Plasma-Assisted Directed Vapor Deposition for Synthesizing Lithium Phosphorus Oxynitride Thin Films

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Yoon Gu Kim

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 Approval Sheet

This Dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Engineering Physics)

Author, Yoon Gu Kim

This dissertation has been read and approved by the examining committee:

Dissertation Advisor, H. N. G. Wadley

Chairman, Robert G. Kelly

Giovanni Zangari

Petra Reinke

Keith A. Williams

Accepted for the School of Engineering and Applied Science:

Dean, School of Engineering and Applied Science
August 2008
Abstract

This dissertation explores a new vapor deposition route for synthesizing lithium phosphorus oxynitride (Lipon) thin-film electrolytes for rechargeable thin-film Li/Li-ion batteries. These batteries operate at a high voltage (around 4.0 V) and exhibit a long cyclic life (over 10,000 charge/discharge cycles). These features stem from the extremely low leakage current of the Lipon film electrolyte when in contact with a lithium anode, and its good Li-ion conductivity (in the $10^{-6}$-$10^{-7}$ S/cm range). Lipon films have usually been synthesized by reactive RF-magnetron sputtering, which suffers from a very low deposition rate (~2 nm/min). It therefore takes many hours to make the 1-2 μm thick films needed for battery applications. Other deposition approaches, such as Pulsed Laser Deposition, Ion Beam Assisted Deposition, and E-beam evaporation, have been investigated but resulted in unsatisfactory Lipon film performance.

Here, a plasma-assisted directed vapor deposition (PA-DVD) approach has been explored to synthesize dense, amorphous Lipon films. Unlike conventional e-beam evaporation, the e-beam based DVD approach employs an annular nozzle to generate a rarefied supersonic inert gas jet around the periphery of an electron beam evaporated source material. The vapor is entrained in the jet and rapidly transferred to a substrate. Because the supersonic gas jet focuses the vapor (it impedes lateral spreading of the vapor flux), most of the evaporant reaches the substrate. As a result, the deposition rate of Lipon films can be potentially much higher than most other processes. The PA-DVD approach used here employs a hollow cathode to create low-energy plasma through
which the vapor is propagated. This plasma ionized some of the evaporant and reactive gases (nitrogen) that were added to the jet. This increased their reactivity and atomic mobility on a substrate enabling the reactive synthesis of lithium phosphorus oxynitride from a lithium phosphate source. This dissertation explores how varying the deposition conditions affected the properties of the Lipon films, and then identifies an optimized process for Lipon film synthesis at rates up to 100 times those reported for sputtering approaches.

The dissertation has systematically investigated the effects of plasma current, nitrogen gas flux, and substrate biasing upon the synthesis of Lipon thin films. Variations to these deposition parameters affect film morphologies, compositions, atomic structures, and the ionic transport properties of the films. When Lipon films were synthesized using systematically varied plasma currents and low substrate bias potentials, entirely amorphous films could be synthesized. The morphologies of the films changed from highly porous to fully dense as the plasma current was increased. As the plasma current increased, the N/P ratio in Lipon films also increased while the Li/P ratio decreased. This decrease of the Li/P ratio was linked to an increase of the N/P ratio as nitrogen atoms replaced oxygen atoms of Li₃PO₄ and created linkages in Li₃PO₄ with doubly and triply coordinated nitrogen bonds. This resulted in lithium losses. X-ray Photoelectron Spectroscopy (XPS) studies indicated that plasma activation was essential for nitrogen atom incorporation in Li₃PO₄ where it substituted for oxygen atoms. The conductivity of the films was highly sensitive to the nitrogen content of the films. When nitrogen atoms were not incorporated into the (Li₃PO₄) films, the Li-ion conductivity was in the ~10⁻⁹
S/cm range. The incorporation of nitrogen atoms at first increased the Li-ion conductivities of Lipon films to \( \sim 10^{-7} \) S/cm. This was accompanied by an expansion of the average Li-O atomic distances, which reduced the activation energy for Li-ion transport in the amorphous structure. However, further increases of the plasma current eventually resulted in lithium losses in the as-deposited Lipon films and a decrease in Li-ion conductivity.

Increasing the plasma activated nitrogen gas flux resulted in the gradual appearance of small regions of local crystallinity in otherwise amorphous Lipon films. It also changed film morphologies from porous to fully dense columnar structures. The phosphorus binding energy was gradually lowered as nitrogen atoms were increasingly substituted for oxygen atoms in \( \text{Li}_3\text{PO}_4 \). When regions of local crystallinity in the amorphous Lipon films occurred, the films also had a reduced Li/P ratio, resulting in a decreased Li-ion conductivity. If insufficient nitrogen was incorporated (by use of too low nitrogen flux) in \( \text{Li}_3\text{PO}_4 \), very low Li-ion conductivities resulted. By optimizing the plasma current and gas jet nitrogen doping, Li-ion conductivities in the range of \( \sim 10^{-7} - 10^{-8} \) S/cm could be readily achieved.

Increasing the negative substrate bias during plasma assisted deposition increased ion bombardment during film growth and this modified the surface morphologies of Lipon films from one covered in growth spirals to a spiral-free (smooth) surface. The use of a negative substrate bias also led to the development of local crystallinity in amorphous Lipon films. The Li/P ratio of the films also increased while the phosphorus
concentration decreased as the negative substrate bias was increased. This result is consistent with preferential acceleration of (lighter) lithium ions across the plasma sheath leading to preferential incorporation. The heavier phosphorus ions were less well incorporated, resulting in an increased Li/P ratio. The Li-ion conductivity of Lipon films was increased as the negative substrate bias was decreased because the high substrate bias resulted in local crystallinity in amorphous Lipon films and these crystalline regions possess very low ionic conductivities. The deposition rates of the Lipon films were also strongly affected by the deposition conditions. Conditions that resulted in Lipon film electrolytes well suited for rechargeable thin-film Li/Li-ion batteries could be synthesized at deposition rates over 60 times those achieved by conventional RF-magnetron sputtering approaches.
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A  Area of electrodes (cm$^2$)
Δ(BE$_i$)  Binding energy chemical shift (eV)
c  Light velocity (3.0×10$^{10}$ cm/s)
C  Capacitance (F)
C$_g$  Geometrical capacitance of Lipon cells (F)
C$_{dl}$  Double layer capacitance between Au and Lipon films (F)
d$_s$  Plasma sheath (mm)
ε$_o$  Dielectric constant (8.84×10$^{-14}$ F/cm)
h  Planck constant (6.62×10$^{-34}$ Joule s)
I  Operating current on an external resistance (A)
j$_i$  Ion current (A)
J$_e$  Electron current density (A/cm$^2$)
J$_i$  Ion current density (A/cm$^2$)
k$_b$  Boltzmann constant (8.617×10$^{-5}$ eV/K)
k  Specific gas constant (8.314 J·K$^{-1}$·mole$^{-1}$)
L  Thickness of films (µm)
m$_e$  Electron mass (9.11×10$^{-31}$ kg)
M  Mach number
M$_a$  Mass of vapor atoms (kg)
M$_i$  Ion mass (i.e., argon: 6.671×10$^{-26}$ kg)
M$_{molecule}$  Mass of the gas molecules (kg)
n  Number of transferred electrons
n$_{es}$  Electron density at plasma sheath edge (cm$^{-3}$)
P$_d$  Downstream pressure
P$_u$  Upstream pressure
P$_c$  Gas pressure in hollow cathode tube
Q$_M$  Mass flow rate through the hollow cathode
Δq$_i$  Change in the atom’s charge
\( R_i \) Internal resistance of a battery (\( \Omega \))

\( R_{Lipon} \) Resistance of Lipon film (\( \Omega \))

\( R_{Au} \) Resistance of Au (\( \Omega \))

\( R_0 \) Resistance at low-frequency ranges (\( \Omega \))

\( R_{\infty} \) Resistance at high-frequency ranges (\( \Omega \))

\( R_h \) Radius of the hollow cathode (cm)

\( R_s \) Specific gas constant (2077 J/(kg K) for helium, 208.1 J/(kg K) for argon)

\( \sigma_e \) Electronic conductivity (S/cm)

\( \sigma_i \) Working ion conductivity (S/cm)

\( t_i \) Transport number

\( T \) Absolute temperature (K)

\( T_e \) Electron temperature (eV)

\( \tau \) \((R_0-R_{\infty})\times C\)

\( u_B \) Bohm velocity (m/s)

\( u_{is} \) Ion velocity at plasma sheath edge (m/s)

\( U \) Speed of a supersonic gas jet (m/s)

\( u_a \) Vapor atom’s velocity (m/s)

\( u_e \) Electron velocity (m/s)

\( \bar{u}_e \) Electron average velocity (m/s)

\( \nu \) Frequency of the radiation (Hz)

\( V_{oc} \) Open-circuit voltage (V)

