Preparation and characterization of lithium thiogermanate thin films using RF magnetron sputtering

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Preparation and characterization of lithium thiogermanate thin films using RF magnetron sputtering

by

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Commercially developed in 1991, lithium ion batteries have long attracted the attention of scientists because of the high electropositivity of lithium. As power requirements become more demanding, batteries are also expected to provide the high energy densities necessary to keep pace. Chalcogenide glasses have long held an interest in battery applications because of the polarizability of the sulfide anion which is believed to be the cause of its superior conductivities. This class of materials exhibits room temperature conductivities on the order of $10^{-2}$ S/cm. Targets in the Li$_2$S–GeS$_2$ binary system have been sputtered in Argon and Nitrogen atmospheres using an RF magnetron sputtering technique with the hope of creating a new class of electrolytes with increased conductivity and stability in contact with lithium. Films were characterized using IR, Raman and X-ray photoelectron spectroscopies in order to evaluate their structure. Our progress in producing and characterizing these ion conducting sulfide thin films will be reported.
CHAPTER 1. INTRODUCTION

The enormous growth in portable consumer electronic devices such as mobile phones, laptops, digital cameras, and personal digital assistants over the past decade has generated a large interest in compact light-weight batteries (1; 2). As power requirements become more demanding, batteries are also expected to provide higher energy densities. Lithium batteries have begun to fill this need due to their use as an attractive anode material. Lithium is extremely lightweight, has a high electrochemical equivalency and a good conductivity. Primary and rechargeable lithium batteries continue to remain attractive for numerous reasons: high voltages, high energy densities, wide operating temperature range, good power density, flat discharge characteristics, and an excellent shelf life. There is an additional interest in specialized lithium batteries for use in the semiconductor industry and printed circuit board applications. Thin film processing of the components can lead to batteries that are 400 x 400 x 2 μm in size (2). These types of batteries are of interest for applications such as nonvolatile computer memory chips. At present, these chips use nonrechargeable batteries that are many times larger than the chip. Developing solid-state thin film batteries will allow close matching with microelectronic components.

Primary single-use and secondary rechargeable lithium batteries began to develop interest through the 1970s and 1980s. At the time, lithium was typically used as the negative electrode in a cell. However, its use in secondary cells came into question because of safety concerns with regard to the cycling behaviour. As a result, lithium-ion cells became commercially available in the 1990s due to intense research on lithium based compounds. These cells use intercalation compounds as the positive and negative materials, eliminating the need to use lithium. Successfully developed positive electrode materials include LiCoO₂, because of the ability to
develop cells with operating voltages as high as 4.5 V, and LiMn$_2$O$_4$, which has high practical energy densities on the order of 220 Wh/kg (3; 4; 5). As for negative materials, graphite-based electrodes remain the most common because they have a low cost, a low mass, and it can host lithium up to a composition of LiC$_6$ (6). While these electrodes are less attractive in terms of capacity when compared to lithium metal (372 vs. 3800 mAh/g, respectively), their ability to prevent lithium dendrite growth and produce a safer battery is worth the reduced efficiency.

Research continues today on various battery chemistries, as well as specific battery components. One such example is the choice of material for the electrolyte, which is responsible for conducting ions between the two electrodes. One promising example is that of a lithium phosphorous oxynitride thin film (7; 8; 9; 10). This material is produced from physical vapor deposition of a lithium orthophosphate target in a 100% nitrogen atmosphere. The result is a thin film with $\sim$6 at% nitrogen that effectively crosslinks the structure. LiPON films are currently one of the primary electrolytes in use because of its stability in contact with lithium and its long shelf life. Characterization studies have confirmed that 6 at% nitrogen is successfully incorporated into the network during deposition and forms a cross-linked structure by replacing bridging oxygens with two and three coordinated nitrogens. This crosslinking in turn increases the ionic conductivity of the material by two orders of magnitude. However, this easily prepared material still has a relatively low conductivity of $10^{-6}$ S/cm compared to other materials such as sulfides. These materials have the potential to further improve lithium primary and/or rechargeable batteries.
CHAPTER 2. BACKGROUND

2.1 Review of Battery Operation

A battery is an assembly of electrochemical cells, connected either in series or parallel, that is used to store electricity. The primary constituents of an electrochemical cell are the positive electrode, the negative electrode, and the electrolyte which allows ions to move between the two electrodes. Chemical reactions take place at the two electrodes during discharging and charging of the battery in order to produce electricity. During discharge, positive ions move towards the positive electrode through the electrolyte and there is an uptake of electrons. Figure 2.1 shows the basic components and operation of a thin film electrochemical cell.

Figure 2.1 Schematic showing the components and operation of a thin film electrochemical cell
2.2 Review of Electrolyte Materials

2.2.1 Polymer Electrolytes

Polymer electrolytes for use in lithium batteries were rapidly developed in the 1970s (6). It was found that these materials could offer a safer battery than those using corrosive, flammable, or toxic liquid electrolytes. Today, the archetypal polymer is poly(ethylene oxide) (PEO). It was found this and other polymers containing a heteroatom, such as oxygen or sulfur, could dissolve lithium salts, such as LiPF₆ and LiAsF₆ (11; 12; 13). The heteroatoms in the polymer are responsible for high electron donor power and a suitable interatomic separation to form multiple coordinate bonds with cations. Furthermore, these polymers have low barriers to bond rotation that allow segmental motion of the chains, providing an ion transport mechanism.

The primary concerns with these electrolytes involve their reactivity with a lithium metal anode and their low room temperature conductivities. Their reactivity with lithium poses safety concerns because lithium dendrites can grow towards the cathode and ultimately short-circuit the cell, which would present safety concerns. This can be overcome by introducing inorganic ceramic particles to form a composite material that is more "solid". As for their conduction properties. These materials have conductivities two or three orders of magnitude lower than aqueous electrolytes. However, thin polymer films on the order of 100 μm thick can compensate for their diminished conductivities. There is also the solution of increasing the operating temperature of the cell to around 90 °C.

2.2.2 Solid State Electrolytes

While commercial cells will continue to be fabricated using organic polymeric electrolytes due to their ease of fabrication and low cost, solid state electrolytes will continue to attract attention for their possible use in special applications. These include, but are not limited to, cells that require extreme operating temperatures, maximum lifetimes, a negligible self-discharge, and/or thin profiles (1). Solid state electrolytes are also attractive because they provide a hard surface that is capable of suppressing side reactions and inhibiting dendritic growth of lithium that is capable of short-circuiting a cell (14). However, one disadvantage of these electrolytes
is their potential to form cracks or voids if there is poor adhesion to the electrode materials.

One of the first commercially viable solid state batteries to emerge came with the invention of the lithium-iodine battery (6). This battery was invented when it was discovered that iodine reacts with poly-2-vinylpyridine to form a tar-like substance. When this material is placed in contact with a sheet of lithium foil, a thin layer of LiI is formed which acts as the electrolyte and the separator. These cells provided a substantial improvement, in terms of volumetric energy density and voltage, over the zinc-mercury oxide cells that were previously employed in pacemaker batteries (6). Additionally, the zinc-mercury oxide cells generated hydrogen as a by-product which prevented good sealing of the cell. Furthermore, catastrophic failure could occur through an internal short-circuit so the average life of the pacemaker was only 2 to 3 years.

