity (σ_b) of the bulk for the LiAl₅O₈ film in Arrhenius format, together with the conductivity of sintered bodies of LiAl₅O₈, a solid solution of LiAl₅O₈–LiFe₅O₈ [Li(Fe_xAl_{1-x})₅O₈], and LiAlO₂.^{10),27)} σ_b of the LiAl₅O₈ film ranged from 10^{-7} to 10^{-5} S cm⁻¹ in the temperature range of 773–1173 K with an activation energy (E_a) of 1.20 eV. This agreed with the conductivity of

Fig. 8. Effect of the electrical conductivity of LiAl₅O₈ films, together with reference values of sintered bodies of LiAl₅O₈¹⁰⁾ and Li(Fe_xAl_{1-x})₅O₈.²⁷⁾

the LiAl₅O₈ sintered body reported in Ref. 10. Li(Fe_xAl_{1-x})₅O₈ consists of insulating LiAl₅O₈ and semiconducting isostructural LiFe₅O₈. Arakawa et al. reported that the electrical conductivity of Li(Fe_xAl_{1-x})₅O₈ increased with an increase in x . σ_b of the LiAl₅O₈ film was two to three orders of magnitude lower than that of Li(Fe_xAl_{1-x})₅O₈ with x of 0.14. Although electron hopping from Fe²⁺ to Fe³⁺ has been reported to be the primary charge transfer mechanism in LiFe₅O₈, Li⁺ ion conduction may occur in addition to electronic conductivity,²⁸⁾ as this material contains Li⁺ ions and has a similar crystal structure to LiMn₂O₄ spinel.²⁹⁾ Among the Li₂O–Al₂O₃ system compounds, Li₅AlO₄ is well known as a Li⁺ ion conductor, and Li⁺ ion conduction in LiAlO₂ has been reported in the literature.^{30),31)} As the primary charge transfer mechanism of LiAl₅O₈ has not been established, further studies are required to elucidate the primary transport carrier and ionic transport number; however, the electrical conductivity in the LiAl₅O₈ film would involve the Li⁺ ion conduction that observed as the strong low-frequency spike in the complex plane plots in Fig. 6.

4. Conclusions

LiAl₅O₈ film were prepared by laser CVD. At lower deposition temperatures ($T_{\text{dep}} < 1050$ K), the LiAl₅O₈ films were highly oriented to (110) with flake-like morphology. The flake-like grains had (111) flatter faces and a (110) top thin surface. At higher deposition temperatures ($T_{\text{dep}} > 1050$ K), dense LiAl₅O₈ films formed with slight (100) orientation at the maximum deposition rate of 70 μm h⁻¹. The surface morphology consisted of pyramidal and terrace facets with {120} and {100} faces. The complex plane plots consisted of a semicircle representing the bulk response and inclined spike at low frequency. The low frequency dispersion in the Z'' spectroscopic plot and an inclined spike at low frequency suggests ionic conduction in LiAl₅O₈. The bulk conductivity of LiAl₅O₈ decreased with increasing temperature with an activation energy of 1.20 eV in the temperature range of 773–1173 K.

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