Preparation and Characterization of Fast Ion Conducting Lithium Thio-Germanate Thin Films Grown by RF Magnetron Sputtering

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Abstract
In this study, amorphous lithium thio-germanate thin films were prepared by radio frequency (RF) sputtering deposition in Ar atmospheres. For the first time, new high quality lithium germanium sulfide nLi$_2$S + GeS$_2$ thin films, n = 1, 2, and 3, have been successfully made by RF sputtering and synthesized as new solid state electrolytes. Although these materials are unstable in air, the starting materials, target materials, and thin films made from them were thoroughly characterized by x-ray diffraction (XRD), Raman spectroscopy, SEM, x-ray photoelectron spectroscopy (XPS), and impedance spectroscopy using special setups to prevent contamination. These high quality thin films did not show any cracks and pits on the surface and the ionic conductivities of the thin films are 2–3 orders of magnitude higher than reported values for similar lithium containing oxide thin films. In this way, this work may provide a new way for developing new thin-film electrolytes for solid state lithium ion batteries.

Keywords
amorphous state electrolytes germanium compounds ionic conductivity lithium compounds materials preparation Raman spectra scanning electron microscopy sputter deposition, thin films, X-ray diffraction, X-ray photoelectron spectra

Disciplines
Materials Science and Engineering

Comments

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Preparation and Characterization of Fast Ion Conducting Lithium Thio-Germanate Thin Films Grown by RF Magnetron Sputtering

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In this study, amorphous lithium thio-germanate thin films were prepared by radio frequency (RF) sputtering deposition in Ar atmospheres. For the first time, new high quality lithium germanium sulfide nLi2S + GeS2 thin films, n = 1, 2, and 3, have been successfully made by RF sputtering and synthesized as new solid state electrolytes. Although these materials are unstable in air, the starting materials, target materials, and thin films made from them were thoroughly characterized by x-ray diffraction (XRD), Raman spectroscopy, SEM, x-ray photoelectron spectroscopy (XPS), and impedance spectroscopy using special setups to prevent contamination. These high quality thin films did not show any cracks and pits on the surface and the ionic conductivities of the thin films are 2–3 orders of magnitude higher than reported values for similar lithium containing oxide thin films. In this way, this work may provide a new way for developing new thin-film electrolytes for solid state lithium ion batteries.

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The enormous growth in portable consumer electronic devices such as mobile phones, laptop computers, digital cameras, and personal digital assistants over the past decade has generated a large interest in compact, high energy density and light-weight batteries.0,1 Rechargeable lithium batteries are attractive for many reasons: high voltages, high energy densities, wide operating temperature ranges, good power densities, flat discharge characteristics, and excellent shelf life.

There is an additional interest in specialized lithium batteries for use in the semiconductor industry and for printed circuit-board applications. These types of batteries are of interest for applications such as nonvolatile computer memory chips, smart cards, integrated circuits, and some medical applications.2,3 Therefore, developing improved solid-state thin-film batteries will allow better compatibility with microelectronic processing and components. Until now LiCoO2 or LiMn2O4 cathode materials and graphite anodes are used commercially. However, graphite-based materials are less attractive in terms of capacity when compared to lithium metal, 372 vs 3800 mAh/g, respectively, in spite of graphite’s higher cyclability and safer operation than lithium anodes.4 Therefore, solid-state lithium secondary batteries have attracted much attention because the replacement of conventional liquid electrolytes with an inorganic solid electrolyte may improve the safety and reliability of lithium batteries utilizing high capacity lithium metal anodes.5