\( V_{sb} \) Substrate bias potential (V)

\( V_f \) Floating potential (V)

\( V_p \) Plasma potential (V)

\( V_s \) Substrate bias (V)

\( \omega \) Angular frequency (Hz)

\( x \) Molar quantity involved in electrochemical reactions

\( Z(\omega) \) Impedance as a function of angular frequency (\( \Omega \))

\( Z' \) Real part of impedance (\( \Omega \))

\( Z'' \) Imaginary part of impedance (\( \Omega \))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_W$</td>
<td>Warburg impedance ($\Omega$)</td>
</tr>
<tr>
<td>$\eta_{ct}$</td>
<td>Charge transfer overvoltage at an anode and a cathode</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>Concentration polarization at an anode and a cathode</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Ratio of specific heats ($5/3$ for helium and argon)</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Overview

The demand for high energy density rechargeable batteries has increased greatly over the last ten years due to the increased use of laptop computers, cellular phones, and other portable electronic devices. Modern rechargeable batteries can be reused many times (around 1,000 cycles) [1]. Rechargeable Li/Li-ion batteries are popularly used in various consumer products because they have a higher stored energy density compared to Lead-acid, Ni-Cd, and Ni-MH battery chemistries, Figure 1-1 [2]. The recent development of microsystems (e.g. micro-electro-mechanical systems (MEMS) devices, implantable medical devices, and smart cards) have led to a growing interest in miniature thin-film Li/Li-ion batteries as rechargeable “on chip” power sources.

Thin-film Li/Li-ion batteries consist of three active layers; a cathode, electrolyte, and an anode [1]. They usually use high voltage cathode materials providing an operating voltage range of ~4.0 V. When charged at this voltage, the thin-film electrolyte between the cathode and anode must not suffer breakdown. To avoid internal leakage currents, ideal thin-film electrolytes should easily conduct lithium ions while blocking electrons; in
other words, they should be a good electronic insulator with an electronic conductivity of $<10^{-14}$ S/cm as well as an ionic conductor with an ionic conductivity of $10^{-6}-10^{-7}$ S/cm or better [3]. Thin-film electrolytes also need to be thin (1-2µm or less) in order to minimize the internal resistive voltage losses of rechargeable thin-film Li/Li-ion batteries [4]. Furthermore, if a pore or a crack exists in thin-film electrolytes, then a localized partial discharge can occur when a voltage is applied to the electrodes. Thus, thin-film electrolytes should have a uniformly dense structure free of through thickness cracks and pores that are elongated across the film thickness (i.e. inter-columnar pores) [5].

![Figure 1.1 Comparison of various batteries in terms of volumetric and gravimetric energy density [2].](image)

Figure 1.1 Comparison of various batteries in terms of volumetric and gravimetric energy density [2].
For three decades, thin-film vapor deposition technologies have been used to make thin cathode, anode, and electrolyte layers [1,6,9]. Today, rechargeable thin-film batteries can be reliably manufactured via vapor phase synthesis routes. They can be extremely small and beneficial over rechargeable bulk batteries in several aspects [6,7]. Using current thin-film fabrication techniques, rechargeable thin-film batteries can be manufactured into almost any size or shape. Sequential vacuum deposition processes can greatly improve reaction areas of rechargeable thin-film batteries because they provide cleaner and more intimate interfaces between a cathode, an anode, and an electrolyte. A parallel or serial connection can easily amplify either their stored energy density or current density. Furthermore, rechargeable thin-film batteries can be fabricated using semiconductor thin-film vapor deposition technologies that are available in microelectronics foundries.

It is noted that even a poor ionic conductor (such as a glassy solid-state electrolyte) can be used as an electrolyte for rechargeable thin-film batteries, provided it is thin enough to permit the passage of the lithium ion flux. For instance, in the early 1990s, Bates et al. first incorporated nitrogen atoms into Li$_3$PO$_4$ by using a Radio-Frequency (RF)-magnetron sputtering approach [8]. They called their nitrogen-doped Li$_3$PO$_4$ films lithium phosphorus oxynitride or Lipon for short. They observed that the Li-ion conductivity of these Lipon films increased from $\sim 6.6 \times 10^{-8}$ S/cm to $\sim 2 \times 10^{-6}$ S/cm as the nitrogen concentration was increased. These Lipon films, when sandwiched between metal layers, did not exhibit voltage breakdown or a significant current flow at applied voltages as high as $\sim 5.5$ V. These films also offered improved performance for cyclic life times (over
10,000 charge/discharge cycle) when used in rechargeable Li/Li-ion batteries. Today, Lipon films are widely used as the thin-film electrolyte in many rechargeable thin-film Li/Li-ion batteries. As shown later (in Table 2-1), many research groups have tried to find better solid-state electrolytes. However, these electrolytes are still under the research phase and their application in rechargeable thin-film Li/Li-ion batteries is uncertain.

1.2 Lipon Deposition Approaches

Lithium phosphorus oxynitride (Lipon) electrolyte films have been synthesized by various vapor deposition approaches. Table 1.1 gives comparisons of various vapor deposition approaches for Lipon film growth. Typically, reactive RF-magnetron sputtering approaches have been used to synthesize the Lipon films [8,10]. Films are typically synthesized from cold-pressed and sintered (at around 900°C) Li$_3$PO$_4$ targets. The deposition chamber is initially evacuated down to $\sim 2 \times 10^{-6}$ Torr and 20 mTorr of either an Ar-N$_2$ mixture or pure N$_2$ is introduced into the chamber. A low RF-sputtering power of 12-40 W is typically used to create vapor while avoiding radial cracking of the target [11]. A substrate-target distance of 5-6 cm is usually used. The low power constraint results in a very low deposition rate (~2.0 nm/min).

Recently, Lipon films have been synthesized by other thin-film deposition approaches, including Pulsed Laser Deposition (PLD) [12], Ion Beam Assisted Deposition (IBAD) [13], and E-beam evaporation [15,16]. The deposition rate of PLD films was between 13.3-50 nm/min, while those synthesized using the IBAD approach could be grown at up
to ~66 nm/min. Both approaches therefore enabled growth at much higher deposition rates than the RF-magnetron sputtering approach. The PLD approach resulted in Li-ion conductivities of $1.6 \times 10^{-6} - 4.7 \times 10^{-8}$ S/cm range. Films made by the IBAD approach had similar Li-ion conductivities of $1.4 \times 10^{-6} - 8.9 \times 10^{-8}$ S/cm. However, PLD-deposited Lipon films had very rough surface morphologies, while those deposited with the IBAD approach contained a high tensile residual stress, which caused cracking of the films and led to electrical shorts in Lipon test cells. Also, because the IBAD approach employed a tungsten boat to melt Li$_3$PO$_4$ sources, a tungsten contamination also occurred [14].

An e-beam evaporation approach using an 8 kW e-beam gun and a 3.54 MHz inductively coupled plasma (ICP) reactor has also been used to synthesize Lipon films [15]. In order to synthesize these films, the deposition chamber was initially evacuated to $\sim 7.5 \times 10^{-7}$ Torr. Ar-N$_2$ gas mixtures were then introduced raising the chamber pressure to $7.5 \times 10^{-5}$ Torr. An Ar-N$_2$ plasma was then formed using an ICP reactor power of 200 W or 300 W. These e-beam evaporated Lipon films had Li-ion conductivities ranging from $10^{-7} - 10^{-8}$ S/cm and could be deposited at a higher deposition rate ($\sim 8.33$ nm/min) than those made by the RF-magnetron sputtering approach [16]. However, the e-beam evaporation approach had a lower deposition rate than either the PLD or IBAD approaches. Nevertheless, the combination of e-beam evaporation and a reactive plasma-assisted processing method appears to be a promising route for the rapid and economical deposition of Lipon films.
Table 1.1 Comparisons of various vapor deposition approaches for Lipon film growth. Here, IBAD represents ion beam assisted deposition and PLD represents pulsed laser deposition. Note that $P_w$ is the working pressure, $T_{sub}$ is the substrate temperature, $d_{sub}$ is the substrate-source distance, $R_{dep}$ is the deposition rate, and $\sigma_{ionic}$ is the Li-ion conductivity.

