Solid electrolyte, *thio*-LISICON, thin film prepared by pulsed laser deposition

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Abstract

$Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte thin films were fabricated by pulsed laser deposition (PLD) method at room temperature. The ionic conductivity of the thin film is 1.7×10^{-4} S cm^{-1} at 25 °C which is about one-fifth of the conductivity of the bulk target material (0.9×10^{-3} S cm^{-1}). The decrement of the conductivity is attributed to the increase of Li content from 3.2 in the target to 3.6 in the thin film, which reduces the number of the lithium vacancy in the structure of the *thio*-LISICON.
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1. Introduction

Solid-state lithium batteries have been studied as a fundamental solution of safety issue of conventional lithium batteries with non-aqueous electrolytes. These batteries have been also anticipated for thin film rechargeable lithium batteries, which will be used as on-chip power source [1–3]. Thin film solid electrolytes for the thin film batteries are required to have a higher ionic conductivity, a negligible electronic conductivity and be stable in contact with the anode and cathode electrodes, i.e. in a cell potential range of several volts. A solid electrolyte categorized in *thio*-LISICON family [4,5], $Li_{3.25}Ge_{0.25}P_{0.75}S_4$, recently reported by Kanno and co-workers exhibited a high ionic conductivity of 2.2×10^{-3} S cm^{-1} at 25 °C, high electrochemical stability, no reaction with lithium metal, and no phase transition up to 500 °C. These features make the *thio*-LISICON thin film especially promising for its use as a thin film solid electrolyte in the thin film rechargeable lithium batteries. Pulsed laser deposition (PLD) method is well known to have the following advantages in fabrication of thin films: high deposition rate, precise control over film thickness, and little deviation in composition of the obtained film from the target. By using this technique, several thin film electrodes of $LiCoO_2$ [6–9], $LiMn_2O_4$ [10–12], and V_2O_5 [13,14] have been prepared. In the present work, the solid electrolyte thin films of *thio*-LISICON were fabricated by PLD and characterized.

2. Experimental

The system for the PLD of the *thio*-LISICON films is composed of a KrF excimer laser ($\lambda = 248$ nm) operated at 10 Hz frequency, a vacuum chamber connected to an Ar-filled glove box via a load lock chamber, a rotating target, and a substrate holder as shown in Fig. 1. Powder of the *thio*-LISICON was prepared by solid-state reaction method from Li_2S, GeS_2, and P_2S_5 powders at a heating temperature of 500 °C for 20 h. The powder was pressed into a pellet, which was used as a target. The laser beam was directed to the target at an incident angle of 60° from normal. The distance from the target to the substrate and the laser power were 4 cm and ~ 0.7 J cm^{-2}, respectively.

The chemical composition of the target and the thin film was examined by inductively coupled plasma atomic emis-
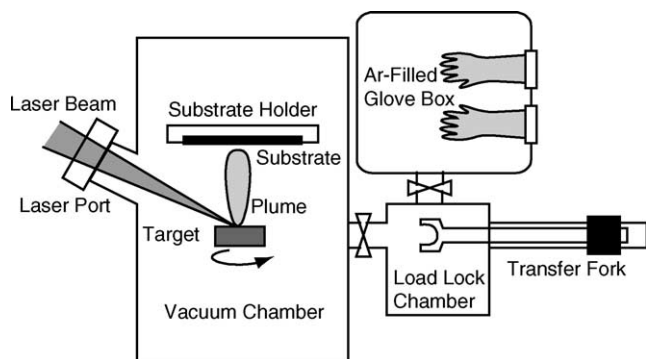
Fig. 1. Schematic representation of the setup for fabrication of the *thio*-LISICON thin film by the pulsed laser deposition (PLD).

sion spectroscopy (ICP-AES). Contents of Li, Ge, and P were determined by the ICP-AES. Residual mass was attributed to S. The $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target and the thin film deposited on sapphire $(0\,0\,0\,1)$ substrates were characterized by X-ray diffraction (XRD) using Cu Kα radiation and Raman spectroscopy in the region of 350–700 cm^{-1}.

For the conductivity measurements, the thin films were deposited on quartz substrates, on which Pt interdigitated array electrode was fabricated. The Pt interdigitated array electrode has two sets of comb-type electrode arrays; each array has 65 electrodes connected in parallel. Each electrode was 10 μm wide, 2.4 mm long, and 0.1 μm thick. Separation between the electrodes in each array was 5 μm. Conductivity of the thin film was measured under vacuum by AC impedance method. The impedance spectra were collected in a frequency range from 10^2 Hz to 10^7 Hz on a computer controlled frequency response analyzer. The AC amplitude used was 100 mV. The thicknesses of the films to calculate the conductivities from the impedances were calculated from the interval of the interference fringes in the infrared reflection spectra of the thin films deposited on Si $(1\,0\,0)$ substrates. Under this deposition condition, a thickness of 3.2 μm was achieved by the irradiation with 7.2×10^4 laser pulses.