A number of candidate materials have been investigated for use as electrolytes in batteries. The most attractive candidates to date are glassy materials. These electrolytes have many advantages over their crystalline counterparts such as physical isotropy, absence of grain boundaries, good compositional flexibility, and good workability. The anisotropy and grain boundaries present in crystalline materials lead to resistive loss, decreasing cell efficiency, as well as chemical attack, raising safety concerns. A number of different systems have been explored and are discussed specifically below.

2.2.2.1 Oxide Glasses

More recently, oxide glasses have received little attention for their use as electrolyte materials. They exhibit very low conductivities and high activation energies. However, they have the primary advantage of being relatively stable in air, allowing for ease of fabrication. The best of the oxide materials appears to be those glasses with mixed formers such as SeO₂ and B₂O₃ (15). Glasses such as these have a room temperature conductivity on the order of \( \sim 10^{-7} \) S/cm. These materials might prove promising if produced into thin films. However, chemistries with a high ionic conductivity are more desirable. Sulfide materials, discussed in more detail below, are of interest for this reason. Figure 2.2 shows ionic conductivity plots
comparing sulfide and oxide fast ion conductiting glasses (16; 17). In terms of conductivity, it is clear that oxide glasses have significantly lower conductivities than their sulfide analogs.

Figure 2.2 Ionic conductivity plots comparing sulfide and oxide fast ion conducting glasses. (16; 17)

2.2.2.2 Oxynitride Glasses

The most commercially viable material in this category is the phosphorus oxynitride glass, called LiPON. This material was first discovered in the 1980s by Marchand (18) but its properties were not fully characterized until 1991 at Oak Ridge National Laboratory (ORNL) (7; 8). It was found that when a high purity lithium phosphate, Li₃PO₄, target was deposited in a
nitrogen plasma using an RF magnetron sputtering technique, the resulting thin film with a typical composition of Li$_{2.9}$PO$_{3.3}$N$_{0.36}$ contained 6 at% nitrogen. This additional nitrogen was found to enhance the room temperature ionic conductivity from $\sim 10^{-8}$ S/cm in the starting Li$_3$PO$_4$ target to a value of $\sim 10^{-6}$ S/cm. Furthermore, these films were found to be highly stable in contact with metallic lithium. It is believed that a thin passivating layer of Li$_3$N is formed between the lithium and electrolyte which prevents lithium dendrite growth but allows ion conduction. A look at the structure of the material further explained the improved properties of this material. The nitrogen was found to substitute for oxygen and form 2 and 3-coordinated nitrogen groups, effectively crosslinking the structure. These structural units can be seen in Figure 2.4. This crosslinking is believed to decrease the electrostatic energy of the overall network, allowing for greater ion conduction. Thin film batteries comprised of Li-LiCoO$_2$ cells and Li-LiMn$_2$O$_4$ cells have been fabricated using the LiPON electrolyte at ORNL and have proven highly successful (9; 10). These types of batteries are being commercialized and target for applications in implantable medical devices, CMOS-based integrated circuits, and RF identification tags for inventory control and anti-theft protection.

2.2.2.3 Sulfide Glasses

Sulfide glasses were first reported on in the 1980s (19; 20; 21; 22). These glasses were based on SiS$_2$, P$_2$S$_5$, and B$_2$S$_3$ after doped with an alkali sulfide such as lithium sulfide. It was found that these materials have exceptional conductivities at room temperature, on the order of $10^{-3}$ S/cm. This is attributed primarily because of the larger ionic radius of sulfur and its high atomic polarizability. This is believed to create weaker covalent bonds between the sulfur and the lithium ions. As a result, the potential energy barrier that must be overcome is decreased, and lithium ion conduction is facilitated. Figure 2.2 shows the conductivities of some of the best compositions. Unfortunately, these glasses have not been widely used because they are highly reactive in air and corrosive with silica containers; an efficient glove box is also necessary to fabricate such glasses.

Thin films in the Li$_2$S + GeS$_2$ + Ga$_2$S$_3$ glass system have recently been prepared using
RF sputtering (23; 24). Successfully deposited films were produced using this method however the authors report that the ionic conductivities of the thin films were diminished compared to that of the starting target material. This was a result of the films being deficient in lithium and enriched in germanium, from the XPS composition analysis performed.

### 2.2.2.4 Oxysulfide Glasses

Efforts to combine the advantage of oxide and sulfide glasses has resulted in the research of a class of oxysulfide materials (25; 26; 27; 28). It was found that adding a small amount, approximately 5 mole%, of different lithium metal oxides to a base sulfide glass, improved the conductivity to $10^{-3}$ S/cm (26). Furthermore, the stability of the structure was observed to improve from thermal analysis results. Structural analysis of these materials has demonstrated
Figure 2.4 Proposed structural units present in LiPON sputtered films. (a) two-coordinated bridging nitrogen unit and (b) three-coordinated nitrogen unit.

that the oxygen typically occupies a bridging anion site, leaving sulfur at the non-bridging sites for lithium mobility. Some solid-state batteries have been fabricated using these oxysulfide compositions, and initial results appear to indicate good electrochemical stability (27; 28).

2.2.2.5 Thionitride Glasses

Work has also been carried out on highly conductive thionitride glasses (29; 30). The motivation behind these materials comes from the fact that lithium nitride, Li$_3$N, which has an impressive ionic conductivity ($1.2 \times 10^{-3}$ S/cm at room temperature (31)), but has poor electrochemical stability in contact with lithium (decomposition voltage of 0.445 (32)). The first report details results of rapid quenching glasses in the $(60 - 3x/2)$ Li$_2$S + SiS$_2$ + x Li$_3$N system (29). The base glass, $x = 0$, had a conductivity of $5.1 \times 10^{-4}$ S/cm while small additions of Li$_3$N, $x = 3$, were found to increase the conductivity to a value of $1.5 \times 10^{-3}$ S/cm. Furthermore, the glasses were found to have a high electrochemical stability in contact with a LiIn alloy, up to 10V.

The second study reported results of mechanical milling powders in the $x$Li$_3$N + (100-)$x$ SiS$_2$ glass system (30). The conductivity in this system was found to exhibit a maximum value of $2.7 \times 10^{-4}$ S/cm at $x = 40$. Structures of the materials were investigated using $^{29}$Si NMR. They report features characteristic of Si–N bonds in the material as well as a crystalline
phase (LiSi$_2$N$_4$). Furthermore, it was reported that these materials had significant oxygen contamination due to initial contamination in the starting materials or to the alumina milling media used during the milling process.

### 2.3 Review of Models of Ionic Conduction in Glass

Ionic conduction is an important property for candidate battery electrolyte materials. In solid state systems, there is typically a single mobile cation, so the total conduction is based on the conductivity of this ion. This value can be expressed by summing all the charge carrying species or by an Arrhenious equation for temperatures below the $T_g$ of a material:

$$\sigma = Z \cdot e \cdot n \cdot \mu = \frac{\sigma_0}{T} \exp \left(-\frac{\Delta E_{\text{act}}}{kT}\right)$$

(2.1)

where $Z$ is the valence of the cation, $e$ is the fundamental unit of charge, $n$ is the concentration of mobile ions, and $\mu$ is the ion mobility, $\Delta E$ is the activation energy, and $\sigma_0$ is the room temperature ionic conductivity.