<table>
<thead>
<tr>
<th></th>
<th>RF-magnetron sputtering</th>
<th>IBAD</th>
<th>PLD</th>
<th>E-beam evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_w$ (Torr)</td>
<td>~0.2</td>
<td>&lt; 6×10^{-6}</td>
<td>0.05-0.2</td>
<td>7.5×10^{-5}</td>
</tr>
<tr>
<td>Working gas</td>
<td>Ar+N$_2$ or N$_2$</td>
<td>N$_2$</td>
<td>N$_2$</td>
<td>N$_2$</td>
</tr>
<tr>
<td>$d_{sub}$ (cm)</td>
<td>5-6</td>
<td>22</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>$T_{sub}$ (°C)</td>
<td>Ambient</td>
<td>Unknown</td>
<td>Ambient</td>
<td>Room</td>
</tr>
<tr>
<td>Source melting method</td>
<td>Physical sputtering</td>
<td>Tungsten boat (1300°C melting)</td>
<td>Q-switched Nd: YAG laser (355 nm)</td>
<td>8 kW e-beam gun (300 W)</td>
</tr>
<tr>
<td>N$_2$ ionization</td>
<td>RF-magnetron discharge</td>
<td>Ion gun</td>
<td>Plasma (unknown)</td>
<td>13.56 MHz inductively coupled plasma</td>
</tr>
<tr>
<td>$R_{dep}$ (nm/min)</td>
<td>1-2</td>
<td>~66</td>
<td>40</td>
<td>8.3</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>Amorphous or Polycrystalline</td>
</tr>
<tr>
<td>$\sigma_{ionic}$ (S/cm)</td>
<td>0.1-2×10^{-6}</td>
<td>0.9-1×10^{-6}</td>
<td>0.64-1.67×10^{-6}</td>
<td>0.81-6×10^{-7}</td>
</tr>
<tr>
<td>Problems</td>
<td>- Very low deposition rate</td>
<td>- Film stress</td>
<td>- Very rough morphology</td>
<td>- Still low deposition rate</td>
</tr>
<tr>
<td></td>
<td>- Race track and cracks of target</td>
<td>- Tungsten contamination</td>
<td>- Difficulty to scale up</td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>[8,10]</td>
<td>[13,14]</td>
<td>[12]</td>
<td>[15,16]</td>
</tr>
</tbody>
</table>
1.3 Goals of the Dissertation

This thesis explores a new deposition route for synthesizing lithium phosphorus oxynitride (Lipon) electrolyte films. It is based upon the use of a plasma-assisted directed vapor deposition (PA-DVD) approach. In this novel e-beam evaporation approach, a supersonic gas jet is used to focus the evaporant and mix it with molecular nitrogen. A hollow cathode plasma technique is used in conjunction with a substrate bias technique to increase the reactivity of the nitrogen with the evaporated $\text{Li}_3\text{PO}_4$ to form an amorphous Lipon film. These processing conditions will potentially enable an increased deposition rate and modify film compositions and properties including the Li-ion conductivity. The goals of this dissertation are to (i) explore the synthesis of Lipon films using this high deposition rate approach and (ii) characterize properties of the resulting films, such as structure, morphology, composition, and Li-ion conductivity. Since these film-processing conditions of the PA-DVD approach can affect deposition rates and film properties, this dissertation also investigates the conditions that most directly influence film properties and seeks to identify optimized process conditions at the fundamental rationale for their existence.

Chapter 2 reviews the solid-state electrolytes of rechargeable thin-film Li/Li-ion batteries. This is followed by a review of the electrochemical properties of lithium phosphorus oxynitride (Chapter 3) and a presentation of the plasma-assisted directed vapor deposition approach (Chapter 4). Detailed film analysis methods are given in Chapter 5. Chapter 6 presents a study of Lipon films synthesis using plasma assistance. In Chapter 7, the effects of the nitrogen flux during the growth of Lipon films are
investigated. In Chapter 8, the effects of a substrate bias are explored. Chapter 9 discusses the findings of this dissertation and its potential impact for synthesizing rechargeable thin-film Li/Li-ion batteries. Finally, conclusions are given in Chapter 10.
Chapter 2

Solid-State Electrolytes in Rechargeable Thin-Film Batteries

2.1 Operational Principles of Rechargeable Li/Li-ion Batteries

Rechargeable Li-ion batteries use lithium-rich cathode and anode materials that form a layered (or other easily penetrated) structure. These materials are chosen to facilitate intercalation of the charge storing ions [1]. In rechargeable Li-ion batteries, the lithium ions move between the cathode and anode through a solid-state electrolyte [1]. This ion transport process is achieved by electrochemically driven diffusion [1,17]. In typical Li-ion batteries, the cathode is a lithium binary transition metal oxide (such as LiCoO$_2$) and the anode consists of a lithium compound (such as Li$_x$C). During a charge cycle, the following reactions occur:

- **Cathode:** $\text{LiMO}_2 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \quad (\text{Oxidation})$
- **Anode:** $\text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C} \quad (\text{Reduction})$
- **Overall:** $\text{LiMO}_2 + \text{C} \rightarrow \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2 \quad (\text{Charge})$. 
During a discharge cycle, the cathode is reduced and the anode is oxidized by Li-ion transport through the electrolyte as shown in Figure 2.1; that is, lithium ions are deintercalated from the anode and then intercalated into the cathode.

![Figure 2.1 Discharge process of a rechargeable Li-ion battery [2]. The electrolyte can be non-aqueous liquids (poly(ethylene oxide)(PEO)-based polymer electrolytes) or solid-state thin films (lithium phosphorus oxynitride film electrolytes).](image)

**2.2 Roles of the Solid-State Electrolytes**

During a discharge cycle, ideal batteries have a flat voltage profile like the open-circuit voltage profile in Figure 2.2. The open-circuit voltage is the voltage across the battery without an external load resistor. The voltage profile of real batteries is rarely so flat, which can be explained by several mechanisms. First, if the internal impedance in a battery is high, then a voltage drop occurs across the battery as current flows. Second,
during a discharge, positive ions move from an anode to a cathode through an electrolyte, Figure 2.1. When they pass through either a cathode-electrolyte interface or an anode-electrolyte interface, the heterogeneous interfaces act as an energy barrier to the charge-transfer reaction [1]. If the barrier to the charge-transfer reaction is high, then the charge-transfer reaction is slow and the voltage across the battery subsequently decreases. Third, during a discharge, if ions move slowly in an electrolyte, then concentration polarization, which is a concentration difference, will occur at either a cathode-electrolyte interface or an anode-electrolyte interface [1]. This concentration polarization acts as a resistance and lowers the battery’s voltage.

Figure 2.2 Voltage losses of batteries as a function of operating current [1]. Here, (a) is internal IR loss, (b) is charge transfer resistance, and (c) is concentration polarization loss.
These three mechanisms usually result in additive voltage drops (Figure 2.2). If an external load resistor (R) is connected across the terminals of the battery, the voltage can be written as [1,17]:

\[ V = V_{oc} - [\eta_{ct}a + (\eta_c)_a] - [(\eta_{ct})c + (\eta_c)_c] - I \cdot R_i = I \cdot R, \]  
(2-1)

where \( V_{oc} \) = Open-circuit voltage of a battery,

\( \eta_{ct} = \) Charge transfer overvoltage at either an anode or a cathode,

\( \eta_c = \) Concentration polarization at either an anode or a cathode,

\( R_i = \) Internal resistance of a battery, and

\( I = \) Operating current on an external resistor.

In view of this, several requirements for a solid-state electrolyte can be identified to optimize battery performance [1,3]. First, internal IR losses should be minimized; that is, a solid-state electrolyte should have the highest possible ionic conductivity (\( \sigma_i \)), because its resistance (\( R_i \)) is inversely proportional to ionic conductivity:

\[ R_i = \frac{h}{\sigma_i \cdot A}, \]  
(2-2)

where \( h \) is the thickness of a solid-state electrolyte and \( A \) is its area. The ionic conductivities can be enhanced by increasing the mobile ion concentration in a solid-state electrolyte, since the conductivities are generally proportional to the number of mobile ions present. Equation (2-2) also indicates that the resistance loss can be decreased by the use of a solid-state electrolyte with the thinnest possible membrane over the area that needs to be coated. This is limited by the variability in thickness of a thin film and can to some extent be controlled by appropriate selection of process conditions. Second, solid-state electrolytes also need to have a transport number for the ion of interest near unity.
where the transport number \( t_i \) is defined as:

\[
t_i \equiv \frac{\sigma_i}{\sigma_t}.
\]  

(2-3)

Here, \( \sigma_i \) is the conductivity of working ions and \( \sigma_t \) is the total conductivity [3]. The total conductivity \( \sigma_t = \sigma_i + \sigma_e + \Sigma \sigma_j \) where \( \sigma_e \) is the electronic conductivity and \( \Sigma \sigma_j \) represents the conductivities of all other mobile ionic species. If mobile counter ions exist in a solid-state electrolyte, they will pile up at an electrode-electrolyte interface and create a counter-internal electric field, which generates a concentration polarization. Solid-state electrolytes need to be electrical insulators (i.e., \( \sigma_e = 0 \)), because an electrical current through a solid-state electrolyte generates an internal power loss and internal leakage currents [3]. Third, the interfacial charge transfer reaction rate should be fast so that the charge transfer resistance is not too high. Fourth, in order for a solid-state electrolyte to remain impervious to reactants, a solid-state electrolyte must retain its mechanical and chemical integrity during repeated charge/discharge cycles [3]. Finally, the voltage window \( (V_g) \) of a solid-state electrolyte between a cathode and an anode should be matched; that is, the open-circuit voltage \( (V_{oc}) \) of a battery should be less than the voltage window \( (V_g) \) of a solid-state electrolyte in order to prevent a decomposition of a solid-state electrolyte [3].