A major challenge in this work is to create solid electrolytes for solid state thin film batteries with high ionic conductivity in order for them to be commercially viable. Until now, LiPON, Lithium phosphorous oxy-nitride, films have been one of the primary electrolytes in use because of its demonstrated good stability in contact with metallic lithium and their resulting long shelf life.6,7 However, these easily prepared oxide materials have relatively low ionic conductivities of ~10−5 S/cm at 25°C compared to bulk sulfide materials which have conductivities in the range of 10−3 S/cm at 25°C (Refs. 9 and 10). A primary requirement for all-solid-state lithium secondary batteries is that the solid electrolytes should possess high lithium ion conductivity at ambient temperatures. Sulfide glasses11 can exhibit conductivities as high as 10−2 S/cm, indicating that the replacement of oxide anions by sulfide anions with larger polarizabilities can substantially improve the ionic conductivity.12 Recently, sulfide glasses have been investigated and include SiS2 (Ref. 13), GeS2 (Refs. 14 and 15), P2S5 (Ref. 16), and B2S3 (Ref. 17). Among these sulfide materials, this study uses GeS2 as a base material because it is less hygroscopic (more oxidatively stable) and enables a more electrochemically stable matrix for lithium ion conduction to be prepared. Since GeS2-based materials are more stable in air than other sulfide materials, GeS2-based nLi2S + GeS2, n = 1, 2, and 3 thin-film electrolytes for Li-ion thin-film batteries were grown by rf magnetron sputtering techniques in Ar atmospheres. Structural properties, compositional properties, and their ionic conductivities were characterized by XRD, Raman spectroscopy, IR, SEM, XPS, and impedance spectroscopy.

Experimental Procedures

Preparation of GeS2 as a starting material.—Glassy GeS2 was prepared by reacting stoichiometric amounts of germanium metal powder (Alfa, 99.999%) and sulfur (Alfa, 99.999%) in an evacuated silica tube at 900°C. First, a bare silica tube was cleaned with a 2% aqueous ammonium bifluoride, NH4HF2, solution. The tube was then fitted with a valve assembly and evacuated to ~4 Pa through a liquid nitrogen trap using a roughing pump. Surface moisture on the inside of the tube was then removed under roughing pump vacuum by passing the tube over a natural gas/oxygen flame. Once this moisture was removed, the tube was transferred to the glovebox where a mixture of appropriate amounts of Ge and S were placed into the tube. The tube was then reconnected to the valve assembly and removed from the glovebox and evacuated with the roughing pump again to a pressure of ~4 Pa. The tube was sealed using a natural gas/oxygen torch.

The sealed tube was then placed into a furnace held at an angle of ~5° where it was heated at a rate of 1°C/min. from room temperature to 900°C. The tube was rotated at about ~7 rpm to promote mixing and reaction of the components. After the tube was held at 900°C for 8 h, it was quenched in air to room temperature. The final product from this process was a homogeneous, transparent, and yellow glass.

Preparation of the target materials.—To make the Li2GeS3, Li4GeS4, and Li6GeS5 target materials, stoichiometric amounts of Li2S (Alfa, 99.9%) and GeS2 (as prepared above) powders were used. These powders were vibratory SPEX milled for 15 min in a steel container with one steel grinding ball inside the glove box to ensure good mixing and to start the reaction process. Batches of 3 to 4 g were then melted in a covered vitreous carbon crucible at 950°C for 15 min inside a Mullite tube lined muffle furnace attached hermetically to the side of a glove box.

The melted charge was poured out of the crucible onto a brass plate and allowed to cool to room temperature. Fifteen grams of the powder was prepared in this way and weighed out and poured into a hardened 2-in.-diameter steel die set. The top press was placed onto the die set and allowed to settle on top of the powder. This assembly was sealed inside a plastic bag to prevent contamination (oxidation)

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during the consolidation process and taken outside the glove box to be uniaxially pressed. The die set assembly was placed with a sheet of 1/16 in. rubber between the press and the die set and loaded and held at ~60 MPa for ~12 h. The target was then adhered to a 2 in. diameter and 0.125 in. thick copper backing plate using silver paste so that it could be water-cooled during the RF deposition process to prevent overheating.

Preparation of Ni coated Si substrates for Raman spectroscopy characterization.—Cut single crystal silicon substrates, 1 cm × 1 cm × 360 μm, size and along the 111 plane were put into a “piranha” solution (aq-H2SO4: aq-H2O2 = 3:1) for 1 h, ultrasonically cleaned with acetone for 20 min and then rinsed with DI water for 20 min. The samples were dried with high purity N2 gas.

The cleaned silicon substrates were loaded into a dc sputtering chamber in the glove box and a Ni adhesion layer of ~120 nm thickness was grown in ~40 min at ~3 nm/min on the surface of the silicon substrates. The Ni/Si substrates then were loaded into the rf magnetron sputtering chamber on which the thin films were grown.