Many authors (33; 34; 35) have attempted to create models for ion conduction in glassy electrolytes, in order to better understand the processes involved. In turn, these models have the potential to provide design criteria when developing new electrolyte chemistries. Two classical models, the Anderson-Stuart model (33) and the weak electrolyte model (34; 35), are presented below.

#### 2.3.1 Anderson-Stuart Model

Anderson and Stuart were the first scientists to explore the activation energy for ion transport in an amorphous material, by examining silica glasses (33). They proposed that the process is comprised of two competing components, a strain energy and a binding energy. The strain energy represents the energy required to deform the glass structure enough to allow an ion to pass from one site to another and the binding energy is the energy required to move the ion an interstitial distance. From their activation energy calculations, these authors deter-
mined an optimal ion radius where smaller ions had excessive binding energies and larger ions had excessive binding energies.

The equation for the strain energy can be seen below in Eq. (2.2). The equation takes into account the difference between the radius of the alkali, $r$, and the radius of the interstitial doorway between cation sites, $r_D$ as well as the shear modulus, $G$, of the glass network.

$$\Delta E_S = 4\pi \cdot G r_D (r - r_D)^2$$  \hfill (2.2)

The equation for the binding energy can be seen below in Eq. (2.3). This component of the total activation energy considers the change in coulombic potential and the energy as the ion makes hops.

$$\Delta E_B = \frac{1}{\gamma} \left( \frac{ZZ_0 e^2}{r + r_0} - \frac{ZZ_0 e^2}{\lambda/2} \right)$$  \hfill (2.3)

where $\gamma$ is a covalency parameter assumed to be approximately the dielectric constant $\varepsilon_\infty$, $Z$ and $Z_0$ are the electrical charges of the alkali and oxygen ions respectively, $r$ and $r_0$ are the ionic radii of the alkali and oxygen ions respectively, and $\lambda$ is the jump distance. It should be noted that this model was developed for oxide-based glasses. From this model, however, it can be determined that replacing oxygen with sulfur will reduce the strain energy term of the equation, since the atomic radius of sulfur is greater than that of oxygen. Furthermore, this substitution will reduce the electrostatic contribution to the activation energy, since the bond energy between the conducting and glass network atoms will be weaker. This model is represented pictorially in Figure 2.5 (36).

### 2.3.2 Weak Electrolyte Model

Ravaine and Souquet (34; 35) developed the weak electrolyte theory to describe ion conducting oxide glasses, using a thermodynamic approach to the problem. More specifically, they developed a relationship between the ionic conductivity of a material and its thermodynamic activity which is the basis for the model:
Figure 2.5  Schematic showing the energy barrier terms used in the Anderson-Stuart model (36).

\[
\sigma = \text{constant} \cdot (a_{Na_2O})^{1/2}
\]  

(2.4)

Their approach is based on the same formalism that is used for the study of weak electrolyte solutions, because of the similarities between glasses and liquids. They compare the network former and the network modifier in glasses to the solvent and solute in liquids, respectively. From the equilibrium dissociation of the modifier oxide in the glass, conventional thermodynamics would then give:

\[
Na_2O \leftrightarrow Na^+ + ONa^- \\
\mu_{Na_2O} = \mu^0_{Na_2O} + RT\ln a_{Na_2O} \\
\approx \mu^0_{Na_2O} + RT\ln[Na^+][ONa^-] \\
\approx \mu^0_{Na_2O} + RT\ln[Na^+]^2
\] 

(2.5)
Furthermore, if this is an ideal solution (so that the activity coefficients are constant), then there exists a relationship between the concentration and the activity:

\[ [Na^+] = constant \cdot (a_{Na_2O})^{1/2} \]  \hspace{1cm} (2.6)

After combining equation 2.3 and 2.5, Ravaine and Souquet concluded that

\[ \sigma = constant \cdot [Na^+] \]  \hspace{1cm} (2.7)

Ravaine and Souquet further conclude that the Na\(^+\) ion mobility is independent of the alkali oxide content and that the dissociated ions are the charge carriers that can overcome the coulombic attraction of the glass network. This coulombic attraction can be considered the activation energy necessary for ion conduction. Therefore, the conductivity of a material can be improved by decreasing this energy needed to dissociate the ions.

The Anderson-Stuart and weak electrolyte models reach similar conclusions despite using different approaches. The electrostatic binding energy from the Anderson-Stuart model is roughly the equivalent of the dissociation energy in the weak electrolyte model.

### 2.4 Review of Thin Film Processing Techniques

There are many vapor deposition techniques that can be employed in order to produce thin film materials (37). These include simple heating of a source material, laser-induced vaporization, or bombarding the material with energetic ions. All of these techniques are performed under vacuum and rely on the kinetic theory of gases in order to understand their behavior.

#### 2.4.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) involves using a powerful laser beam in order to vaporize the surface of a target material (37). The experimental arrangement is represented schematically in Figure 2.6. One of the most common lasers used is the KrF excimer laser, operating at 248 nm with the following parameters: a pulse on the order of 25 ns, a power density of
2.4×10^8 W/cm², and a repetition rate of 50 Hz (38). In general, the PLD process can be divided into four stages. First, the laser beam is focused onto the target material. The elements in the target are rapidly heated to their evaporation temperature when there are sufficiently high flux densities and a short pulse duration. This ablation process involves many complex physical phenomena such as collisional, thermal and electronic exfoliation, exfoliation and hydrodynamics. Second, the ablated target elements move towards the substrate according to the laws of gas-dynamics. In the third stage, the high energy atoms bombard the substrate surface where a collision region is formed between the incident flow and the sputtered atoms. A film begins to grow after a thermalized region develops and when the condensation rate is higher than the rate of sputtered atoms. Finally, nucleation and growth of a thin film occurs on the substrate. This step depends on many factors such as the density, energy, ionization degree, and the temperature of the substrate. PLD has some advantage over other techniques in that many different materials can be deposited, the technique is conceptually simple, and deposition rates can be as high as 0.5 μm/minute (39)

Figure 2.6 Schematic of the pulsed laser deposition setup showing the laser path, the target, the plume, and the substrate material.
2.4.2 DC and RF Sputtering

Sputtering is a technique whereby energetic ions from a plasma are used to bombard a target (which is the cathode of the discharge), and ejecting atoms into the plasma (37). These atoms then impinge upon the substrate (the anode) and form a coating. The two fundamental diode arrangements that can be used are the direct current (DC) discharge, and the radio frequency (RF) discharge, both of which can be seen schematically in Figure 2.7. Additionally, a magnet can be added to these two setups in order to enhance the deposition rates. In DC sputtering, a high-voltage DC source is used as the power supply.

