Li₄GeS₄–Li₃PS₄ electrolyte thin films with highly ion-conductive crystals prepared by pulsed laser deposition

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Highly ion-conductive thin films in the pseudobinary system Li₄GeS₄–Li₃PS₄ were prepared by pulsed laser deposition (PLD). Raman spectra showed that the obtained thin films were mainly composed of Li⁺, (PS₄)^{3–}, (GeS₄)^{4–} and (GeS_{1/2}S₃)^{3–} ions. The 33Li₄GeS₄·67Li₃PS₄ (mol %) thin film showed glass transition phenomenon at about 160°C, suggesting that the obtained amorphous thin film was in a glassy state. The thin film exhibited higher ionic conductivity than the Li₄GeS₄ and Li₃PS₄ thin films because of the so-called “mixed anion effect”. Furthermore, the structural rearrangement and crystallization after heat treatment for the thin film increased ionic conductivity from 1.1×10^{-4} to 1.8×10^{-3} S cm^{–1} at 25°C, and decreased activation energy from 42 to 28 kJ mol^{–1}. Highly lithium-ion conductive thin films prepared in this study are promising for the application to bulk-type all-solid-state lithium secondary batteries.

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1. Introduction

Lithium secondary batteries are capable of a high energy density, high power and long cycle life.¹⁾ High-performance lithium batteries have attracted much attention as large-scale power storage systems for electric vehicles. However, safety issues become more important with the increasing size.²⁾ All-solid-state lithium secondary batteries with inorganic solid electrolytes have been widely studied as next generation batteries. Various advantages have been reported so far; no electrolyte leakage, long cycle performance, wide operation temperature range^{3–5)} and potential application of new electrode materials that are difficult to use in conventional batteries. In general, all-solid-state batteries are divided into two types. One is a film-type battery and the other is a bulk-type battery. Especially, bulk-type batteries, which use composite electrodes of active materials and electrolyte powders, are anticipated as power sources with high energy density and thus are suitable for large-scale batteries.

It should be noted that highly lithium ion-conductive solid electrolytes are indispensable for improving the performance of all-solid-state batteries. Lithium thiophosphates have been intensively studied as promising solid electrolytes for them. In our previous study, glass-ceramic electrolytes in the system Li₂S–P₂S₅, which were prepared by mechanical milling and subsequent heat treatment, showed a high ionic conductivity of more than 10^{-3} S cm^{–1} at room temperature.⁶⁾ A recent report by Kamaya et al. showed that Li₁₀GeP₂S₁₂ has an extremely high ionic conductivity of about 10^{-2} S cm^{–1} at room temperature, which is comparable to that of organic liquid electrolytes used in conventional lithium-ion batteries.⁷⁾ Moreover, inorganic glassy electrolytes are famous among solid electrolytes. They have various advantages, such as wide selection of compositions, single ion

conduction, higher ionic conductivity and easy film formation.⁸⁾ In oxide-based solid electrolytes, the glasses in the pseudobinary system Li₄SiO₄–Li₃BO₃ were prepared by rapid quenching of melts with a twin-roller quenching apparatus. At a middle composition of $x\text{Li}_4\text{SiO}_4 \cdot (100 - x)\text{Li}_3\text{BO}_3$, the $x = 60$ glass showed the highest conductivity of 6×10^{-6} S cm^{–1} at 300 K.⁹⁾ This phenomenon is generally called the “mixed anion effect” or “mixed former effect”. The increase of ionic conductivity probably relates to the structural changes of glasses with mixing two kinds of anions.^{10,11)} In this study, we focus on the “mixed anion effect” to increase ionic conductivity of sulfide glassy electrolytes. The glasses in the pseudobinary system Li₄GeS₄–Li₃PS₄ are expected to have high ionic conductivity because of the coexistence of (GeS₄)^{4–} and (PS₄)^{3–} ions. In general, sulfide electrolytes have higher ionic conductivities than oxides. However, it is difficult to prepare Li₄GeS₄–Li₃PS₄ glasses by the conventional rapid quenching method since these materials with high lithium-ion concentrations tend to crystallize easily.