3. Results

The chemical compositions of the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target and the thin film are shown in Table 1. The ratios of Ge/P and (Ge + P)/S for the thin film were about 1/3 and 1/4, re-

Table 1
Chemical compositions of the thin film prepared by PLD and the bulk sample for target measured by ICP-AES

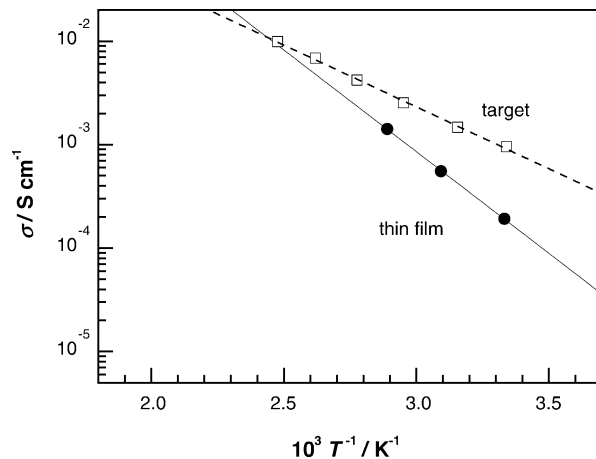|	Thin film		Target	
	Mass ratio/mass %	Atomic ratio	Mass ratio/mass %	Atomic ratio
Li	12.7	13.8	11.7	13.1
Ge	9.7	1.0	9.4	1.0
P	11.7	2.8	12.3	3.1
S (calc.)	65.9	15.5	66.7	16.1

Fig. 2. Arrhenius plots of the conductivity for the *thio*-LISICON thin film prepared by PLD and the bulk sample for target.

spectively, which were consistent with those of the target. The ratio of Li/(Ge + P) for the thin film was about 3.6/1 which was slightly larger than that for the target (3.2/1).

The temperature dependences of the conductivity for the target material and the thin film are shown in Fig. 2. The conductivities of the target and the thin film at 25 °C were deduced by extrapolation to be 0.9×10^{-3} and 1.7×10^{-4} S cm^{-1}, respectively. The conductivity of the thin
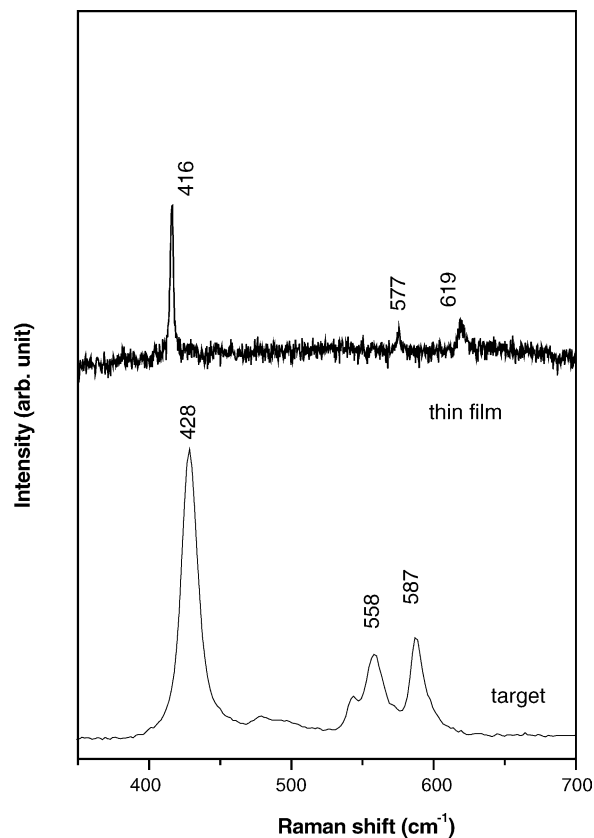