RF Magnetron Sputtering is a reliable technique used to deposit many different types of films, including electrically insulating samples (41). A high-voltage RF source at a frequency of 13.56 MHz is used to ionize a sputtering gas which produces the plasma. The ionized gas then bombards the target where multiple collisions take place, releasing atoms of the target material into the plasma. These atoms condense upon the substrate which is placed in front of the target. A blocking capacitor is placed in the circuit, and a matching network is used to optimize the power transfer. A permanent magnet is added to the sputtering gun in order to enhance the deposition rate. This is done by the trapping of electrons, from a Hall effect near the target surface (37). This magnet creates lines of magnetic flux that are perpendicular to the electric field, or parallel to the target surface. This static magnetic field retains secondary electrons in that region which drift in a cycloidal path on the target and increase the number of collisions that occur.

RF Magnetron sputtering was chosen for this particular application for a variety of reasons. First, DC sputtering of thiogermanate materials is not possible because they are electrically insulating. Next, it is known that RF sputtering produces thin films that have a high density and are relatively smooth when compared with films produced from PLD processes (41). Additionally, RF deposition offers good compositional control so that the resulting thin films have compositions similar to that of the target material.
Figure 2.7  Schematic of the RF magnetron sputtering setup, showing the blocking capacitor and impedance-matching network that enables sputtering of insulative materials. (37)
CHAPTER 3. PROPOSED WORK

Research will be performed in order to examine the role that nitrogen has upon fast-ion conducting chalcogenide glasses, specifically within the Li$_2$S + GeS$_2$ system. The base material GeS$_2$ is an excellent glass former that is also relatively stable in contact with atmospheric moisture and oxygen. Li$_2$S will be used in order to modify the glass and improve the ionic conductivity. Initially, the compound that will be examined in this study is Li$_4$GeS$_4$. This material is not typically glass forming because of the high fractions of lithium sulfide. However, it is believed from previous studies that thin films are deficient in lithium as compared with the starting target material (23; 24).

The motivation for this research stems from the success of LiPON thin films presented in the previous chapter. While the improved conductivity of these films is impressive, it is still well below the best of the sulfide materials. The aim of this work is therefore to determine if sulfide thin films can be deposited with high lithium ion conductivities, if nitrogen can be incorporated into the material, and what the effect this additional component has on its structure and properties. Only few attempts have attempted to explore thionitride chemistries (29; 30), and this was completed only with bulk materials. Furthermore, there has been few reports of sulfide thin films, and those authors never report sputtering in a nitrogen plasma in order to alter the structure and composition (23; 24).

There are many steps to this project. First, the deposition system and equipment must be assembled and tested. This will be carried out by reproducing the work of Yu and Bates (7; 8). Once this step has been completed, work on target preparation will be conducted in order to produce strong and long lasting targets that can be used to deposit multiple thin films. Next, thin films will be deposited in both 100% Ar and 100% Nitrogen atmospheres.
and mixtures thereof to optimize the sputtering process as to maximize the amount of N in the film. Characterization of these films will determine if nitrogen can be incorporated into these materials, how the nitrogen affects the bonding and structure of these films, and how the resulting ionic conductivity is either improved or diminished.
CHAPTER 4. EXPERIMENTAL METHODS

4.1 Sputtering Target Development

4.1.1 Preparation of Germanium Sulfide

Glassy GeS$_2$ was prepared by reacting stoichiometric amounts of germanium metal powder (Cerac, 99.999$\%$) and sulfur (Cerac, 99.999$\%$) in an evacuated silica tube at 900 °C. First, a bare silica tube was cleaned with a 2$\%$ ammonium bifluoride, NHF-HF, solution. The tube was then fitted with a valve assembly and evacuated to 30 mtorr using a roughing pump. Surface moisture on the inside of the tube was removed by passing the tube over a gas/oxygen flame. Once this moisture was removed, the tube was transferred to the glovebox where the appropriate amounts of Ge and S were placed into the tube. The tube was then removed from the glovebox and evacuated with the roughing pump again to a pressure of 30 mtorr. Following evacuation, the tube was sealed using a high-temperature gas and oxygen torch. The sealed tube was then placed into a furnace held at an angle of 5$^\circ$C/min where it was slowly heated from room temperature to 900 °C at a rate of 1 $^\circ$C/min. The tube was also slowly rotated, at about 20 rpm, to promote full reaction and mixing of the components. Once the tube was held at 900 °C for 16 hours, it was air quenched down to room temperature. The final product from this process was a homogenous transparent yellow glass.

4.1.2 Li$_4$GeS$_4$ Target Preparation

Li$_4$GeS$_4$ powders were prepared using stoichiometric amounts of Li$_2$S (Sigma-Aldrich, Lorrad) 99.8$\%$ and GeS$_2$ prepared above. These powders were mechanically milled for 15 minutes in a steel container with one steel grinding ball in order to ensure good mixing and to start the
reaction process. Batches of 3 to 4 grams were melted in a covered vitreous carbon crucible at 940 °C for 15 minutes inside a mullite tube lined muffle furnace attached hermetically to the side of a glove box. Figure 4.1 shows the glovebox with extension arm and graphite crucible used to melt the materials. The samples were then poured out of the crucible onto a brass plate and allowed to cool.

Once enough material, ~15 grams, was prepared using the aforementioned method, the material was ground into a fine powder using a vibratory milling process for 15 minutes. Fifteen grams of the powder was weighed out and poured into a steel die set with a two-inch diameter. The die set was agitated so as to make the powder level as smooth as possible. Then, the top loading bearing was placed into the shaft and allowed to settle on top of the powder. This assembly was loaded into a plastic bag, to prevent contamination (oxidation) during the

Figure 4.1  Picture of the glovebox with extension arm and graphite crucible used to melt the materials.
consolidation process, and taken outside the glovebox to be biaxially pressed, by placing a sheet of rubber between the press and the die set, into a disc under a 15000 lb load, or about 5000 psi. After consolidation, the pellet was removed from the die and placed into the furnace for a sintering operation in an effort to improve the density. Pellets were initially sintered on top of an alumina sheet, but there were concerns that this oxidized the target material, so a boron nitride sheet was used instead.

Additionally, two other techniques were employed in order to optimize the density of the target. First, cold isostatic pressing was attempted to further compact the powders prior to sintering. A uniaxially pressed pellet was inserted into a rubber sleeve and then this assembly was inserted into a thin metal sleeve. This assembly was evacuated to prevent air contamination and to prevent rupture of the sleeve during the pressing operation. When the sleeve was evacuated, the sleeve was heat sealed. Next, the bag was introduced into the cold isostatic press chamber and then pressed to ~50ksi.

In a second process, a two-inch diameter graphite mold was fabricated in order to attempt a hot pressing technique. Powder samples produced during the aforementioned melting operation were placed into the graphite mold. This mold was placed into a box furnace inside the glovebox and heated to 940 °C, held for 1 hour, and then slowly cooled down to room temperature. This operation allowed the material to consolidate into a 2-inch cast disc.

For all targets produced using these three techniques, the final target was then adhered to the back of a 2” diameter, 0.125” thick copper plate, using silver paste or indium foil, so that it may be sufficiently water-cooled during the deposition process to prevent thermal shock.