We previously fabricated amorphous Li₂S–P₂S₅ and Li₂S–GeS₂ thin films with high lithium-ion concentrations by pulsed laser deposition (PLD).^{12,13)} PLD is a useful technique to prepare thin films by depositing plume species, ablated from target materials with irradiation of high energy pulsed laser.¹⁴⁾ This technique allows us to use target materials with high melting points and prepare amorphous solid electrolyte thin films with high quality. Furthermore, we applied this technique to coat solid electrolyte thin films on electrode particles, which resulted in the formation of an ideal electrode–electrolyte interface and the considerable decrease of solid electrolyte contents in composite electrodes. Consequently, the increase of energy density of all-solid-state batteries normalized by the total weight of the composite electrode was achieved by using this coating technique.^{13,15)} Bulk-type all-solid-state batteries with smaller amounts of solid electrolyte in the composite electrode will be fabricated by an increase in ionic conductivity of coating electrolytes.

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In this study, the $\text{Li}_4\text{GeS}_4\text{--Li}_3\text{PS}_4$ solid electrolyte thin films were prepared by PLD to achieve high ionic conductivity in thin film electrolytes. The morphology, structure and ionic conductivity were investigated for the obtained thin films. In addition, the influences of the heat-treatment for as-deposited thin films on their morphology, structure and ionic conductivity were evaluated.

2. Experimental

$x\text{Li}_4\text{GeS}_4\cdot(100-x)\text{Li}_3\text{PS}_4$ ($x = 25, 33, 50$ and 75 mol %) solid electrolyte thin films were prepared by PLD with a KrF excimer laser ($\lambda = 248$ nm, LPXPro, Lambda Physik). The pulsed laser energy was 200 mJ/pulse and its repeating frequency was 10 Hz. The energy density was estimated about 2 J/cm² at the target. The pellets of the mixture of Li_2S (Idemitsu Kosan, 99.9%), GeS_2 (Furuuchi Chem., 99.9999%) and P_2S_5 (Aldrich, 99%) crystalline powders without sintering were used as a target. Si or SiO_2 glass substrates were placed at the distance of 7 cm from the target. In order to prevent the obtained thin films from exposure to air atmosphere, an Ar-filled glove box was connected to a vacuum chamber for PLD. Each thin film was prepared at room temperature and under Ar gas pressure of 5 Pa. In addition, the heat treatment for as-deposited thin films was conducted in an Ar-filled glove box for 1 h.

The morphology of thin films deposited on Si substrates for 30 min was observed with a scanning electron microscope (SEM; JSM-6610A, JEOL). The chemical compositions of thin films were determined from inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7800, Seiko Instruments). X-ray diffraction (XRD) measurements ($\text{Cu K}\alpha$) were performed using a diffractometer (Ultima IV, Rigaku). Differential thermal analysis (DTA) was conducted using a thermal analyser (Thermo Plus TG8110, Rigaku) at a heating rate of $10^\circ\text{C min}^{-1}$. Raman spectra of thin films were obtained using a spectrometer (LabRAM HR-800, Horiba) equipped with a green laser (532 nm). Electrochemical impedance spectroscopy measurements of thin films were performed using an impedance analyzer combined with a dielectric interface (SI 1260 and SI 1296, Solartron Analytical). Comb-like gold electrodes sputtered on SiO_2 glass substrates were used to measure the conductivities of thin films parallel to the film surface. The thickness of SE thin film was estimated from cross-sectional SEM observations. The length and cross-sectional area of the comb-like gold electrodes were 5.0×10^{-2} cm and 8.5×10^{-4} cm², respectively. All the measurements were conducted under an Ar atmosphere. In this report, the obtained thin films are denoted by a nominal composition.

3. Results and discussion

The surface morphology and cross-sectional image for the thin film at the nominal composition of $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol %) are shown in Figs. 1(a) and 1(b), respectively. The thin film on a Si substrate had a relatively smooth surface and was dense with a thickness of about 1.3 μm . The estimated thicknesses of thin films with other compositions were ranging from 1.1 to 1.3 μm .

The XRD patterns of the $x\text{Li}_4\text{GeS}_4\cdot(100-x)\text{Li}_3\text{PS}_4$ ($x = 25, 33$ and 50 mol %) thin films are shown in Fig. 2(a). The thin films did not exhibit any diffraction peaks in the XRD patterns, indicating that as-deposited thin films prepared by PLD were amorphous. Figure 2(b) exhibits the DTA curve of the powder sample, obtained by peeling off the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin film from a Si substrate. There was an endothermic change corresponding to a glass transition phenomenon at around 160°C , suggesting that the amorphous thin film was in a glassy state.