2.3 Fabrication of Rechargeable Thin-Film Li/Li-ion Batteries

Figure 2.3 shows the structure and layer thickness of a typical rechargeable thin film Li/Li-ion battery. The electrolyte and cathode layers of thin-film Li/Li-ion batteries have usually been fabricated by the RF-magnetron sputtering approach [18-20]. The lithium
metal anode is deposited by a resistive thermal evaporation method since lithium metal has a low melting point of 180.5°C [21]. However, because lithium metal is highly reactive in air (especially humid air), it should be handled in a dry, inert gas atmosphere (argon or nitrogen) in order to avoid possible environmental contamination. For this reason, a resistive thermal evaporator is usually built in a glove box. After the glove box is filled with either argon or nitrogen, the lithium anode can be carefully handled without any environmental contamination. As shown in Figure 2.3, the rechargeable thin-film lithium battery has a multi-layer structure with a total thickness typically less than 15.0 µm. Thin-film electrolytes prevent direct contact between the cathode and the anode, thus enabling the fabrication of the rechargeable thin-film Li/Li-ion batteries of any size and on substrate of a variety of shapes.

Figure 2.3 Cross-sectional illustration of a rechargeable thin-film lithium battery showing the general layout and stacking order of the film components.
Rechargeable thin-film Li/Li-ion batteries usually have inorganic solid-state electrolytes. Both crystalline and amorphous electrolytes have been widely investigated for rechargeable Li/Li-ion batteries (Table 2-1). Even though some of crystalline electrolytes have higher Li-ion conductivities than amorphous electrolytes, they suffer from either low voltage windows or electron conductions. These properties cause difficulties in fabricating rechargeable Li/Li-ion batteries, such as failure or internal current leakage of the batteries. When inorganic solid-state electrolytes are deposited at ambient temperature using thermalized vapor, the low atomic mobility on the film growth surface typically generates an amorphous film structure [43]. While crystalline electrolytes must be annealed at a high temperature for crystallization to occur, amorphous electrolytes do not require the annealing process, which is advantageous when multi-layered stacks made up of materials with widely varying thermal expansion coefficients. Also, because amorphous glass electrolytes have a usually higher and more isotropic ionic conductivity than crystalline counterparts of the same composition, they can reduce internal voltage losses [3,44]. Because of these considerations, amorphous electrolytes are generally preferred for fabricating rechargeable thin-film Li/Li-ion batteries.

As Table 2-1 indicates, both sulfide and oxide glasses have been investigated as amorphous glass electrolytes. Sulfide glass electrolytes have a higher Li-ion conductivity than oxide glass electrolytes. However, since sulfide glass electrolytes are highly reactive with moisture, they must be isolated from the ambient atmosphere during the manufacturing process. Also, sulfide glass electrolytes corrode processing equipment and
are therefore not really practical. Thus, even though the ionic conductivity of oxide glass electrolytes is lower than that of sulfide glass electrolytes, oxide glass electrolytes are usually preferred for use as an thin-film electrolyte, since they are stable in an ambient atmosphere and do not corrode processing equipment. Bates et al. successfully synthesized lithium phosphorus oxynitride (Lipon) films using a reactive RF-magnetron sputtering approach [8,10]. When the current-voltage characteristics of these Lipon films were measured, they did not exhibit any voltage breakdown up to 5.5 V. This indicated that Lipon films have a wide voltage window of 0-5.5 V that is well matched to the operating voltage window (~4.0 V) of rechargeable Li/Li-ion batteries. Lipon films also had an acceptable Li-ion conductivity of $10^{-6}$-$10^{-7}$ S/cm range.

When Lipon films were synthesized using the reactive RF-magnetron sputtering approaches, Li-ion conductivities of Lipon films increased with the increase of N/P ratio, Figure 2.4 (a) [10,108,109,112]. When the N/P ratio is higher than 0.2, Lipon films have Li-ion conductivity greater than $1\times10^{-7}$ S/cm. Overall, these literature studies indicate that Li-ion conductivities of Lipon films were higher than $1\times10^{-7}$ S/cm range when N/P ratio is between 0.3 and 1.4 and Li/P ratio is between 2.4 and 3.3, (Figure 2.4 (a) and (b)).
Figure 2.4 N/P ratio versus Li-ion conductivity (a) and Li/P ratio (b) in Lipon films synthesized by the reactive RF-magnetron sputtering approaches [10,108,109,112].
Table 2-1 Comparisons of solid-state electrolytes. Here, $E_a$ is the activation energy for ion transportation (eV), $t_e$ is the electron transport number and $\Delta V$ is the voltage window of solid-state electrolytes (V).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_{ionic}$ (S/cm) at 25°C</th>
<th>$E_a$ (eV)</th>
<th>$t_e$</th>
<th>$\Delta V$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O-SeO$_2$-B$_2$O$_3$</td>
<td>8x10^{-7}</td>
<td>unknown</td>
<td>unknown</td>
<td>0-5</td>
<td>[22]</td>
</tr>
<tr>
<td>Li$_3$PO$_4$N$_2$</td>
<td>2x10^{-6}</td>
<td>0.57</td>
<td>&lt; 10^{-8}</td>
<td>0-5.5</td>
<td>[23]</td>
</tr>
<tr>
<td>Li$_2$BO$_4$N$_2$</td>
<td>6x10^{-8}</td>
<td>0.84</td>
<td>&lt; 10^{-8}</td>
<td>0-6</td>
<td>[24]</td>
</tr>
<tr>
<td>Li$_2$S-P$_2$S$_5$</td>
<td>2x10^{-4}</td>
<td>0.38</td>
<td>10^{-4}</td>
<td>0-1</td>
<td>[25]</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$</td>
<td>1x10^{-4}</td>
<td>0.31</td>
<td>10^{-4}</td>
<td>unknown</td>
<td>[26]</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$-Li$_3$MO$_4$ (M=Si, P, Ge)</td>
<td>1x10^{-3}</td>
<td>0.31</td>
<td>10^{-4}</td>
<td>0-10</td>
<td>[27]</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$-Li$_3$PO$_4$</td>
<td>1.5x10^{-3}</td>
<td>0.30</td>
<td>unknown</td>
<td>0-4.5</td>
<td>[28,29]</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$-xMS$_y$ (M=Sn, Ta, Ti)</td>
<td>0.6-1.6x10^{-3}</td>
<td>0.30-0.31</td>
<td>&lt; 10^{-2}</td>
<td>unknown</td>
<td>[30]</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$-Li$_3$N</td>
<td>1.5x10^{-3}</td>
<td>0.28</td>
<td>10^{-4}</td>
<td>0-10</td>
<td>[31]</td>
</tr>
<tr>
<td>Li$_3$N-SiS$_2$</td>
<td>2.7x10^{-4}</td>
<td>0.30</td>
<td>10^{-4}</td>
<td>0-10</td>
<td>[32]</td>
</tr>
<tr>
<td>La$<em>{2/3-x}$Li$</em>{3x}$TiO$_3$</td>
<td>1x10^{-3}</td>
<td>0.29</td>
<td>10^{-6}</td>
<td>1.5-4</td>
<td>[33,34]</td>
</tr>
<tr>
<td>La$<em>{1/3-x}$Li$</em>{3x}$TaO$_3$</td>
<td>9x10^{-6}</td>
<td>unknown</td>
<td>10^{-4}</td>
<td>unknown</td>
<td>[35]</td>
</tr>
<tr>
<td>La$<em>{1/3-x}$Li$</em>{3x}$NbO$_3$</td>
<td>4x10^{-5}</td>
<td>0.36</td>
<td>unknown</td>
<td>0-1.8</td>
<td>[36]</td>
</tr>
<tr>
<td>Li$<em>{1.3}$Ti$</em>{1.7}$Al$_{0.3}$(PO$_4$)$_3$</td>
<td>3x10^{-4}</td>
<td>unknown</td>
<td>unknown</td>
<td>0-2.4</td>
<td>[37]</td>
</tr>
<tr>
<td>Li$<em>{0.6}$V$</em>{0.61}$Si$<em>{0.39}$O$</em>{5.56}$</td>
<td>1x10^{-4}</td>
<td>0.50</td>
<td>10^{-4}</td>
<td>0-3.5</td>
<td>[38]</td>
</tr>
<tr>
<td>Li$<em>{4-x}$Ge$</em>{1.3}$Ga$_x$S$_4$</td>
<td>6x10^{-5}</td>
<td>0.57</td>
<td>10^{-3}</td>
<td>0-5</td>
<td>[39]</td>
</tr>
<tr>
<td>Li$<em>{4-x}$Ge$</em>{1.3}$P$_x$S$_4$</td>
<td>2x10^{-3}</td>
<td>0.21</td>
<td>10^{-6}</td>
<td>0-5</td>
<td>[40]</td>
</tr>
<tr>
<td>Li$_3$Bi$_2$Cl$_3$</td>
<td>7x10^{-7}</td>
<td>0.47</td>
<td>10^{-4}</td>
<td>0-1.5</td>
<td>[41]</td>
</tr>
<tr>
<td>Li$_3$SiAlO$_8$</td>
<td>2x10^{-7}</td>
<td>0.56</td>
<td>10^{-4}</td>
<td>0-6.5</td>
<td>[42]</td>
</tr>
</tbody>
</table>
Chapter 3

Lithium Phosphorus Oxynitride

3.1 Overview

Li or Li-ion batteries can be made using liquid [45], polymeric [46], and inorganic electrolytes [47]. Their charging and discharging rates are controlled by the electrochemical diffusion rate of lithium ions, which is characterized by the Li-ion conductivity. High ionic conductivities are preferred and this poses a significant challenge to the inorganic electrolytes, which have quite dense atomic structures. These electrolytes can only be used as a very thin-film in rechargeable thin-film batteries.