### 4.2 Deposition Equipment

Figure 4.2 shows a schematic of the specific deposition setup used to produce the thin films. It is comprised of a dry nitrogen glovebox with a series of two chambers (6” and an 8”) and two gate valves between these three components so that samples can be inserted and removed from the chambers. Inside both chambers, a track system was built and installed so that substrates can be introduced into the sputtering chamber via a sliding tray that is pulled
and pushed with a mechanical loading arm. Both chambers have a mechanical roughing pump to achieve low vacuum and turbomolecular pumps to achieve a high vacuum. The pressures were measured from two convectron gauges connected to each of the roughing pumps, and with ionization gauges connected to each of the chambers. A commercially available sputtering gun (Kurt Lesker, Inc) was purchased and fitted on to the deposition chamber using a viton gasket to allow quick installation and removal of new targets.

![Schematic of sputtering system showing the principal components.](image)

In order to test the deposition equipment, a target of Li$_3$PO$_4$ was obtained commercially from SCI Engineered Materials, Inc. This target was installed in the sputtering gun and attached to the deposition equipment. The system was baked out for ~2 days in order to remove any moisture on the chamber walls. Films were produced at 100 Watts power and 30 mtorr dynamic N$_2$. In order to determine reproducibility of the literature results, the films were examined using X-ray photoelectron spectroscopy. The results can be seen in 4.3. As can
be seen, the results obtained experimentally match well with those from literature

![N1s spectra](image)

**Figure 4.3** N1s spectra for films produced from a Li$_3$PO$_4$ target in an nitrogen atmosphere.

### 4.3 Deposition of Thin Films

In order to produce the desired thin films, the target assembly was attached to the sputtering gun inside the glove box. The sputtering gun was then removed from the glovebox and quickly attached to the deposition chamber, after which both the roughing and turbo pumps were turned on to achieve a high vacuum. Figure 4.4 shows a picture of the home built sputtering system where the films were prepared. Additionally, the deposition chamber was heated for two days using tape heaters so as to drive off any remaining water in the system. Table 4.1 shows the typical base pressure as well as partial pressures of different gases in the sputtering
Table 4.1  Typical base pressure and partial pressures of different gases in the sputtering chamber.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>6.0 x 10^{-7}</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.1 x 10^{-8}</td>
</tr>
<tr>
<td>N₂</td>
<td>1.6 x 10^{-7}</td>
</tr>
<tr>
<td>O₂</td>
<td>3.6 x 10^{-8}</td>
</tr>
</tbody>
</table>

chamber. Presputtering was performed for two hours on the target in order to clean the surface of the target of any impurities from the brief exposure to atmospheric moisture.

Substrates were then introduced into the deposition chamber through the glovebox via a sliding track system. The substrates were shielded to initially prevent thin film growth so that the target could be cleaned and the plasma could stabilize. Then, the plasma was lit by turning on the RF power to the target and filling the chamber with the selected gas (Ar, N₂) to about 100 mtorr. Once the plasma was lit, the gas pressure was reduced to 30 mtorr and was allowed to stabilize for 15 minutes. After this time, the shield was withdrawn and deposition continued for 4 hours to produce thin films. All films were produced with a power level of 25 Watts and a 30 mtorr dynamic pressure of the specific sputtering gas, Argon or Nitrogen.

4.4 Thin Film Characterization

4.4.1 Raman Spectroscopy

Raman spectroscopy is a nondestructive technique that is used to probe the local structure of a material. For this, it uses scattered radiation of sample from a laser beam. This scattered radiation comes from the energy transfer between the incident radiation and the scattering system. Two types of scattering can occur, Stokes and anti-Stokes. Stokes scattering occurs when the system is placed into an excited state, the resulting scattered radiation is at a lower frequency that the incident radiation. In anti-Stokes scattering, an incident photon is destroyed while another photon is created simultaneously, which gives scattered radiation that has a higher frequency than the incident radiation. This can be represented mathematically.
Figure 4.4  Picture of sputtering system showing the deposition chamber, load-lock chamber, and the sputtering gun.

represented as,

\[ \hbar v_s = \hbar v_o \pm \hbar v_e \]  

(4.1)

where the subscripts s, o, and e refer to the scattered, incident, and excited radiation frequencies.

Raman spectra were collected using a Renishaw in Via spectrometer using a 488 nm line from an Ar\(^+\) ion laser with a power of 25 mW. The instrument was calibrated using an internal silicon standard with a peak centered at 520.4 cm\(^{-1}\). All samples were placed into holders which were covered with a transparent tape to prevent exposure to atmospheric moisture and oxygen.
4.4.2 Infrared Spectroscopy

Infrared spectroscopy is a non-destructive technique that uses photons in order to examine the structural units present within a material. As photons of a specific frequency interact with a molecule, the photons are absorbed and the molecule is vibrationally. The frequency required to vibrationally excite a specific molecule is a function of the interatomic potential energy well of that molecule. It should be noted that IR and Raman spectroscopy techniques are complimentary in that some vibration modes that are IR-inactive are Raman-active, and vice versa.

Infrared spectra were obtained using a Bruker IFS 66 V/S machine. Films were deposited onto 0.20 mm thick polyethylene sheets. Films were mounted onto the holders inside the glovebox and introduced into the machine without exposure to atmospheric moisture or oxygen. Samples were inserted into the chamber and measured under vacuum in transmission.

4.4.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a destructive chemical surface analysis technique. XPS uses a high-energy, nearly monochromatic beam of x-rays that are focused onto the sample. These x-rays are capable of liberating photoelectrons, with unique energies, from the material. The difference between the incident beam energy and the photoelectron energy is the binding energy of the electron. Since the photoelectron energies are unique based on their electronic environment, information about the bonding preference of elements can be determined. Furthermore, XPS is useful in quantitatively analysing the composition of a sample.

X-ray photoelectron core level spectra were obtained using a Scienta ESCA-300 spectrometer with monochromatic $K\alpha$ X-rays (1486.6 eV). Shirley backgrounds were subtracted for each element. XPS was performed on the starting target material and films sputtered both in 100% Argon and 100% Nitrogen atmospheres, in order to determine the composition as well as the nature of the bonding for each element. The samples were introduced into the XPS chamber through a glovebag that had been purged and refilled three times with dry nitrogen.
gas before opening the sample container. The target material, in a compacted powder pellet, was fractured in the glovebag before introducing it into the XPS chamber so as to provide a fresh, nearly uncontaminated surface. Survey scans were performed on all samples to confirm elements present in the sample. Next, scans on each of the specific elements (Li, Ge, S, O, N, C) were performed in order to acquire high resolution spectra. The XPS signals were analyzed using a peak synthesis program in which a nonlinear background is assumed. In the case of the S2p doublets, curve fits were obtained using fixed amplitude ratios (S_{3/2}/2P_{1/2}).

4.4.4 Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS) is a technique used to identify and quantify the elemental composition of a sample area. When this sample area is bombarded with electrons, from an electron beam instrument such as an SEM, characteristic X-rays are produced which can be measured using an energy dispersive spectrometer. In order to conduct these measurements, thin film samples deposited onto polished stainless steel substrates were loaded into a Hitachi S2460-N VP-SEM maintained by the Materials Analysis Research Laboratory. Spots were measured at different magnifications as well as different areas in order to obtain compositional information.