Deposition of the thin films.—After pumping down the chamber to ~10−11 Pa and baking the chamber with heating tapes to drive off moisture, the chamber was filled high purity Ar gas (99.9999%) to ~13 Pa and the plasma was lit by turning on the rf power to the target. Presputtering was performed for ~30 min on the target with the substrate shielded in order to clean the surface of the target of any residual impurities (oxygen and water) from the brief exposure to the atmosphere.

After presputtering, the shield was withdrawn and deposition continued to produce thin films. All films were produced with a power of 50 W and a ~3.3 Pa dynamic pressure of the argon sputtering gas.

X-ray diffraction (XRD).—To verify the structural phase of the GeS2 glass powder, Li2S crystalline powder and target materials, powder x-ray diffraction data were collected on finely ground samples at room temperature using a Scintag XDS 2000 diffractometer using CuKα radiation (λ = 1.5406 Å). It was operated at 40 kV and 30 mA in the 20 range of 30° – 80° in continuous scan mode with step size 0.03° and scan rate 2.0 deg/min. Because GeS2, Li2S, Li4GeS4 crystalline powder and target materials are unstable in air, these powder materials were covered by an amorphous polymer thin film (~10 μm) to prevent contamination by air during measurements.

X-ray photoelectron spectroscopy (XPS) analysis.—X-ray photoelectron core level spectra were obtained using a Scienta ESCA-300 spectrometer with monochromatic Al-Kα (1486.6 eV). Photoelectron spectra were determined at a take-off angle of 45°. The pressure inside the chamber was ~6.7 × 10−10 Pa at room temperature. The starting materials, GeS2 glass and Li2S crystalline powder were characterized by XPS to calibrate these elements, Li, Ge, and S and to verify the amount bridging, Ge-S-Ge, and non-bridging, Li3S/Li+ sulfur.

In the case of thin films, after being sputtered, the thin films on the Ni coated Si substrate the thin films were moved directly into the XPS chamber in a tightly closed sample jar loaded in the glove box. Tests were conducted on freshly sputtered films exposed for varying times to the glove box atmosphere to ensure that the film was not being contaminated by loading it into sample jars in the glove box likewise tests were made to ensure that moving to and loading the films in the XPS chamber did not contaminate the films. In order to get more accurate compositional data, Ar etching for 1 and 5 min at ~1 nm/min etching rate were performed to remove residual contaminants on the surface.

Raman spectroscopy.—The Raman spectra were collected at room temperature with a Renishaw inVia spectrometer using the 488 nm line of an Ar+ laser at 50 mW power. The instrument was calibrated using an internal silicon reference and the band positions were accurate to within ±1 cm−1. The samples were placed into a small cuplike plastic sample holder and then covered with clear amorphous tape to prevent air contamination. It was found by using the confocal feature of the Raman microscope that good quality spectra could be obtained by focusing through the tape and directly on the powdered samples of Li2S, GeS2, targets, and the thin films. Examination of multiple spots showed that the samples were homogeneous.

Impedance spectroscopy.—Sapphire substrates (Al2O3) were loaded into a dc sputtering chamber covered by a stainless steel mask with two 2 mm × 16 mm slits 2 mm apart parallel to each other to produce two 2 mm × 10 mm parallel electrodes 2 mm apart on the sapphire substrate. Au electrodes of ~100 nm thickness were sputtered in ~20 min. at a sputtering rate of 5 nm/min through the mask. Lastly, the substrate was loaded into the rf magnetron sputtering chamber to which the thin-film electrolytes were grown for impedance spectroscopy measurements.

Because the lithium thio-germanate materials are sensitive to moisture and air, the thin-film samples were put into specialized air-tight sample container. Impedance spectroscopy measurements were performed on the deposited Li2GeS3, Li4GeS4, and Li6GeS5 thin films at temperatures from −25 to 100°C with 25°C increments and from 0.1 Hz to 1 MHz using a 50 V ac signal using a Novocontrol Technologies impedance spectrometer.

Results and Discussion

XRD of the starting materials and targets.—The Li2GeS3, Li4GeS4, and Li6GeS5 target materials were characterized by XRD and the data are shown in Fig. 1a. The Li2GeS3 target shows an amorphous pattern without dominant peaks because the melt-quenching technique combined with its 50 mol % GeS2 glass former composition is sufficient to make this phase amorphous on cooling. The XRD patterns of the Li4GeS4 and Li6GeS5 targets, on the other hand, are polycrystalline and show sharp peaks because the Li4GeS4 and Li6GeS5 targets contain only 33 and 25 mol % GeS2 glass former, respectively, which are not sufficient to vitrify these melts on quenching.