Chapter 2 indicates that amorphous lithium phosphorus oxynitride (Lipon) is the best candidate electrolyte for rechargeable thin-film Li/Li-ion batteries. When a voltage scan of Lipon cells sandwiched by metal layers was conducted, Lipon cells did not fail in the range of 0.0-5.5 V [8,9]. This property indicates that when thin-film batteries are designed to operate at high voltages (~4.0 V), a Lipon electrolyte provides an acceptable voltage window. Also, because amorphous Lipon films have higher Li-ion conductivity ($10^{-6}$-$10^{-7}$ S/cm) than crystalline Lipon electrolytes ($\sigma_{\text{ionic}} \sim 10^{-12}$ S/cm), they have reduced the internal voltage [1]. Unlike crystalline Lipon film electrolytes, amorphous...
Lipon film electrolytes do not require an annealing process at a high temperature. Amorphous Lipon films are therefore the preferred electrolytes for multi-layered structures where a differential thermal expansion contraction becomes an issue if annealing is necessary.

### 3.2 Classification of Lithium Phosphates

Lithium phosphates are a combination of a base glass, $P_2O_5$, and a network modifier, $Li_2O$ [48]. The $PO_4$ tetrahedra consist of a framework of phosphate glasses. The chemical bond structure of phosphates can be understood by the structure of $Li_3PO_4$. Because the outer electrons ($3s^23p^3$) of phosphorus form $sp^3$ hybrid orbitals, the structure of $Li_3PO_4$ can be represented by the Lewis structure, Figure 3.2.1 (a). In chemical terminology, a dash represents a covalent bond, and, thus, Figure 3.2.1 (a) can be simply represented by Figure 3.2.1 (b). As shown in Figure 3.2.1 (b), four P outer electrons form covalent $\sigma$ bonds with the oxygen 2p electrons. The fifth electron forms a strong covalent $\pi$ bond with the oxygen 2p electron because it is promoted to a 3d orbital of phosphorus or donated to oxygen [48]. Likewise, the $Li_3PO_4$ forms the tetrahedral bond structure where a phosphorus atom is located in its center and four oxygen atoms are located at the vertices of the $PO_4$ tetrahedron. Lithium and oxygen form ionic bond, and this ionic bond acts as one of the activation energy barriers and decreases the Li-ion conductivity of $Li_3PO_4$. The chemical bond structure also reveals that mobile electrons are not available in the $Li_3PO_4$. The energy band gap of 5.75 eV indicates that the $Li_3PO_4$ is an electrical insulator [49].
Figure 3.2.1 Chemical bond structure of Li$_3$PO$_4$: (a) Lewis structure and (b) simplified structure. As shown in the above figure (right), phosphorus, which forms “sp$^3$ hybrid orbitals,” has four covalent $\sigma$ bonds and one covalent $\pi$ bond with oxygen.

The PO$_4$ tetrahedra are classified by the Q$^i$ terminology where ‘$i$’ represents the number of bridging oxygen per tetrahedron [50]. Figure 3.2.2 shows the tetrahedral sites of phosphate glasses. The structures of phosphate glasses can be represented by a ratio of M$_2$O to P$_2$O$_5$ (R=M$_2$O/P$_2$O$_5$, M=Li, or Na), Figure 3.2.3 [48]. Alternatively, networks of phosphate glasses can be represented by a composition ratio: i.e., $x$M$_2$O·$(1-x)$P$_2$O$_5$. Depending on the ratio (R=M$_2$O/P$_2$O$_5$), phosphate glasses are classified as ultraphosphate (R<1), metaphosphate (R=1), pyrophosphate (1<R<3), and orthophosphate (R=3), Figure 3.2.3.
The literature indicates that nitrogen atoms have usually been incorporated into either metaphosphates or orthophosphates. Here, nitrided lithium metaphosphates and nitrided lithium orthophosphates will be discussed.

![Diagram of Tetrahedral sites of phosphate glasses](image)

Figure 3.2.2 Tetrahedral sites of phosphate glasses [50].

![Diagram of Schematic structures as a function of a ratio, R](image)

Figure 3.2.3 Schematic structures as a function of a ratio, R (i.e., R=M2O/P2O5, M=Li, or Na) [50].
3.2.1 Nitrided Lithium Metaphosphates

Lithium metaphosphates (LiPO$_3$) have $R=1$ (or $x=0.5$). As shown in Figure 3.2.2, they consist of only $Q^2$ tetrahedra, which form chain and ring structures. Bounir et al. studied nitridation of lithium metaphosphates (LiPO$_3$) [51]. They observed that as the Li/P ratio decreases and the N/P ratio increases, the glass transition temperature (and hardness) increases and the thermal expansion coefficient decreases. Larson et al. observed the effects and noted that the chemical durability increased during nitridation [52].

The nitridation of metaphosphates has been achieved by melting metaphosphates at $\sim 800^\circ$C under flowing ammonia atmospheres. This environment results in a metaphosphate reaction with ammonia gases of the form:

$$3O^{2-} \text{(glass)} + 2NH_3 \rightarrow 2N^{3-} \text{(glass)} + 3H_2O \uparrow.$$  \hspace{1cm} (3-1)

This indicates that two $N^{3-}$ ions replace three $O^{2-}$ ions, and water is generated as a reaction product.

When nitrogen atoms are substituted for oxygen atoms in metaphosphates, they form one of two nitrogen bonds: a doubly coordinated nitrogen state or triply coordinated nitrogen state [53-57]. As shown in Figure 3.2.4, nitrogen replaces both non-bridging (=O) and bridging (−O−) oxygen. Wang et al. observed that the Li-ion conductivity of nitrided lithium metaphosphates ($\sim 3.7 \times 10^{-7}$ S/cm) was higher than that of lithium metaphosphates ($2.5 \times 10^{-9}$ S/cm) [58]. The reason for this is that the nitridation of lithium metaphosphates lowers the activation energy for Li$^+$ ion transport from 0.74 eV to 0.57
eV. This occurs because the nitridation generates either a linkage or a structural distortion in lithium metaphosphates [58].

![Diagram of nitrogen incorporation in metaphosphates](image)