4.4.5 Impedance Spectroscopy

Impedance spectroscopy is a study of the frequency response in alternating current. This is accomplished by applying a voltage across the sample and measuring the resulting response from the material. When the sample is stimulated, many processes take place of which one is the flow of ions in the material. This flow depends on the ohmic resistance of the electrodes and the electrolyte as well as any reactions between the electrodes and the electrolyte.

Measurements were performed on both sets of thin films at room temperature from 0.10 Hz to 10 MHz with a sinusoidal voltage of 0.050 V across the sample. Electrodes were sputtered beneath and above the thin film to optimize the geometric cell constant. The sputtered films were placed into an airtight sample container in the glove box. The sample container was
connected to a Solartron 1260 Impedance Gain-Phase Analyzer to measure the magnitude and phase angle of the impedance of the sample. The conductivity was then determined from the resulting complex impedance diagrams.

As mentioned, the geometric cell constant was optimized in order to effectively measure thin film materials. The equation used to measure the ionic conductivity is dictated by the equation below:

\[ \sigma = \frac{1}{R} \times \frac{t}{A} \]  \hspace{1cm} (4.2)

where \( t/A \) is the cell constant. Since the films are \( \sim 1 \) micron thick and the electrodes are typically at least \( \sim 1 \) mm wide, resulting impedances are either small, on the order of 100 \( \Omega \), or large, on the order of 1 M\( \Omega \). The configuration used for these films can be seen below in Figure 4.5. Each gold electrode strip is 2 mm wide which leads to an area of 0.04 cm\(^2\). Furthermore, this results in a cell constant of 0.0025. For this specific cell constant, resistances are on the order of 100 \( \Omega \).

![Figure 4.5](image)

Figure 4.5  Schematic showing the interdigitated electrode masking arrangement used for impedance spectroscopy measurements.
CHAPTER 5. RESULTS AND DISCUSSION

5.1 Target Characterization

5.1.1 Structure and Composition

Figure 5.1 shows the XRD results obtained for the target material Li₄GeS₄ as prepared according to the previous discussion. The signal to noise ratio of the experimental pattern is low because a polyimide tape was used to cover the sample material to prevent contamination. Furthermore, the powder used for the experiment tended to agglomerate easily which would raise concern about preferential orientation of the powder in the sample holder. Despite this low signal to noise ratio, the pattern of this material appears to closely represents the reported literature pattern (40). The structure of this material is related to the \( \gamma \)-Li₃PO₄ type. It is comprised of hexagonal close-packed sulfide ion arrays with germanium ions in the tetrahedral sites. Lithium ions are found in both octahedral and tetrahedral sites.

5.1.2 Sintering and Density

Figure 5.2 presents the results obtained for the sintering experiments. As the graph presents, the average green density for each of the three pellets at each sintering temperature is consistently 1.60 g/cm\(^3\). After sintering the material, the density of the material increased slightly to an average value of 1.70 g/cm\(^3\). This compares to the theoretical density which is 2.25 g/cm\(^3\) (40). Table 5.1 presents the data along with the standard deviation for the sintered pellets.
5.2 Thin Film Characterization

5.2.1 Profilometry

Surface profilometry involves placing a diamond stylus in contact with the sample in order to measure film thicknesses (41). The stylus electromagnetically senses its position as it traces the topography of a step created between the substrate and thin film. Figure 5.4 shows the profilometry scan for a thin films sputtered in argon and nitrogen. The vertical distance for the Ar film is shown to be approximately 12,000 Å, which would be 1.20 μm. The vertical distance for the N₂ film indicated by the stylus is shown to be approximately 8,000 Å, or 0.80 μm. This indicates a sputtering rate of about 3000 Å/hr in Ar and about 2000 Å/hr in N₂. Similar results have been obtained in the literature.
Table 5.1  Physical density measurements performed on sets of pellets fired at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Sintered Density</th>
<th>Standard Deviation</th>
<th>% Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>2</td>
<td>1.68</td>
<td>0.023</td>
<td>74.7</td>
</tr>
<tr>
<td>820</td>
<td>2</td>
<td>1.72</td>
<td>0.028</td>
<td>76.4</td>
</tr>
<tr>
<td>840</td>
<td>2</td>
<td>1.76</td>
<td>0.091</td>
<td>78.2</td>
</tr>
<tr>
<td>860</td>
<td>2</td>
<td>1.76</td>
<td>0.017</td>
<td>78.2</td>
</tr>
<tr>
<td>880</td>
<td>2</td>
<td>1.74</td>
<td>0.013</td>
<td>77.3</td>
</tr>
</tbody>
</table>

5.2.2 Raman Spectroscopy

Raman spectroscopy was carried out on the target material as well as films sputtered both in 100% argon and 100% nitrogen atmospheres, in order to qualitatively determine the structural units present. First, a literature review of existing Raman spectra allows for a more complete analysis. In pure GeS₂, a strong peak appears at ~342 cm⁻¹ which has been assigned to the symmetric stretching of the GeS₄/2 tetrahedra (42; 43). Upon addition of an alkali sulfide, such as lithium sulfide, non-bridging sulfurs become incorporated into the network, generating additional peaks in the spectra. It has been suggested that the Raman spectra of Li₂S + GeS₂ binary glasses have structures that resemble those of the Na₂S + GeS₂ system (44). Peaks at ~469, 419, and 390 cm⁻¹ in this glass system have therefore been assigned to germanium tetrahedral units with three, two, and one non-bridging sulfurs, respectively (44; 45). Examples of these types of units can be seen in Figure 5.5

The Raman spectra of the target and resulting films sputtered in Ar and N₂ can be seen in Figure 5.6. Looking first at the spectrum of the target material, there is one sharp peak centered at ~380 cm⁻¹. This peak has been attributed to germanium sulfide tetrahedral units with three non-bridging sulfurs, or (GeS₄)⁴⁻ units. This sharp narrow peak is also evidence that the starting target material is crystalline.

Next, the film sputtered in Ar was analyzed. It is noted that the peaks are much broader than those in the target material. This suggests that the films are amorphous in nature. The main peak in this Raman spectra is at 345 cm⁻¹. This peak has been assigned to the symmetric stretching mode of the GeS₂ tetrahedra. There is also an intense peak from about 360 to 450
cm$^{-1}$, which can be deconvoluted into two peaks. These peaks are assigned to germanium tetrahedra with three and two non-bridging sulfur units. The last peak located around 480 cm$^{-1}$ is assigned to GeS$_{3/2}$S$^-$ tetrahedra with a single non-bridging sulfur unit.