Fig. 1. SEM images of the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol %) thin film prepared on Si substrate: (a) surface and (b) cross-section of the thin film.

Fig. 2. (a) XRD patterns of the $x\text{Li}_4\text{GeS}_4\cdot(100-x)\text{Li}_3\text{PS}_4$ ($x = 25, 33$ and 50 mol %) thin films prepared by PLD and (b) DTA curve of the powder sample obtained by peeling off the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin film from Si substrate.

Table 1. Chemical compositions, ionic conductivities at 25°C and activation energies for the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=0-100$ mol %) thin films. Pseudobinary system expressions, $\text{Li}_y\text{GeS}_z\text{-Li}_3\text{PS}_4$ for the thin films were determined by ICP-AES

x	Li/ (Ge+P)	P/Ge	$\text{Li}_y\text{GeS}_z\text{-Li}_3\text{PS}_4$	σ_{25} (S cm^{-1})	E_a (kJ mol^{-1})
100	— (—)	— (—)	—	8.8×10^{-5}	43
75	3.1 (3.7)	0.2 (0.3)	$\text{Li}_{3.1}\text{GeS}_{3.6}\text{-Li}_3\text{PS}_4$	9.0×10^{-5}	—
50	3.2 (3.5)	0.7 (1.0)	$\text{Li}_{3.3}\text{GeS}_{3.7}\text{-Li}_3\text{PS}_4$	6.0×10^{-5}	45
33	3.4 (3.3)	1.4 (2.0)	$\text{Li}_{4.0}\text{GeS}_{4.0}\text{-Li}_3\text{PS}_4$	1.1×10^{-4}	42
25	3.5 (3.2)	2.1 (3.0)	$\text{Li}_{4.6}\text{GeS}_{4.3}\text{-Li}_3\text{PS}_4$	8.0×10^{-5}	44
0	— (—)	— (—)	—	8.7×10^{-5}	50

Moreover, an exothermic peak corresponding to the crystallization was also observed. The following heat treatment for as-deposited thin film was conducted at 200°C, which is higher than the crystallization temperature determined by DTA.

The atomic ratios of Li/(Ge+P) and P/Ge in the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=25, 33, 50$ and 75 mol %) thin films measured by ICP-AES are listed in Table 1. The figures in parentheses represent the calculated values of nominal compositions. It was confirmed from a comparison between measured and calculated compositions, that the higher the value of x was in nominal compositions, the lower lithium concentrations were in obtained thin films. We previously prepared thin films in the system $\text{Li}_2\text{S-GeS}_2$ by PLD, in which large elemental loss for lithium in thin films occurred in comparison with target compositions.¹³⁾ This is probably because light elements such as lithium tend to be scattered by ambient Ar gas during the deposition. Similarly in this study, lithium concentrations decreased with increasing germanium concentrations in obtained thin films.

The Raman spectra of the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=25, 33, 50$ and 75 mol %) thin films are shown in Fig. 3. Peaks at around 300, 365, 385, 420 and 475 cm^{-1} are observed in the spectra of as-deposited thin films. The peak at 300 cm^{-1} is assigned to a Si substrate. Tachez et al. reported that the peak at 418 cm^{-1} was assigned to $(\text{PS}_4)^{3-}$ ions in Li_3PS_4 crystal.¹⁶⁾ The peaks at around 220 and 475 cm^{-1} are attributable to S-S bonds in elemental sulfur and lithium polysulfides Li_2S_x ,¹⁷⁾ respectively. Kim et al. reported that the peak at 340 cm^{-1} was assigned to $(\text{GeS}_4)_2$ units with bridging sulfurs, and the peaks at 385, 415, and 460 cm^{-1} were assigned to $(\text{GeS}_{1/2}\text{S}_3)^{3-}$, $(\text{GeS}_{2/2}\text{S}_2)^{2-}$, and $(\text{GeS}_{3/2}\text{S})^-$ ions with non-bridging sulfurs, respectively.¹⁸⁾ Yao et al. reported the peak at 372 cm^{-1} was assigned to $(\text{GeS}_4)^{4-}$ ions in the Raman spectra of sodium-ion conductive sulfide materials;¹⁹⁾ the peak at 365 cm^{-1} in this study is assigned to $(\text{GeS}_4)^{4-}$ ions. From the above assignment for the Raman spectra shown in Fig. 3, the obtained thin films were considered to be mainly composed of Li^+ , $(\text{PS}_4)^{3-}$, $(\text{GeS}_{1/2}\text{S}_3)^{3-}$ and $(\text{GeS}_4)^{4-}$ ions.