**Figure 3.2.4** Nitrogen incorporation in metaphosphates (MPO₃, M=Li, or Na).

**3.2.2 Nitrided Lithium Orthophosphates**

Lithium orthophosphates (Li₃PO₄) have R=3 (or x=0.75 in xLi₂O·(1-x)P₂O₅). Because lithium orthophosphates form the Q⁰ structure, oxygen atoms do not have bonds between PO₄³⁻ tetrahedra, Figure 3.2.3. Reculeau et al. indicated that the crystalline Li₃PO₄ had a phase transformation as the temperature was increased: β → γ at 500°C and γ → α at 1170°C [58]. As shown in Figure 3.2.5, β-Li₃PO₄ has a Wurtzite structure where Li and P
are located in the middle of tetrahedral sites and all of the tetrahedra share corners and point in the same direction [59]. The $\beta$-Li$_3$PO$_4$ has only corner-linked tetrahedra. Oxygen atoms of the $\beta$-Li$_3$PO$_4$ are shared by three LiO$_4$ tetrahedra and one PO$_4$ tetrahedron, Figure 3.2.5. The $\gamma$-Li$_3$PO$_4$ forms orthorhombic, space group Pmnb with $Z=4$, Figure 3.2.6. Wang et al. divided lithium atoms into Li$_I$ and Li$_{II}$, depending on their atomic position in the $\gamma$-Li$_3$PO$_4$ structure [59]. These are represented by the Li$_I$O$_4$ and Li$_{II}$O$_4$ tetrahedra, Figure 3.2.7. Each Li$_{II}$O$_4$ tetrahedron shares adjacent edges with two Li$_I$O$_4$, which in turn share only corners with other Li$_I$O$_4$ tetrahedra. There are twice as many tetrahedral Li$_I$O$_4$ units as Li$_{II}$O$_4$ units. In addition, because the darkest shaded PO$_4$ tetrahedra are isolated from each other, the $\gamma$-Li$_3$PO$_4$ does not contain P-O-P bonds.
Figure 3.2.5 Polyhedral crystal structure of $\beta$-Li$_3$PO$_4$: (a) (001) and (b) (100). PO$_4$ are the darker shaded tetrahedra, and LiO$_4$ are the lighter shaded tetrahedra [59].
Figure 3.2.6 Crystal structure of $\gamma$-Li$_3$PO$_4$: orthorhombic, space group Pmn$\bar{b}$ with Z=4 [59]. In this figure, lithium is represented as a blue solid circle, oxygen as a red solid circle, and phosphorus as a yellow solid circle.
Figure 3.2.7 Polyhedral crystal structures of $\gamma$-Li$_3$PO$_4$: (a) (001) and (b) (100). The darkest shaded tetrahedra are PO$_4$, and the lighter shaded tetrahedra are LiO$_4$. The Li$_{I}$O$_4$ tetrahedra are gray shaded and Li$_{II}$O$_4$ tetrahedra are dot shaded. Black, gray, and white shaded represent the three oxygen atoms (O$_{I}$, O$_{II}$, and O$_{III}$) [59].
Using a solid-state reaction method, Wang et al. reacted Li$_3$N and LiPO$_3$ to synthesize polycrystalline Lipon [59]. They used X-ray and neutron diffraction to analyze a polycrystalline $\gamma$-Li$_3$PO$_4$ and a nitrided Li$_3$PO$_4$ (i.e., Li$_{2.8}$PO$_{3.73}$N$_{0.14}$). These studies indicate that the nitrogen incorporation in the $\gamma$-Li$_3$PO$_4$ increased the average Li-O bond distances from 1.99 Å to 2.0 Å. It is worth noting that because the effective ionic radius of N$^{3-}$ (1.32 Å) is larger than that of O$^{2-}$ (1.24 Å), the nitridation induces a structural distortion of $\gamma$-Li$_3$PO$_4$. Because the binding energy between lithium and oxygen is inversely proportional to the Li-O bond distances, the increase of average Li-O bond distances reduces a Li-O binding energy. In the nitrided Li$_3$PO$_4$, lithium ions can easily break their bonds from oxygen compared to lithium ions in the $\gamma$-Li$_3$PO$_4$. Also, because lithium ions are located in the LiO$_4$ tetrahedra of the nitrided Li$_3$PO$_4$, they must pass through one of the triangular faces of the tetrahedra. Increasing average Li-O bond lengths enlarges the triangular face of the LiO$_4$ tetrahedron, and this enables easier lithium ion transport through the triangular faces. The X-ray and neutron diffraction studies conducted by Wang et al. could not directly provide the nitrogen positions in the nitrided $\gamma$-Li$_3$PO$_4$ [59]. They tried to infer the nitrogen position by comparing the atomic spacing changes of $\gamma$-Li$_3$PO$_4$ and Li$_{2.8}$PO$_{3.73}$N$_{0.14}$. As shown in Figure 3.2.8, the gray solid circles represent nitrogen atoms that substitute for oxygen atoms in polycrystalline $\gamma$-Li$_3$PO$_4$. Unfortunately, the positions of the nitrogen atoms that Wang et al. proposed did not predict any bond linkages between nitrogen atoms and phosphorus atoms in the polycrystalline Li$_{2.8}$PO$_{3.73}$N$_{0.14}$. Wang et al. assumed that a disordering between phosphorus and lithium might exist in the polycrystalline Li$_{2.8}$PO$_{3.73}$N$_{0.14}$. 
Using chromatography and XPS measurements, Wang et al. showed that nitrogen could be incorporated into two nitrogen bonds: a doubly coordinated nitrogen state and a triply coordinated nitrogen state [59]. As shown in Figure 3.2.7, the structure of $\gamma$-Li$_3$PO$_4$ shares corners and edges. If nitrogen atoms are incorporated, they will substitute for oxygen atoms. When nitrogen atoms are locally incorporated in either triply or doubly coordinated states, the resulting composition is either Li$_2$PO$_3$N$_{0.33}$ or Li$_{2.5}$PO$_3$N$_{0.5}$. Lithium vacancies must then exist in crystalline Li$_{2.8}$PO$_{3.73}$N$_{0.14}$.

Wang et al. also measured the Li-ion conductivity of a polycrystalline $\gamma$-Li$_3$PO$_4$ and a nitrided Li$_3$PO$_4$ [59]. The nitrided Li$_3$PO$_4$ had a higher Li-ion conductivity ($\approx 1.4 \times 10^{-13}$ S cm$^{-1}$) compared to polycrystalline $\gamma$-Li$_3$PO$_4$ ($\approx 1.4 \times 10^{-18}$ S cm$^{-1}$), because the nitrogen incorporation in the polycrystalline $\gamma$-Li$_3$PO$_4$ decreased the activation energy from 1.24 eV to 0.97 eV. Also, because the nitrogen incorporation in $\gamma$-Li$_3$PO$_4$ increased the average Li-O bond length, it reduced the lithium-oxygen binding energy resulting in enlarged triangular faces of the LiO$_4$ tetrahedra. These changes make it easier for lithium ions to break its bond with oxygen and pass more easily through the dilated triangular faces of the PO$_4$ tetrahedra. This is experimentally observed as a reduced Li-ion migration activation energy for nitrided Li$_3$PO$_4$ and increased Li-ion conductivity.
Figure 3.2.8 Crystal structure of polycrystalline lithium phosphorus oxynitride (Lipon) [59]. In this figure, lithium is represented as a blue solid circle, oxygen as a red solid circle, phosphorus as a yellow solid circle, and nitrogen as a gray solid circle.

Yu et al. synthesized Lipon films by using the reactive RF-magnetron sputtering approach and characterized them, Table 3.1 [10]. The typical composition of Lipon films synthesized by the reactive RF-magnetron sputtering approach was Li$_{2.9}$PO$_{3.3}$N$_{0.36}$. The Lipon films had the wide voltage window of 0-5.5 V versus lithium metal and the Li-ion conductivity of $\sim$2×10$^{-6}$ S/cm. Their electronic conductivity was lower than $\sim$10$^{-11}$ S/cm. Also, an energy band gap of $\sim$3.75 eV indicates that Lipon films are electrical insulators. These Lipon properties are well suited for the fabrication of rechargeable thin-film lithium batteries, which have an operational voltage range of 3.5-5.0 V.
Table 3.1 Typical characteristics of lithium phosphorus oxynitride (Lipon) films synthesized by the RF-magnetron sputtering approach [10].

<table>
<thead>
<tr>
<th>Deposition &amp; composition</th>
<th>Deposition method</th>
<th>RF-magnetron sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Source target</td>
<td>Li₃PO₄</td>
</tr>
<tr>
<td></td>
<td>Typical composition</td>
<td>Li₂₉PO₃₃N₀₃₆</td>
</tr>
<tr>
<td>Electrochemical, electrical &amp; optical properties</td>
<td>Stability window versus Li</td>
<td>0-5.5 V</td>
</tr>
<tr>
<td></td>
<td>Li-ion conductivity (S/cm)</td>
<td>2(±1)×10⁻⁶ at 25°C</td>
</tr>
<tr>
<td></td>
<td>Transport number of Li⁺ ions</td>
<td>~1</td>
</tr>
<tr>
<td></td>
<td>Intrinsic diffusion coefficient (cm²⋅s⁻¹)</td>
<td>~10⁻¹¹ at 25°C</td>
</tr>
<tr>
<td></td>
<td>Electronic conductivity (S/cm)</td>
<td>&lt; 10⁻¹⁴ at 25°C</td>
</tr>
<tr>
<td></td>
<td>Optical energy band gap</td>
<td>3.75 eV</td>
</tr>
</tbody>
</table>
Chapter 4

Plasma-Assisted Directed Vapor Deposition

4.1 Overview

Directed vapor deposition (DVD) is a high-rate electron beam physical vapor deposition (PVD). It employs a supersonic gas jet and a low-vacuum environment of $7.5 \times 10^{-3} - 0.75$ Torr. The supersonic gas jet can entrain vapor atoms and rapidly transport them toward a substrate [60,61]. Vapor atoms are strongly thermalized in the DVD environment and deposited films typically form porous columnar structures, because of the low vacuum pressure used in DVD. So far, the DVD approach has been mainly used for thermal barrier coatings (TBC), because the TBC coatings require porous columnar structures [62]. However, some applications, such as microelectronics and solid electrolytes, require dense film structures. During the DVD deposition of films, the vapor thermalization was not desirable to synthesize dense films. Recently, a plasma-assisted directed vapor deposition (PA-DVD) approach has been used for dense film depositions. This approach employs a hollow cathode plasma technique and a substrate bias technique to synthesize dense films and modify the microstructures of films.
4.2 Directed Vapor Deposition