The Raman spectrum of the film sputtered from the target in a 100% nitrogen atmosphere is also shown in this figure. As can be seen, the primary peak in this spectrum is the peak centered around 490 cm$^{-1}$. As with the Ar-sputtered film, this peak is assigned to a germanium unit with a single non-bridging sulfur unit, GeS$_{3/2}$S$^-$. It is noted that there are no peaks in the range of the symmetric stretching mode of GeS$_2$ tetrahedra. No other peaks appear to indicate the nature of the nitrogen bonding in the material, the concentration is perhaps too low to get a large enough signal.
5.2.3 Infrared Spectroscopy

Infrared spectroscopy was carried out on the films sputtered in argon and nitrogen atmospheres, in order to qualitatively determine the structural units present. Attention is focused on both the far infrared region (400 to 100 cm\(^{-1}\)), in order to evaluate the nature of the glassy GeS\(_2\), as well as the mid infrared region (4000 to 400 cm\(^{-1}\)), in order to determine how nitrogen might be incorporated into the nitrogen sputtered films. The resulting spectra can be seen in Figure 5.7. The starting materials used, GeS\(_2\) and Li\(_2\)S, as well as the reacted Li\(_4\)GeS\(_4\) powders are shown on the bottom half. In all of the spectra shown, the peak located at \(\approx 374 \text{ cm}^{-1}\) is assigned to the symmetric stretching of Ge-S bonds in a germanium tetrahedral with bridging sulfurs. Two different batches of lithium sulfide are displayed in gray. The dark gray spectra represents a relatively pure Li\(_2\)S powder as compared to the spectra shown in light gray. The contaminated Li\(_2\)S displays a doublet around 1469 cm\(^{-1}\) which is representative of vibrations from the CO\(_3\) structural unit.

As for the sputtered thin films, it is first noted that the spectra contain interference fringes from the polyethylene on which the films are deposited. Additionally, both the argon and nitrogen samples contain the bridging sulfur stretching unit at 347 cm\(^{-1}\). The spectra from the nitrogen sputtered thin film shows additional peaks located at higher wavenumbers. In order to further identify these peaks, the literature was consulted. According to (46), sulfur-nitrogen
bonding is located at $\sim 1204 \text{ cm}^{-1}$. A peak centered around this frequency is also noted in the nitrogen sputtered thin films. It is therefore believed that the nitrogen sputtered in these films is associated with the sulfur. Furthermore, the appearance of an additional peak centered around $1010 \text{ cm}^{-1}$ is believed to be associated with sulfate bonding, as per (46). Finally, it should be noted that the peak around $800 \text{ cm}^{-1}$ is assigned to a polyethylene absorption mode that is subtracted out while acquiring the background.

5.2.4 X-ray Photoelectron Spectroscopy

Table 5.2 shows the compositional analysis that was performed from the experiments performed. This was carried out using a curve integration program and the appropriate sensitivity
Figure 5.5 Possible structural units present in lithium thiogermanate glasses and crystals. (a) 100% bridging sulfur units, representative of the GeS₂ material, (b) one non-bridging sulfur, LiGeS₃/₂S, (c) two non-bridging sulfurs, Li₂GeS₂/S₂, (d) three non-bridging sulfurs, Li₃GeS₁/S₃ (e) all non-bridging sulfurs, representative of the Li₄GeS₄ structure.

factors for each element (47). It is observed that the target composition is near the theoretical values of the material, except for the 12.1% oxygen contamination. This oxygen is believed to primarily come from the starting Li₂S material obtained from Lorad Inc. (St. Petersburg, FL), as this material is difficult to produce in pure form. In the resulting thin films, the lithium content appears to decrease by about 10 at%, confirming the results found in (23). It is confirmed that nitrogen can be successfully incorporated into these materials, on the order of 10 at%. Additionally, it was confirmed that the argon sputtered films contained no nitrogen. Furthermore, the sulfur content in the argon deposited films as compared to that of the films deposited in nitrogen is increased by a factor of two. There is also a dramatic increase in the oxygen content of the nitrogen sputtered films. Both of these effects are brought about by the nitrogen plasma, which is considered to be more reactive as compared to the argon plasma.
Table 5.2  Approximate composition of the the target material and result­
ing thin films deposited in Ar and N\textsubscript{2} atmospheres. Sensitivity   

<table>
<thead>
<tr>
<th>Atom measured</th>
<th>Li\textsubscript{4}GeS\textsubscript{4} Target</th>
<th>Li\textsubscript{4}GeS\textsubscript{4} in Ar</th>
<th>Li\textsubscript{4}GeS\textsubscript{4} in N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>37.2</td>
<td>25.6</td>
<td>26.8</td>
</tr>
<tr>
<td>Ge</td>
<td>14.4</td>
<td>14.3</td>
<td>10.3</td>
</tr>
<tr>
<td>S</td>
<td>36.2</td>
<td>28.3</td>
<td>14.9</td>
</tr>
<tr>
<td>N</td>
<td>–</td>
<td>0</td>
<td>12.8</td>
</tr>
<tr>
<td>O</td>
<td>12.1</td>
<td>9.8</td>
<td>16.8</td>
</tr>
<tr>
<td>C</td>
<td>–</td>
<td>21.8</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Nitrogen ions will have a stronger tendency to combine with oxygen atoms inside the chamber or impurity oxygen from the nitrogen tank.

As can be seen in Figure 5.8, it is confirmed that no nitrogen was incorporated into the films that were deposited in a 100% Argon atmosphere. As for the films sputtered in a nitrogen atmosphere, the N1s spectra can be deconvoluted into 2 separate peaks. It is initially suggested that these two peaks represent S-N bonding and O-N bonding.

Figure 5.9 shows the S2p spectra of the starting target material from which the films are deposited. The doublet in this graph can be attributed to Ge-S bonding based on its binding energy.

Figure 5.10 shows the S2p spectra of the argon sputtered thin film. This spectrum was deconvoluted into 3 separate doublets in order to fit the curve. The information in (48) provides the key information when determining the nature of the sulfur in these films. Doublets 2 and 3 of this spectrum were found to correspond to non-bridging sulfur units and bridging sulfur units, respectively, when compared to the results of (48). It is believed that the first doublet of this spectrum might be assigned to pure sulfur units, suggesting that elemental sulfur is be sputtered into our film, or the high power of the XPS equipment is separating the sulfur out of the film.

Figure 5.11 shows the deconvoluted S2p spectra of the nitrogen sputtered thin film. Many of the peaks from the previous S2p spectra are also observed, such as the non-bridging and bridging sulfur units. These doublets are seen again as Doublets 2 and 3. However, at higher
binding energies, there are two additional doublets that are not found in previous spectra. It is believed that these doublets represent more strongly covalent bonding, can be attributed to sulfate (SO₂) bonding and S-N bonding within the structure of the material. The doublet at \(~164.5\) eV is believed to be associated with S-N bonding, as compared to \(164.6\) eV for \(\text{S}_2\text{N}_2\) measured by others \((49; 50)\). The doublet centered at \(~166\) eV is assigned to \(\text{SO}_2\), based on the results of \((51; 52)\).