From the Li2S + GeS2 phase diagram, it is expected that the Li2GeS3 target will be comprised of polycrystals of the Li2GeS3 phase and this is supported by the XRD pattern of the Li2GeS3 target material shown in Figs. 1a and 1b. From its composition and the Li2S + GeS2 phase diagram, the Li2GeS3 target material is expected to be comprised of a mixture in a 1:1 ratio of polycrystalline Li2GeS3 and Li2S. In order to verify that Li4GeS4 contained Li2GeS3 and Li2S in the XRD experimental data, Li2S, Li4GeS4, and Li6GeS5 XRD data are shown in Fig. 1b. While the XRD powder pattern of Li4GeS4 does not show peaks related to those of Li2S as expected the XRD powder pattern of Li4GeS4 show peaks related to those of Li2S and Li6GeS5. The filled stars indicate the peaks from Li2S and the filled triangles indicate the peaks from Li6GeS5 in the XRD data of Li6GeS5. This indicates that the XRD data in the experiments agrees with the hypothesis that the Li4GeS4 phase is a mixture of Li2GeS3 and Li2S.

Raman spectroscopy of the starting materials, targets, and thin films.—GeS2, Li2S, target materials, and thin films sputtered by the target materials were characterized by Raman spectroscopy in order to analyze their purities and to determine the atomic level structure of these materials and their Raman spectra are shown in Fig. 2. In the Raman spectrum of GeS2, a strong main peak appears at 340 cm−1 and agrees well with that seen in the literature.18 This peak has been assigned to the symmetric stretching mode of the GeS4 tetrahedra.19 The Raman spectrum of Li2S crystalline powder shows a single strong peak centered at 375 cm−1 and this peak is assigned to stretching modes the ionic Li+S. In the Raman spectrum of the Li2GeS3 target, there are three dominant peaks at 340, 375, and 415 cm−1. The peak at 340 cm−1 is found in GeS2 and is assigned to bridging sulfur (Ge-S-Ge bonding, BS) structures. The peak at 375 cm−1 is found in the Raman spectra of Li2S and for this
reason this mode is assigned to \( \text{Li}^{+}\text{S}^{-} \) bonding structures. The peak at \( 415 \text{ cm}^{-1} \) is assigned to the vibration of nonbridging sulfur (NBS) \( \text{Ge-S} \) structures. All three of these Raman modes are relatively broad features and this arises because of the amorphous nature of the \( \text{Li}_2\text{GeS}_3 \) target material. While there are three peaks in the Raman spectra of \( \text{Li}_2\text{GeS}_3 \) target, the Raman spectra of the \( \text{Li}_4\text{GeS}_4 \) and \( \text{Li}_6\text{GeS}_5 \) show only one quite sharp dominant peak at \( 375 \text{ cm}^{-1} \). The strong main Raman peak in the \( \text{Li}_4\text{GeS}_4 \) and \( \text{Li}_6\text{GeS}_5 \) target materials appears at \( 375 \text{ cm}^{-1} \) which is at the same peak position as in \( \text{Li}_2\text{S} \). This indicates that \( 375 \text{ cm}^{-1} \) peak in the target materials is related to that of the \( \text{Li}_2\text{S} \) component. The narrowing of the Raman peaks in the spectra of \( \text{Li}_4\text{GeS}_4 \) and \( \text{Li}_6\text{GeS}_5 \) phases compared to that of \( \text{Li}_2\text{GeS}_3 \) arises from the polycrystalline structure of the former and the glassy structure of the latter.