Fig. 3. Raman spectra of the thin film prepared by PLD and the bulk sample for target. Excitation wavelength was 514.5 nm.
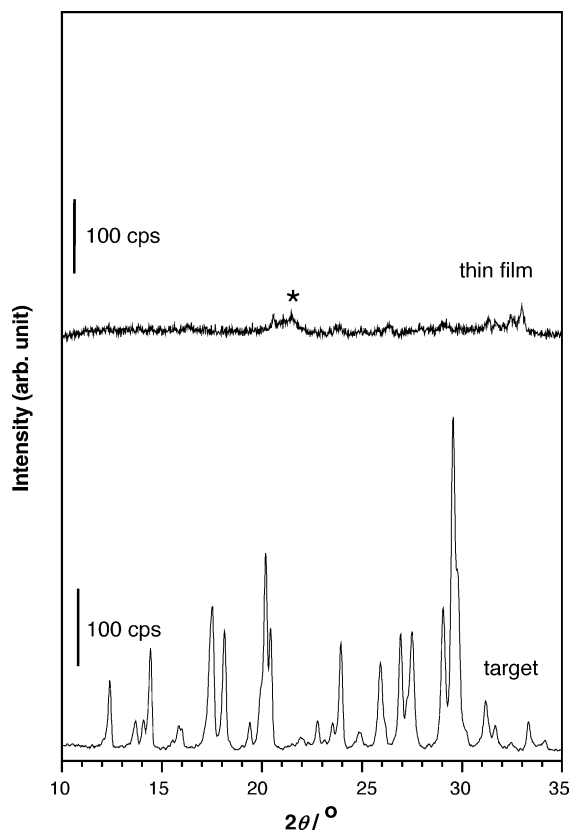
Fig. 4. XRD patterns of the thin film prepared by PLD and the bulk sample for target. A diffraction peak coming from to the sapphire substrate was indicated by asterisk.

film is about one-fifth of the conductivity of the target. The activation energies for the target material and the thin film were calculated to be 0.24 and 0.38 eV, respectively from the slope of the plot. The activation energy of the thin film was greater than that of the target.

Raman spectra for the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target and the thin film are shown in Fig. 3. They were very similar to each other, both of them had three lines and resembled that observed for Li_3PS_4 [15], which is the one of the end members in the *thio*-LISICON family. In the 410–430 cm^{-1} range, the target and the thin film gave strong lines at 428 and 416 cm^{-1}, respectively, which were attributable to symmetric stretching mode of P–S bonds [15]. The two other Raman lines in the 550–620 cm^{-1} range are related to the splitting of the B mode of P–S bonds which occurs when the anion symmetry is lowered [15,16].

The XRD pattern of the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target is shown in Fig. 4, which was consistent with the published data [4]. The thin film prepared by PLD did not show any intense peaks in the XRD pattern.

4. Discussion

The comparison between the Raman spectra for the target material and the thin film suggested that the local struc-

tures of the frameworks formed by PS_4 and GeS_4 tetrahedra are similar to each other, which indicates that the ablated fragments from the target were deposited on the substrate without changing the framework structure. However, the room temperature ionic conductivity of 1.7×10^{-4} S cm^{-1} for the thin film was about one-fifth of the conductivity of the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target (0.9×10^{-3} S cm^{-1}), and the activation energy of the thin film (0.38 eV) is greater than that of the target (0.24 eV). These differences in ionic conductivity and activation energy were considered to be attributable to the different compositions. The thin film had a larger Li content than the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ target. The high ionic conductivity in the *thio*-LISICON system is originated from the lithium vacancy introduced by the aliovalent substitution of $Ge^{4+} + Li^+ \leftrightarrow P^{5+}$ [4]. The increase of Li content from 3.2 in the target to 3.6 in the thin film reduces the number of lithium vacancy and, thus, is considered to decrease the conductivity. In fact, the conductivity at room temperature and the activation energy of $Li_{3.6}Ge_{0.6}P_{0.4}S_4$ powder, whose Li content is larger than one optimum for high ionic conduction, were reported to be about 2×10^{-4} S cm^{-1} and 0.34 eV [4], which are close to those of our thin film.

The room temperature ionic conductivity of 1.7×10^{-4} S cm^{-1} for the thin film showed its potential for application to thin film rechargeable lithium batteries, since the conductivity is much higher than that of LIPON (2×10^{-6} S cm^{-1}) [17,18], which has been regarded as one of the most promising thin film solid electrolytes so far. Furthermore, it should be noted that the highly conductive thin film electrolyte was obtained without heating or annealing. To construct solid-state thin film batteries, it is necessary to deposit a solid electrolyte thin film on a cathode active material. Heating during and annealing after electrolyte film deposition on a film of cathode active material is not recommended, because the two films may react and/or be unstuck owing to the differences in thermal expansion coefficient, even though the heating and annealing may improve the crystallinity.

5. Conclusion

$Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte thin films were fabricated by PLD method at room temperature. The ionic conductivity of the thin film was 1.7×10^{-4} S cm^{-1} at 25 °C and the activation energy for conduction was 0.38 eV. The ionic conductivity is about one-fifth of that of the bulk target material (0.9×10^{-3} S cm^{-1}). The decrement of the conductivity is considered to be caused by the difference in the chemical compositions between them.

Acknowledgements

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