The original directed vapor deposition (DVD) redirects vapor atoms to a 90° angle from the vapor’s trajectory, Figure 4.1. The redirection of vapor atoms limits DVD abilities when films are deposited at a low gas flow or when a high deposition rate is required. The experimental and model-based research enabled the design of a new DVD system, Figure 4.2. Because an electron beam (e-beam) bombards a source material by a 45° incidence angle, a supersonic gas jet can vertically carry vapor atoms toward a substrate: thus, the supersonic gas jet and vapor atoms have the same direction in the new DVD system and films can be synthesized by a low gas flow. The new e-beam gun operates with a maximum power of 10 kW and a beam accelerating voltage of 70 kV. It also has a high-speed e-beam scanning system of up to 100 kHz and a minimal e-beam spot diameter of 0.3 mm. It is possible to create several vapor fluxes by placing source targets close together and scanning the focused e-beam at an extremely high rate. The focused e-beam and high speed scanning create a uniform temperature distribution across the surface of each source target.
Figure 4.1 Directed vapor deposition (DVD I) approach. During the DVD deposition process, the supersonic carrier gas jet redirects vapor atoms to a 90° angle toward the substrate.

Unlike a conventional e-beam evaporation method, the DVD approach can artificially create a supersonic gas jet through an annular nozzle (inner diameter: 3.0 cm), Figure 4.2. The supersonic gas jet rapidly transports vapor atoms toward a substrate under a low vacuum pressure range ($7.5 \times 10^{-3}$-0.75 Torr). During the deposition process, the upstream pressure ($P_u$) is higher than the downstream pressure ($P_d$), creating a supersonic gas jet through an annular nozzle near the source rod. The speed of a supersonic gas jet, $U$, is proportional to Mach number, $M$ [60]:

$$U = M \sqrt{\gamma R_s T},$$

(4-1)
where \( \gamma \) = Ratio of specific heats (5/3 for helium),

\[ T = \text{Absolute temperature (K)}, \] and

\[ R_s = \text{Specific gas constant (2077 J/(kg K) for helium)}. \]

The Mach number is determined by a pressure ratio \( (P_u/P_d) \) [59]:

\[
\frac{P_u}{P_d} = \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}},
\]

where \( M \) is the flow’s Mach number.

Equations 4-1 and 4-2 indicate that increasing the pressure ratio \( (P_u/P_d) \) increases the speed of the supersonic gas jet. Because increasing an upstream pressure \( (P_u) \) between 0.0 slm and 20 slm can focus vapor atoms towards the substrate, it increases material utilization efficiency. By mixing oxygen or nitrogen (between 0.0 slm and 1.0 slm) into the supersonic gas jet, a reactive film deposition can be achieved. Therefore, the use of the supersonic gas jet increases the deposition rate and material utilization efficiency [60,61].
4.3 Hollow Cathode Plasma Technique

Since the DVD approach is typically conducted under a low-vacuum environment (7.5×10⁻³-0.75 Torr), vapor atoms are strongly thermalized and the DVD deposited films typically form porous columnar structures [60]. Thornton divided the microstructure of sputtered films into four different zones (that is, zone I, zone T, zone II, and zone III) depending on gas pressure and substrate temperature, Figure 4.3 [63]. Thornton’s diagram indicates that a high gas pressure and a low substrate temperature generate a porous columnar film structure because vapor atoms have limited atomic mobility during film deposition.
Figure 4.3 Thornton diagram [63]. This diagram indicates that a high gas pressure and a low substrate temperature generate a porous columnar film structure.

Previously, cathodic arc evaporation was used to increase the mobility and reactivity of vapor atoms, because a conventional evaporation method had the limited atomic mobility of ~0.2 eV or less [64,65]. Unfortunately, the cathodic arc evaporation generated macroparticles from the cathode surface and these macro-particles contaminated the films. Goedicke et al. employed a spotless-arc-activated deposition (SAD) process, because the SAD process did not generate the macroparticles [66]. Later on, Morgner et al. combined a high-rate evaporation process and a hollow cathode plasma technique to create a hollow cathode-activated deposition (HAD) process, Figure 4.4 [67]. The HAD process successfully achieved dense films. Schiller et al. also deposited aluminum oxide films using various discharge currents, Figure 4.4 [68]. The density and hardness of aluminum oxide films increased with the increase of discharge currents.
Figure 4.4 Hollow cathode-activated deposition (HAD) process [67,68]. The HAD process employs the hollow cathode plasma unit and the e-beam gun. The hollow cathode arc discharge provides a high electron density of $\sim 10^{12} \text{ cm}^{-3}$.

<table>
<thead>
<tr>
<th>Without plasma</th>
<th>Discharge current: 100A</th>
<th>Discharge current: 200A</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
<td><img src="image3.png" alt="Image 3" /></td>
</tr>
</tbody>
</table>

| Hardness: 3.2 GPa | Hardness: 5.2 GPa | Hardness: 6.3 GPa |

Figure 4.5 Reactive e-beam evaporation of aluminum oxide. Plasma was activated by the hollow cathode technique [67]. The deposition rate was around 6 $\mu$m/min.
The hollow cathode arc discharge creates a 100-times higher electron density ($\sim 10^{12}$ cm$^{-3}$ versus $\sim 10^{10}$ cm$^{-3}$) than the RF discharge. As shown in Figure 4.6, the high electron density can be explained by the electron energy distribution function (EEDF). The EEDF consists of a Maxwell distribution of isotropic electrons and a superimposed group of directed electrons. Directed electrons are called the low-voltage electron beam (LVEB) ranging from 0-25 eV [67-70]. By using the hollow cathode arc discharge, vapors can be ionized up to approximately 30% or more. If an insulated (floating) substrate is placed near the plasma, then the ion current becomes the same as the electron current on the substrate. A floating potential ($V_f$) can be estimated by [43]:

$$V_f = \frac{kT_e}{2e} \ln \left( \frac{\pi m_e}{2 M_i} \right),$$  \hspace{1cm} (4-3)

where $k =$ Boltzmann constant ($8.617 \times 10^{-5}$ eV/K),

$T_e =$ Electron temperature (K),

$m_e =$ Electron mass ($9.11 \times 10^{-31}$ kg), and

$M_i =$ Ion mass (for example, argon: $6.671 \times 10^{-26}$ kg).

As shown in Figure 4.7, if a negative potential is applied to a substrate, then it attracts positive ions and creates a plasma sheath near the substrate. Because the plasma sheath generates a sheath potential ($V_{ps}$) between the substrate and the plasma itself, the sheath potential strongly accelerates positively ionized vapor atoms towards the substrate. Likewise, the vapor ionization and the plasma potential can increase kinetic energy of the vapors from 0.2 eV to about 6.0 eV, create a vapor incidence angle perpendicular to a film surface, and increase the reaction rate between vapor atoms and reactive gases [67].
Figure 4.6 Electron energy distribution of the hollow cathode plasma [51]. The square-shaped line represents the electron energy distribution function close to the cathode, which is described as Maxwell distribution superimposed by the directed LVEB. The solid line represents the electron energy distribution at a distance of 5-7 cm from the core of hollow cathode plasma in a longitudinal magnetic field.

In this study, a hollow cathode plasma (HCP) technique was employed between a source rod and a substrate, Figure 4.7. HCP currents between 60 A and 200 A can be adjusted with an external power supply. Argon is used as a working gas, and the emitted electrons from a heated hollow cathode create the argon plasma. In the PA-DVD approach, since vapor atoms entrapped by the supersonic He+N\(_2\) gas jet are carried through the argon plasma, emitted electrons and argon ions are able to ionize some of vapor atoms and He+N\(_2\) gas while simultaneously transferring higher thermal energy. In the plasma sheath, the ionized vapor atoms and gases are strongly attracted by the sheath
potential ($V_{ps}$), Figure 4.7. Furthermore, the low-vacuum environment of the PA-DVD system provides a high collision rate between vapor atoms and nitrogen, which might increase their reaction rate. Therefore, the use of HCP plasma activation can affect the growth mechanism of films, allowing film structures to be modified.