The Raman spectrum of the \( \text{Li}_2\text{GeS}_3 \) thin-film also shows three dominant peaks at \( 340, 375, \) and \( 415 \text{ cm}^{-1} \). The peak at \( 340 \text{ cm}^{-1} \) is coincident with the \( \text{GeS}_2 \) main peak position and is assigned to the BS (Ge-S-Ge) mode. The \( 375 \text{ cm}^{-1} \) peak is assigned to the \( \text{Li}^{+}\text{S}^{-} \) mode and the \( 415 \text{ cm}^{-1} \) peak is assigned to the NBS (Ge-S-) mode. Among the three peaks, the peak at \( 340 \text{ cm}^{-1} \) has the highest intensity and this is consistent with the higher (50 mol %) \( \text{GeS}_2 \) content in this film compared to the other, \( n = 2 \) and \( 3 \) thin films. The spectrum of the \( \text{Li}_4\text{GeS}_4 \) thin-film also shows three peaks at \( 340, 375, \) and \( 415 \text{ cm}^{-1} \), like the spectrum of the \( \text{Li}_2\text{GeS}_3 \) thin-film, and another broader peak of lower intensity at \( 460 \text{ cm}^{-1} \). As expected, the intensities of the peaks at \( 375 \text{ cm}^{-1} \) (\( \text{Li}^{+}\text{S}^{-} \)) and \( 415 \text{ cm}^{-1} \) are increased compared to those of the \( \text{Li}_2\text{GeS}_3 \) thin-film. This is consistent with the increased \( \text{Li}_2\text{S} \) content in the \( \text{Li}_4\text{GeS}_4 \) compared to \( \text{Li}_2\text{GeS}_3 \) which would increase the concentration of both \( \text{Li}^{+}\text{S}^{-} \) and \( \text{Ge-S}^{-} \) NBS modes. As described above, the peak at \( 340 \text{ cm}^{-1} \) is assigned to the bridging sulfur (Ge-S-Ge bonding) and the peaks at \( 340 \) and \( 460 \text{ cm}^{-1} \) are assigned to modes of the NBS (Ge-S-). The peak at \( 460 \text{ cm}^{-1} \) is assigned to 1 NBS and the peak is not present significantly in thin films. The peak at \( 415 \text{ cm}^{-1} \) is assigned to 2NBS and the peak is present in thin films. On the other hand, the peak at \( 340 \text{ cm}^{-1} \) is assigned to 0 NBS and the peak is present in thin films. The \( \text{Li}_4\text{GeS}_4 \) thin-film which has an even higher \( \text{Li}_2\text{S} \) content compared to the other two films shows only one dominant peak at \( 375 \text{ cm}^{-1} \) which is assigned to the \( \text{Li}^{+}\text{S}^{-} \) vibrational mode. This is consistent with the fact that \( \text{Li}_4\text{GeS}_4 \) thin films contain a higher \( \text{Li}_2\text{S} \) content compared to the \( \text{Li}_2\text{GeS}_3 \) and \( \text{Li}_4\text{GeS}_4 \) thin films.

The Raman spectra of all of the thin films do not show sharp peaks, but rather show broad peaks compared to those of crystalline targets (\( \text{Li}_4\text{GeS}_4 \) and \( \text{Li}_6\text{GeS}_5 \)) and are consistent with the films being amorphous. As the \( \text{Li}_2\text{S} \) content increases in the targets up to \( n = 3 \), the \( \text{Li}_2\text{S} \) content in the thin-film is also increased. This suggests that the rf sputtering conditions in this study for these targets were optimized and the thin films compositions are expected to be consistent with the target compositions. Although the previous reported literature showed \( \text{Li}_2\text{S} \) deficiency in \( \text{GeS}_2 \)-based thin films after sputtering compared to that of target,\(^{19}\) the compositions of the thin films up to \( n = 3 \) in this study are consistent with chemical composition of the targets.

Figure 1. X-ray diffraction data of experimental target materials (a) and comparison of x-ray diffraction of \( \text{Li}_6\text{GeS}_5 \) target to that of \( \text{Li}_2\text{S} + \text{Li}_4\text{GeS}_4 \) target (b).

Figure 2. Raman spectra of starting materials, \( \text{GeS}_2 \) and \( \text{Li}_2\text{S} \) target materials, and their thin films grown in Ar atmosphere.
Thin-film morphology and deposition rate.— Figure 3a shows the surface morphology of the Li4GeS4 thin-film produced by RF Ar+ sputtering. The thin-film surface is mirrorlike without any defects or cracks. This suggests that the thin-film electrolytes are homogeneous and have a flat surface morphology. The smooth surface enables the thin films to improve the contact adhesion and thereby decrease the contact resistance between thin-film and the electrodes.

