

Aluminum Migration during Deposition of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Thin Films on Aluminum Oxide SubstratesJung Hoon Park<sup>1,2</sup>, Wan-Shick Hong<sup>1,3,\*</sup>, Joong Sun Park<sup>3</sup>, Lei Cheng<sup>3</sup>, Jordi Cabana<sup>3</sup>, Guoying Chen<sup>3</sup>, Marca M. Doeff<sup>3</sup>, Thomas J. Richardson<sup>3</sup>, and Ji-Won Son<sup>2</sup><sup>1</sup>Dept. of Nano Science and Technology, University of Seoul, Seoul 130-742 Korea<sup>2</sup>High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea<sup>3</sup>Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.

Al-doped cubic phase  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) garnet is a promising solid electrolyte for lithium metal batteries, owing to its high Li-ion conductivity ( $>10^{-4} \text{ Scm}^{-1}$ ). Another advantage is the capability of stabilizing the cubic phase at a relatively low temperature ( $\sim 1100^\circ\text{C}$ ). Capping a porous membrane with a thin layer of LLZO will allow construction of a liquid-solid hybrid electrolyte system that exhibits both fast ion transport and minimal reactivity with the lithium metal anode.

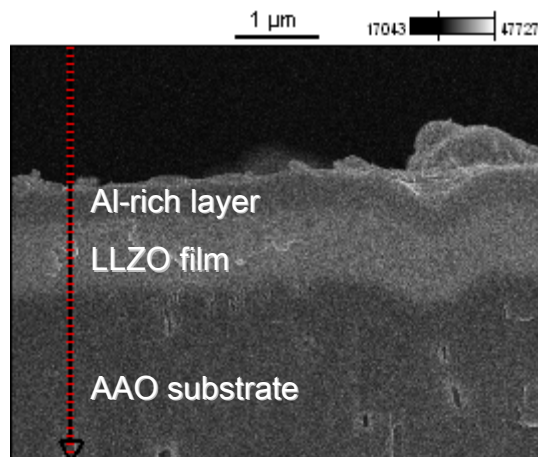
In this study, we attempted to deposit LLZO films containing 6 mole% Al onto anodized aluminum oxide (AAO) substrates by a pulsed laser deposition (PLD) technique. The target material for laser ablation was prepared by sintering an LLZO powder compact at  $1000^\circ\text{C}$  for 5 hours, and the cubic symmetry was confirmed by X-ray diffraction. The film deposition was performed at room temperature and  $700^\circ\text{C}$ , respectively. The LLZO films were also deposited on sapphire substrates to examine how the substrate profile influenced the film morphology.

1  $\mu\text{m}$ -thick films were obtained in an hour when the laser having an energy density of  $3 \text{ J/cm}^2$  was pulsed at 10 Hz. X-ray diffraction (XRD) revealed that the as-deposited films were amorphous regardless of the substrates. A columnar growth was observed in films grown at room temperature and was more distinctive on AAO than on sapphire. The columns merged with each other as they grew and effectively filled up the channels of AAO. In some regions of AAO specimens, the LLZO penetrated several microns into the channels. Vertical cracks developed between columns in room temperature films on AAO whereas the  $700^\circ\text{C}$  film on sapphire exhibited a homogeneous morphology.

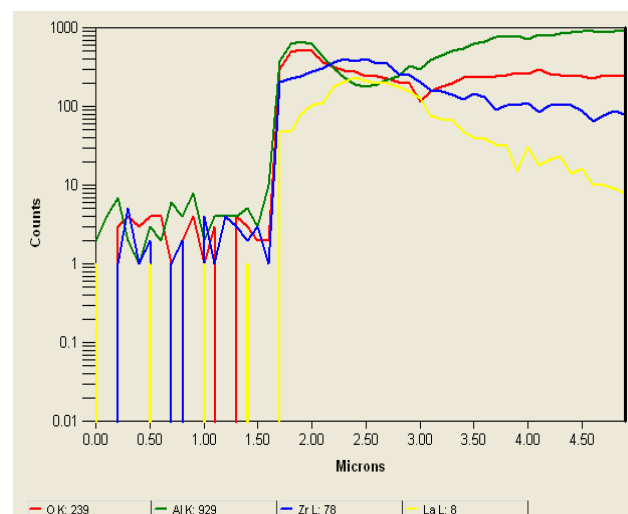
During the film deposition, aluminum was found to diffuse from the substrate into the film. The aluminum migration was more pronounced at an elevated temperature. Fig.1(a) shows a cross section of a film deposited at  $700^\circ\text{C}$  on an AAO substrate, which was polished with an Ar ion beam. The film was divided into two distinct regions with different shades. As shown in Fig.1(b), the Energy Dispersive Spectroscopy (EDS) scan along the dotted arrow in Fig.1(a) indicates that the upper region of the film is rich in aluminum and oxygen. Notably, the aluminum count in this region is comparable to that of the substrate. The driving force of this active migration of aluminum and its segregation on the film surface is not clear, but it is assumed that the Li supply either from the ablated radicals or from the contaminated reactor wall may attract aluminum to diffuse out to react to form lithium aluminum oxide. The Al-rich top layer was not observed in the films prepared at room

temperature, but thermal annealing at  $700^\circ\text{C}$  for 1 hour resulted in the same profile shown in Fig.1. The Al-rich layer was formed more readily when the crucible used for annealing was contaminated previously with Li from calcination of the source powder than when a fresh crucible was used.

These results suggest that a careful design of the film deposition procedure is called for in order to control the incorporation of Al into the film. Ideally, it should not exceed what is required for stabilization of the cubic phase.



(a)



(b)

Fig. 1 (a) Cross sectional SEM of the LLZO film deposited on an AAO substrate at  $700^\circ\text{C}$ , (b) EDS scan profile along the arrow indicated in (a)

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\* corresponding author : wshong@uos.ac.kr