### 5.2.5 Energy Dispersive Spectroscopy

Elemental dispersive spectroscopy was performed in order to examine the germanium, oxygen, and sulfur contents of the two different sets of thin films. Table 5.3 presents the results of the EDS carried out on argon and nitrogen sputtered thin films. It should be noted that lithium atomic percentages cannot be measured using EDS because the lithium atom contains only one outer shell electron. Therefore, with this element missing, the atomic percentages measured were not accurate. However, these results can be modified and adjusted by assuming that the lithium content in the XPS is measured accurately and representative of the amount of lithium in the films measured using EDS. While this assumption may be incorrect, it does allow for an improved understanding of the composition of the films. In comparing these new results to those obtained through XPS, the results are similar. The oxygen content of the films from EDS is lower, this is because a more pure lithium sulfide material (see IR results) was used in making the target.

Instead, the focus of this analysis technique was to examine the Ge/S ratio and compare to the same ratio obtained in the XPS results. In the case of the argon sputtered thin films, the Ge/S ratio measured with EDS was 0.39 while measured with XPS was 0.5053. For the nitrogen sputtered thin films, the EDS ratio was 0.72 while the XPS ratio was 0.69. These values can then be compared to the theoretical ratios for typical binary \(\text{Li}_2\text{S}-\text{GeS}_2\), where the ratio can range from 0 (for high amounts of lithium sulfide) to 0.50 (for low amounts of lithium sulfide).
Table 5.3  Results of EDS as performed on argon and nitrogen sputtered thin films.

<table>
<thead>
<tr>
<th>Atom measured</th>
<th>Li$_4$GeS$_4$ in Ar</th>
<th>Li$_4$GeS$_4$ in N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ge</td>
<td>26.5</td>
<td>27.8</td>
</tr>
<tr>
<td>S</td>
<td>67.7</td>
<td>38.8</td>
</tr>
<tr>
<td>N</td>
<td>–</td>
<td>26.0</td>
</tr>
<tr>
<td>O</td>
<td>5.9</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Table 5.4  Results of EDS adjusted to account for lithium content by using values measured using the XPS.

<table>
<thead>
<tr>
<th>Atom measured</th>
<th>Li$_4$GeS$_4$ in Ar</th>
<th>Li$_4$GeS$_4$ in N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>26.3</td>
<td>25</td>
</tr>
<tr>
<td>Ge</td>
<td>20.1</td>
<td>20.9</td>
</tr>
<tr>
<td>S</td>
<td>49.5</td>
<td>28.9</td>
</tr>
<tr>
<td>N</td>
<td>–</td>
<td>19.0</td>
</tr>
<tr>
<td>O</td>
<td>4.1</td>
<td>6.1</td>
</tr>
</tbody>
</table>

5.2.6 Lithium Ion Conductivity

Impedance spectroscopy was performed on thin film samples sputtered in Argon and Nitrogen. Physical masking was done in order to place electrodes on the sample. The different arrangements used can be seen in Figure 4.5. The first masking arrangement involved depositing gold on to a masked piece of alumina, depositing the thin film electrolyte, and then another layer of gold. Initial tests performed at room temperature indicated a short circuit, and it was determined that the top layer of gold was likely penetrating the film. Furthermore, it was found that the cell constant of this arrangement is $\sim 0.0001$. Therefore, there was a small signal to noise ratio because of the small impedances that were recorded. A second masking arrangement was tested whereby both the electrodes were deposited on top of the film with a 1 mm gap in between for the measurement. This gave a cell constant of $\sim 400$. This was found to improve the signal to noise ratio so that impedances could be measured more accurately. However, at the same time, the impedances measured approached the limit of the spectrometer being used (100 M$\Omega$). The results of the argon sputtered thin films can be seen
in Figure 5.12 while the nitrogen sputtered films can be seen in Figure 5.13. The data from both sets of sputtered thin films were fitted with arcs in order to measure the resistance. The resistance was taken to be the diameter of the fitted arc. In the case of the argon sputtered films, an average value of 137.4 Ω and standard deviation of 78.9 Ω was observed. This would represent a room-temperature conductivity value of $1.82 \times 10^{-5}$ S/cm. The data from the nitrogen films shows an average of 285.8 Ω with a standard deviation of 127.8 Ω, which would give a conductivity value of $6.99 \times 10^{-6}$ S/cm. It appears that the nitrogen sputtered thin films have a slightly lower conductivity as compared to the argon sputtered thin films. While this may be the case, it is anticipated that this nitrogen will make the amorphous films stable in contact with metallic lithium.
Films sputtered from Li₄GeS₄ target
30 mtorr Nitrogen, 25W

Films sputtered from Li₄GeS₄ target
30 mtorr Argon, 25W

Li₄GeS₄ target material
before sputtering

Figure 5.6 Raman spectra of the starting Li₄GeS₄ target material and the resulting films produced in argon and nitrogen atmospheres.
Figure 5.7 Infrared spectra of the starting GeS$_2$ and Li$_2$S powders, and Li$_4$GeS$_4$ target material and the resulting films produced in argon and nitrogen atmospheres.
Figure 5.8  Deconvoluted N1s spectra for films produced from a Li₄GeS₄ target in argon and nitrogen atmospheres.
Figure 5.9  Deconvoluted S2p spectra for the starting Li$_4$GeS$_4$ target material.
Figure 5.10  Deconvoluted S2p spectra for films produced from a Li$_4$GeS$_4$ target in an argon atmosphere.
Figure 5.11 Deconvoluted S2p spectra for films produced from a Li₄GeS₄ target in an nitrogen atmosphere.
Figure 5.12 Room-temperature complex plane plots of the argon sputtered thin films
Figure 5.13  Room-temperature complex plane plots of the nitrogen sputtered thin films
An RF Magnetron sputtering system has been constructed and coupled to a nitrogen glovebox so that moisture and oxygen sensitive films can be deposited without contamination. Films can be sputtered in both argon and nitrogen atmospheres, under an RF power ranging from 0-100 Watts. The system was tested by preparing films of LiPON, and reproducing the results of Bates et al (7; 8).

Targets have been prepared from a Li₄GeS₄ material, which was prepared by reacting stoichiometric amounts of Li₂S and GeS₂. Attempts have been made to improve the bulk density of the target material, including pressing and sintering operations and a pressureless consolidation technique. Sintering experiments appeared to improve the target density, but fully dense targets could not be obtained and consolidation of the material could also not be carried out. As a result, the sputtering system was reconstructed to accommodate the mechanically weaker targets.

Films have been deposited from these targets, with powers ranging from 25 to 50 Watts, in both argon and nitrogen atmospheres. It appears that the lithium content of the films is significantly decreased, which will dramatically reduce the ionic conductivity. Targets with higher fractions of lithium sulfide are needed to make ionically conductive films.

Lithium thiogermanate thin films have been sputtered for the first time in a 100% nitrogen atmosphere. XPS confirms the incorporation of nitrogen into the structure, at approximately 10 at%. The nitrogen appears to be interacting primarily with the sulfur in the film as confirmed with both IR spectroscopy and XPS. Initial impedance spectroscopy experiments appear to suggest that nitrogen sputtered films have a decreased conductivity as compared with argon sputtered thin films. While the conductivity might be adversely affected, it is believed that
the added nitrogen will improve the stability of the structure in contact with metallic lithium.

Future work on this project can include many different processes. First, targets with higher fractions of lithium sulfide need to be used in the sputtering system in order to improve the ionic conductivity of the resulting thin films.
BIBLIOGRAPHY