In order to examine the sputtering rate, one thin film was sputtered to a larger thickness, \( \sim 1.3 \mu m \), than the other thin films, \( \sim 0.4 \mu m \), used for the Raman and ionic conductivity measurements. The thin film was characterized in the cross-sectional direction by FE-SEM as shown in Fig. 3b. The Ni adhesion layer (\( \sim 120 \) nm) is used to improve the adhesive between the Si wafer and the thin film. A sputtering power and pressure of 50 W and \( \sim 4 \) Pa were used, respectively, and the total thickness of the thin film after 4 h of sputtering was \( \sim 1.3 \mu m \) which gives a sputtering rate of \( \sim 5 \) nm/min.

\[ \text{Figure 3. (Color online) Surface morphology (a) of the Li4GeS4 thin-film and cross sectional view (b) of the thin film grown in Ar atmosphere by FE-SEM.} \]

\begin{table}[h]
\centering
\caption{The XPS compositional analysis of the thin films grown in Ar atmosphere.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Thin films & Li is & C is & O is & Ge_{2}P_{3} & S_{2}P & Remarks \\
\hline
Li2GeS3 & 32 & 0 & 4 & 16 & 48 & After 1 min Ar etching \\
& 33 & 0 & 0 & 17 & 50 & Theoretical values \\
Li4GeS4 & 42 & 0 & 5 & 12 & 41 & After 1 min Ar etching \\
& 44 & – & – & 12 & 44 & Theoretical values \\
Li6GeS5 & 45 & 0 & 3 & 11 & 41 & After 1 min Ar etching \\
& 50 & – & – & 8 & 42 & Theoretical values \\
\hline
\end{tabular}
\end{table}

XPS measurements of the thin films.— Table I gives the XPS compositional analysis of the thin films grown in Ar atmosphere and shows that residual carbon and oxygen are present on the surface of the films. However, after Ar etching for 1 min at 1 nm/min etching rate, the carbon and oxygen contents became 0% and \( \sim 3\% \), respectively. This suggests that the contaminated thickness by carbon is only \( \sim 0.25\% \) of the total thickness of the thin film, \( \sim 0.4 \mu m \), and further suggests that the thin films in this study are homogeneous throughout their thickness. Table I shows that all of the films show a background oxygen contamination of \( \sim 3\% \). This contamination appears to increase lightly with the nominal Li2S content (n) in the film and this suggests that the Li2S may well be the source of this contamination. Indeed, similar XPS measurements, not reported here, on the Li2S and GeS2 starting materials used to prepare the targets from which the film were grown, showed that the GeS2 was completely free of any oxygen where as the Li2S showed slightly measureable oxygen contamination. Table I shows that when this residual oxygen is ignored, all three films, n 1, 2, and 3 all show very good agreement between the measured concentrations of the elements and their expected values. This is in agreement with the Raman spectra as discussed above.

Ionic conductivities of the thin films.— In order to measure ionic conductivity for the thin films, the thin films, \( \sim 0.4 \mu m \), were grown with the widths and thicknesses are shown in Table II. In the electrode geometry given here, the electrical field applied from the impedance analyzer would be across very thin cross-sectional area of height \( \sim 0.4 \mu m \) and width of \( \sim 10 \) mm. The thickness (depth) that the electrical field is applied over is 2 mm. This give a geometrical cell constant, \( k = t/A, 0.2 \text{ cm}/(0.4 \times 10^{-4} \text{ cm} \times 1 \text{ cm}) = 5000 \text{ cm}^{-1} \). Such a geometry to create such a large cell constant was required because with a typical conductivity of 10\(^{-3}\) S/cm, measuring through the 0.4 \( \mu m \) thickness of the film over an area of 1 cm\(^2\), would give a net impedance of only 0.04 \( \Omega \) and this could not be differentiated from the contact resistances in the measurements. A representative plot of the ac ionic conductivity over the temperature range from \(-25\) to 100\(^\circ\)C at 25\(^\circ\)C increments for the Li2GeS2 thin-film electrolyte is shown in Fig. 4. The impedance was remeasured at room temperature after the temperature cycle to check if the impedance data had changed as a quality check against the cell leaking or the thin film changing in some other way. The red filled triangles indicate the ionic conductivity at room temperature before heating and the open circles indicates the ionic conductivity at room temperature after cooling from 100\(^\circ\)C. The agreement between the before and after measurements suggests that the impedance data are very reversible and thin films are very thermally stable and there was no chemical change during the impedance measurements. The ionic conductivities for the thin films, the thin films, \( \sim 0.4 \mu m \), were grown with the widths and thicknesses are shown in Table II. 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\begin{table}[h]
\centering
\caption{Width and thickness of the thin films.}
\begin{tabular}{|c|c|c|}
\hline
Composition & Width (\( \pm 0.01 \) mm) & Thickness (\( \pm 0.05 \) micron) \\
\hline
Li2GeS3 thin film & 2 mm & 0.4 \\
Li4GeS4 thin film & 2 mm & 0.4 \\
Li6GeS5 thin film & 2 mm & 0.4 \\
\hline
\end{tabular}
\end{table}
conductivities of the Li2GeS3 thin film in Ar atmosphere at 25 and at 100°C are 1.1 × 10^{-5} S/cm and 2.9 × 10^{-3} S/cm, respectively. As the temperature increases from -25 to 100°C, the conductivity continually increased and was found to be stable over this temperature range. The ac and dc ionic conductivities for Li4GeS4 and Li6GeS5 thin films at 25 to 100°C show the same pattern and the data are available in supporting materials.