We reported that acid-base reactions for preparing oxide glasses were deeply related to the acidity of glass formers and the basicity of glass modifiers. Phosphate components showed stronger acidity than borate and silicate components in reacting with alkali oxides.²⁰⁾ It is speculated that the P_2S_5 component has stronger acidity than the GeS_2 component, and thus P_2S_5 preferentially reacts with Li_2S to form $(\text{PS}_4)^{3-}$ ions rather than $(\text{GeS}_4)^{4-}$ ions. Therefore, $(\text{PS}_4)^{3-}$ ions are considered to be mainly formed in thin films prepared by PLD. On the basis of this assumption and the ICP-AES data, the expression of pseudobinary system $\text{Li}_y\text{GeS}_z\text{-Li}_3\text{PS}_4$ determined for the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=25, 33, 50$ and 75 mol %) thin films is listed in Table 1. Deviation in chemical compositions from targets was confirmed at the

Fig. 3. Raman spectra of the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=25, 33, 50$ and 75 mol %) thin films prepared by PLD.

compositions of $x=50$ and 75 . This is probably because not only $(\text{GeS}_4)^{4-}$ ions but also $(\text{GeS}_{1/2}\text{S}_3)^{3-}$ ions were present in the obtained thin films. In addition, deviation in chemical compositions from targets was also seen at the composition of $x=25$. On the other hand, chemical compositions of the thin films at $x=33$ were almost identical to the nominal compositions. However, the peak attributable to $(\text{GeS}_4)^{4-}$ ions was not clearly observed in the Raman spectra of both thin films at $x=25$ and 33 . This is probably because unreacted Li_2S existed in lithium polysulfides Li_2S_x and thus $(\text{GeS}_4)^{4-}$ ions were not dominantly formed in the as-deposited thin films.

The ionic conductivities of the $x\text{Li}_4\text{GeS}_4(100-x)\text{Li}_3\text{PS}_4$ ($x=0, 25, 33, 50, 75$ and 100 mol %) thin films were measured with comb-like gold electrodes as blocking electrodes. A large semicircle and a subsequent straight line were observed in the complex impedance plots for the thin films, suggesting that each thin film is an ion conductor. Especially, for the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin film, the peak top frequency of the semicircle was 40 kHz . The estimated capacitance at the frequency was $1.8 \times 10^{-12}\text{ F}$, which indicates that the resistance of the semicircle is attributable to the bulk resistance because the typical bulk capacitance of ionic conductors is known to be $10^{-11}\text{--}10^{-12}\text{ F}$.²¹⁾ Temperature dependence of ionic conductivity obeyed the Arrhenius law; the activation energy for ionic conduction was calculated from the slope of the plots. The ionic conductivities at room temperature and activation energies are listed in Table 1 (Temperature dependence of ionic conductivity for the thin film at $x=75$ was not measured). In particular, the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin film showed the highest ionic conductivity of $1.1 \times 10^{-4}\text{ S cm}^{-1}$, which is almost identical to the ionic conductivity of amorphous $25\text{Li}_4\text{GeS}_4\cdot 75\text{Li}_3\text{PS}_4$ thin film prepared by PLD.²²⁾ Moreover, the thin film exhibited higher ionic conductivity than the Li_4GeS_4 and Li_3PS_4 thin films because of so-called “mixed anion effect” by the coexistence of $(\text{GeS}_4)^{4-}$ and $(\text{PS}_4)^{3-}$ ions. In contrast, the thin films at the composition of $x=25$ and 50 exhibited lower ionic conductivities in comparison with $x=33$. In general, the structural unit of S-S and the lower lithium

Fig. 4. Raman spectra of the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol%) thin films with and without heat treatment at 200°C .

concentrations tend to decrease the ionic conductivity of glassy electrolytes. The existence of insulative lithium polysulfides Li_2S_x for $x = 25$ and low lithium concentrations for $x = 50$ probably decreased ionic conductivity of thin films.