Figure 5 shows a representative Nyquist plot of the complex impedance for the Li2GeS3 thin film grown in Ar atmosphere over the temperature range from 25 to 100°C. The frequency increases for each point from right to left starting at 0.1 Hz and finishing at 1 MHz. The spike at low frequencies represents polarization of the Li^+ ions due to the use of Au blocking electrodes. The dc resistance can be calculated from the intercept of the semicircle as -Z'' goes to 0 as shown in Fig. 5. The dc ionic conductivities were calculated from this effective dc resistance of the Li2GeS3, Li4GeS4, and Li6GeS5 thin films grown in Ar atmosphere.

The ionic conductivity can be obtained by Eq. 1.

\[ \sigma_{dc} = \frac{1}{Z_{dc}} \times \frac{t}{A} \]

where t = 0.2 cm, and A = 0.4 μm × 1 cm.

The ionic conductivities at 25°C of the Li2GeS3, Li4GeS4, and Li6GeS5 thin films grown in Ar atmospheres were 1.1 × 10^{-5} (S/cm), 7.5 × 10^{-4} (S/cm), and 1.7 × 10^{-3} (S/cm), respectively. These values are 2 to 3 orders of magnitude higher than those of oxide thin films (LiPON) which are used commercially in thin-film batteries. As shown in Table III, the ionic conductivities at 25°C for Li6GeS5 thin film was 1.7 × 10^{-2} (S/cm) which is better than that of Li2GeS3 and Li4GeS4 due to higher Li content in the Li4GeS4 thin films.

### Table III. The ionic conductivities over the temperature range from -25 to 100°C at 25°C increments for the Li2GeS3, Li4GeS4, and Li6GeS5 thin films grown in Ar atmosphere.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Li2GeS3 (S/cm)</th>
<th>Li4GeS4 (S/cm)</th>
<th>Li6GeS5 (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-25°C</td>
<td>4.0 (±0.05) × 10^{-6}</td>
<td>4.6 (±0.05) × 10^{-5}</td>
<td>9.7 (±0.05) × 10^{-5}</td>
</tr>
<tr>
<td>0°C</td>
<td>2.5 (±0.05) × 10^{-5}</td>
<td>2.2 (±0.05) × 10^{-4}</td>
<td>4.8 (±0.05) × 10^{-4}</td>
</tr>
<tr>
<td>25°C</td>
<td>1.1 (±0.05) × 10^{-4}</td>
<td>7.5 (±0.05) × 10^{-4}</td>
<td>1.7 (±0.05) × 10^{-3}</td>
</tr>
<tr>
<td>50°C</td>
<td>3.8 (±0.05) × 10^{-4}</td>
<td>2.2 (±0.05) × 10^{-3}</td>
<td>5.0 (±0.05) × 10^{-3}</td>
</tr>
<tr>
<td>75°C</td>
<td>1.1 (±0.05) × 10^{-3}</td>
<td>5.8 (±0.05) × 10^{-3}</td>
<td>1.3 (±0.05) × 10^{-2}</td>
</tr>
<tr>
<td>100°C</td>
<td>2.9 (±0.05) × 10^{-3}</td>
<td>1.3 (±0.05) × 10^{-2}</td>
<td>3.0 (±0.05) × 10^{-2}</td>
</tr>
</tbody>
</table>

Figure 4. (Color online) The ionic conductivity over the temperature range from -25 to 100°C at 25°C increments for Li2GeS3 thin films grown in Ar atmosphere.

Figure 5. (Color online) Nyquist plot of the complex impedance for the Li2GeS3 thin film grown in Ar atmosphere over the temperature range from 25 to 100°C at 25°C increments.

Figure 6. (Color online) The ionic conductivities of the Li2GeS3, Li4GeS4, and Li6GeS5 thin films at 25°C.

Figure 7. (Color online) The comparison of Arrhenius plots of ionic conductivities between the thin films and LiPON.21
The thin films show slight oxygen contamination but the slight oxygen contents do not affect to the thin-film properties significantly. The mixed content glasses and thin films are at least two orders of magnitude higher than that of LiPON thin films. This means that the thin films are very stable over the temperature range compared to a liquid electrolyte.

In order to compare how much different of the ionic conductivities for three thin films, the Arrhenius plots at 25°C are shown in Fig. 6. The Arrhenius temperature plots for the Li2GeS3, Li4GeS4, and Li6GeS5 thin films are shown and compared to that of LiPON in Fig. 7 and the ionic conductivities of the thin films are at least two orders of magnitude higher than that of LiPON at 25°C and the maximum ionic conductivities of the Li6GeS5 thin films show lithium ion conductivities approximately three orders of magnitude higher than that of LiPON.

The dc ionic conductivities of all thin films are 1, 2, and 3 in the nLi2S+GeS2 system at 25°C and their activation energies are shown in Fig. 8. The filled and open circles represent the ionic conductivities and activation energies, respectively, for the thin films in Fig. 8. In order to compare ionic conductivities between thin films and bulk glasses (published reference data), the ionic conductivities of the bulk glasses at 25°C and their activation energies are shown in Fig. 8. The filled and open triangles indicate the ionic conductivities of the bulk glasses and their activation energies, respectively. The ionic conductivities of the Li2GeS3 thin film, 50 mol % Li2S content, are higher than that of bulk glass. It is possible that although thin films and bulk glasses are amorphous structures, the bulk glasses are produced with a slower cooling rate than the thin films. This large difference in cooling rate will produce glasses with higher fictive temperature for the thin films which will have higher conductivity. The thin films show that as Li2S content increases, the ionic conductivities increase up to n = 3 (75 mol % Li2S). This behavior continues the trend of the bulk sulfide glasses where the conductivity increases with 35 to 50 mol % Li2S. The maximum in the lithium ion conductivity results in a minimum in the activation energy and this appears to occur near n = 3.

Conclusions

An RF magnetron sputtering system has been constructed and coupled to a nitrogen filled glove box so that moisture and oxygen sensitive films can be deposited without contamination. Li2GeS3, Li4GeS4, and Li6GeS5 thin-film electrolytes have been deposited from corresponding targets with 50 W power and ~3.3 Pa pressure in Ar atmospheres.

The sputtering condition was optimized and the samples were handled with care at every processing step to minimize contamination by moisture and air. The surface morphology of the thin films showed mirrorlike surface and was very smooth without any defects or cracks. In addition, the Raman spectra show that the thin films are consistent with the target materials. The XPS compositional data of the thin films show slight oxygen contamination but the slight oxygen contents do not affect to the thin-film properties significantly. The ionic conductivities of the thin films at 25°C appear to be the highest so far reported for Li+ ion conductivity glasses and thin amorphous films and are 2–3 orders of magnitude higher than those of commercial LiPON thin-film electrolytes. In addition, as the temperature increases from −25 to 100°C with 25°C increments, the ion conductivity continuously increases. This means that the thin films are stable over wide temperature ranges, so lithium ion batteries based on these sulfide materials should be very stable over wide temperature ranges and are therefore very promising for use in new thin-film lithium batteries. Further extensive investigations of solid state batteries fabricated from these films, however, are needed before this thin-film electrolyte is put to practical use.

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