The effects of heat treatment for as-deposited thin films on their morphology, structure and ionic conductivity were examined. The as-deposited $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin films were heated at 200°C , which is beyond the crystallization temperature as shown in Fig. 2(b). A cross-sectional SEM observation showed the thin film after heat treatment still stuck to a Si substrate and the film thickness was not changed. **Figure 4** shows the Raman spectra of $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ thin films with and without heat treatment at 200°C . By the heat treatment, the peak intensity at 385 and 475 cm^{-1} decreased, while that at 365 cm^{-1} increased. This suggests the rearrangement of structural units was brought about by heat treatment, and $(\text{GeS}_4)^{4-}$ ions were dominantly formed instead of $(\text{GeS}_{1/2}\text{S}_3)^{3-}$ ions. Therefore, it was considered that the heat-treated thin film was mainly composed of Li^+ , $(\text{PS}_4)^{3-}$ and $(\text{GeS}_4)^{4-}$ units.

In the XRD pattern of the heat-treated thin film on a Si substrate, diffraction peaks were not clearly observed. This is probably because the crystallite size was too small to be detected in the XRD measurement. However, some diffraction peaks were observed in the XRD pattern of the powder sample, which was obtained by heat treatment for the powder peeled off from a Si substrate (**Fig. 5**). It is expected that the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) crystal phase⁷⁾ can be precipitated in the heat-treated thin films in terms of the nominal composition of $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol%), corresponding to the composition of LGPS crystal. Although the diffraction peaks attributable to LGPS crystal were observed in the XRD pattern, additional peaks at $2\theta = 18.3, 19.5, 22.6$ and 26.2° also appeared. All the peaks were assigned to thio-LISICON $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ crystal at region II ($0.6 < x < 0.8$), which showed the highest ionic conductivity of $2.2 \times 10^{-3}\text{ S cm}^{-1}$.²³⁾ **Figure 6**(a) exhibits complex impedance plots of thin films with and without heat treatment at 200°C . It was found that the resistance of the semicircle, attributable to bulk resistance, significantly decreased after heat treatment. **Figure 6**(b)

Fig. 5. XRD patterns of the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol%) powder sample obtained by heat treatment at 200°C of the thin film peeled off from Si substrate.

Fig. 6. (a) Complex impedance plots and (b) temperature dependence of ionic conductivity of the $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol%) thin film with and without heat treatment at 200°C .

shows temperature dependence of ionic conductivity for the as-deposited and heat-treated thin films. Their ionic conductivities were 1.1×10^{-4} and $1.8 \times 10^{-3}\text{ S cm}^{-1}$ at room temperature; their activation energies for ionic conduction were 42 and 28 kJ mol^{-1} , respectively. The heat-treated thin film showed higher ionic conductivity and lower activation energy than the as-deposited thin film. Heat treatment brought about structural rearrangement to form high lithium-ion conductive phase “thio-LISICON”, resulting in the increase of the ionic conduction of the thin film. In the near future, we will clarify the size and

distribution of crystalline phase precipitated in thin films by TEM observations.

We previously reported that the solid electrolyte coatings on electrode particles improved the energy density in bulk-type all-solid-state batteries. Therefore, highly lithium-ion conductive thin films will be effective in the formation of sufficient lithium-ion conduction paths even by using small amounts of solid electrolyte in the composite electrodes. Moreover, the thin films are anticipated for the further improvement of energy density, utilization of active materials and rate performance in bulk-type all-solid-state batteries.

4. Conclusions

Amorphous $\text{Li}_4\text{GeS}_4\text{-Li}_3\text{PS}_4$ thin films were prepared by pulsed laser deposition. The thin films were dense with a smooth surface. The $33\text{Li}_4\text{GeS}_4\cdot 67\text{Li}_3\text{PS}_4$ (mol %) thin film showed glass transition phenomenon at about 160°C , suggesting that the obtained amorphous thin film was in a glassy state. Raman spectra showed that the as-deposited thin film was mainly composed of Li^+ , $(\text{PS}_4)^{3-}$, $(\text{GeS}_4)^{4-}$ and $(\text{GeS}_{1/2}\text{S}_3)^{3-}$ ions. The thin film exhibited higher ionic conductivity than the Li_4GeS_4 and Li_3PS_4 thin films because of mixed anion effect. The heat-treated thin film showed higher ionic conductivity and lower activation energy than the as-deposited thin film. This is probably due to the precipitation of high lithium-ion conductive phase “thio-LISICON” in the thin film. Highly lithium-ion conductive thin films prepared by PLD in this study are promising for use as electrolytes for the improvement of bulk-type all-solid-state batteries.

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