Figure 4.7 Schematic illustration of the plasma generation process. The hollow cathode (left) uses thermionic electron emission to create a low-voltage electron beam (LVEB) in the 0-25 eV range. These electrons are injected with an Ar gas jet into the deposition chamber through the end orifice of the hollow cathode toward the anode plate. A plasma consisting of electronically excited, ionized evaporants and working gas atoms/molecules is formed. If a negative potential is applied to the substrate, a plasma sheath is formed near the biased substrate and this sets up plasma sheath potential ($V_{ps}$), which draws the ion flux toward the deposition surface. Note that M: vapor molecules, M*: excited vapor molecules, and M$: ionized vapor molecules.
4.4 Substrate Bias Technique

Even though the HCP technique creates a dense argon plasma environment, LVEB-electrons are still thermalized, which prevents the generation of a sufficient floating potential near the substrate [60]. Previously, ion plating during the deposition process was used to modify film properties, such as film density, film adhesion, and film composition [71,72]. If a substrate bias is applied, then the ion current ($j_i$) of the substrate can be modified by [43]:

$$j_i = \frac{4}{9} \varepsilon_o \left( \frac{2e}{M_i} \right)^{1/2} \frac{(V_p - V_{sb})^{3/2}}{d_s^2},$$

(4-4)

where $M_i$ = Ion mass (for example, argon: 6.671×10^{-26} kg), $V_p$ = Plasma potential (V), $V_{sb}$ = Substrate bias potential (V), $\varepsilon_o$ = Dielectric constant (8.84×10^{-14} F/cm), and $d_s$ = Plasma sheath (mm).

As shown in Equation (4-4), if a negative bias is applied on the substrate, then the ion current of the substrate will increase. The increased current causes more ion bombardments of the growing film surface, which can manipulate surface morphology and composition. Mattox et al. used a planar dc diode sputtering approach to deposit tantalum [73]. When the negative substrate bias increased, it could modify film structures from columnar to dense structures. However, the negative substrate bias resulted in energetic ion bombardments, which increased a film stress and reduced the deposition rate. Furthermore, since energetic ion bombardments heat the substrate, they can enhance the atomic diffusional energy and chemical reactions.
Here the PA-DVD approach employs a substrate bias technique, which can provide either a constant potential or an alternating bias of ±200 V. As shown in Figure 4.7, while the supersonic He+N₂ gas jet carries neutral vapor atoms toward the substrate, the supersonic gas jet and the neutral vapor atoms pass through the argon plasma and are then ionized. If a negative bias is applied on the substrate, then ionized vapor atoms are strongly accelerated towards the substrate. On the other hand, ionized gases (such as Ar, He, and N₂) enhance the surface adatom mobility of vapor atoms and simultaneously sputter the growing film surface. The negative substrate bias can therefore modify properties of Lipon films.
Chapter 5

Film Analysis Methodologies

5.1 Overview

In this dissertation, lithium phosphorus oxynitride (Lipon) films were synthesized by the plasma-assisted directed vapor deposition (PA-DVD) approach. The analysis of Lipon films was carried out by various methods, including Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and Electrochemical Impedance Spectroscopy (EIS). This chapter presents the analysis methodologies of Lipon films.

5.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to investigate morphologies of Lipon films [74]. In this study, JEOL 6700 SEM was used to investigate surface morphologies and cross-sectional microstructures of Lipon films. Pd/Au was coated on Lipon films in order to avoid a charging effect on the film images. In order to take a cross-sectional image, Lipon films were mounted on a carbon epoxy and then mechanically polished by wet sand papers and alumina powders of 0.3 μm and 0.05 μm. Gatan Precision Etching
Coating System (PECS) etched the polished cross-sections with sputtering by an argon
ion gun because the mechanical polishing made the Lipon films smeared. The films were
finally coated with Pd/Au to prevent charging.

5.3 X-ray Diffraction

The crystallinity of Lipon films was measured by X-ray diffraction (XRD) [75]. In
order to measure XRD patterns of Lipon films, the 2θ angle was scanned and a
diffractometer, which has a CuKα1 radiation source of λ =1.5405 Å, was employed.

5.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was employed to determine the N/P ratio of
Lipon films and investigate the bond state of Lipon films [76]. Here, the Perkin-Elmer
560 system was employed to measure XPS spectra and the excitation source was the Al
Kα X-ray of 1486.6 eV. The survey scans were carried out from 1100 eV to 0.0 eV and
high-resolution scans were performed in the N1s, P2p, and C1s regions. Because the
charging effect of Lipon films shifted the peaks, C1s of 285 eV was taken as a reference
peak in order to correct a position of XPS spectra. The atomic fraction of each element is
determined by:

$$ C_x = \frac{I_x}{S_x} \left( \sum_{i=1}^{n} \frac{I_x}{S_x} \right)^{-1} $$

(5-1)

where Iᵢ is the peak intensity of XPS spectra and Sᵢ is the sensitivity factor of each
element, which was provided by Perkin-Elmer [77]. Atomic fraction is determined within
a ±10% error.
5.5 Inductively Coupled Plasma Optical Emission Spectroscopy

In general, a compositional analysis of Lipon films is very challenging when using conventional chemical analysis equipment, such as Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). EDS cannot detect lithium in Lipon films. Because the signals of XPS come from the surface (~2 nm thick) of samples, XPS cannot provide a bulk composition of Lipon films. Also, because the XPS sensitivity factor to lithium is very low, it induces inaccurate results. Previously, Dudney et al. employed proton-induced gamma ray emission (PIGE) spectroscopy and atomic spectroscopy (AS) in order to determine a lithium concentration in Lipon films [11]. They indicated that the PIGE spectroscopy was more reliable than the AS because the result of the AS was inconsistent.

In this study, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was employed to investigate a concentration of lithium and phosphorus [78]. This ICP-OES measures the intensity of lights that plasma-excited atoms or ions emit with a wavelength. The measured intensity of lights provides elemental concentrations in materials. In order to measure the concentration of Li and P, five standard samples were prepared from the Li$_3$PO$_4$ powder: that is, 40 mg/L, 20 mg/L, 10 mg/L, 5 mg/L, and 0.5 mg/L. They were completely dissolved by a solution of 20% HNO$_3$ and 80% Milli-Q water (~18.2 MΩ) at around 75±5°C. Also, Lipon films were dissolved using the same method as the standard samples. The ICP-OES measured Li and P concentrations in Lipon films. In ICP-OES, the peak position of Li and P was selected as a wavelength: that is, Li=610.365 nm and P=213.618 nm. The ICP-OES scanned intensities of the Li$_3$PO$_4$
powder standard samples at around the wavelength of Li and P and then similarly scanned the intensities of the Lipon samples. From the results of the Li$_3$PO$_4$ powder standard samples, the intensity versus the concentration of Li and P was plotted and fitted by a linear or quadratic equation. The fit results yielded a Li and P concentration of Lipon samples within ±5% error.

5.6 Fourier Transform Infrared Spectroscopy

Infrared light interacts with a material as it passes through materials. If the infrared frequencies are equal to the molecular vibrational frequencies of materials, then they are absorbed in materials and otherwise they are transmitted. In this manner, the infrared spectra can be obtained and nondestructively provides information about their chemical bond structures in a short-range order [79]. Molecular vibrations are unique physical properties of molecules in the material, allowing both amorphous and crystalline materials to be investigated by Fourier Transform Infrared (FTIR) spectrometry. In this study, a Nicolet Impact 400D spectrometer was employed to investigate the chemical bonds of Lipon films.

5.7 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was employed to measure the Li-ion conductivities of Lipon films [80,81]. The EIS technique provides information about the ionic motion in an ionic conductor by scanning a frequency of AC voltage. If a high-frequency AC voltage is applied to an ionic conductor sandwiched by an ion-blocking electrode (e.g., Gold or Platinum), ions cannot move across the interface. This is
attributed to an ion’s speed that is much slower than the speed of the AC voltage changing cycle. As the frequency of AC voltage is lowered, ions begin to move in the direction of the voltage drop. If AC voltage is in the low frequency range, then ions will stop moving at one of two interfaces between the ion conductor and the ion-blocking electrode, forming an interfacial capacitor. The EIS technique thus is useful to investigate the interfacial phenomena between materials and measure the ionic conductivity of materials. In this study, a metal/Lipon/metal test cell was prepared to obtain Li-ion conductivities. Since ion-blocking electrodes have a high charge transfer resistance, they should not undergo oxidation or reduction with a solid-state electrolyte. Here, gold was used as the ion-blocking electrode.

The EIS plot is conveniently represented in a complex plane along a frequency called the “Nyquist plot.” Alternatively, if the real and imaginary parts of impedance can be represented along a frequency axis, then this plot is called the “Bode plot.” If an AC voltage is applied into an electrochemical test cell as a function of frequency (ω) and the current is measured, then an impedance of the electrochemical test cell can be obtained. Here, AC voltage, V(t), and current, I(t), can be given by:

\[ V(t) = V_{\max} \cdot e^{j(\phi t - \theta)} \]  
\[ I(t) = I_{\max} \cdot e^{j(\phi \omega t - \theta)} \],  \hspace{1cm} (5-3)

where \( \theta \) is the phase difference and \( \omega \) is the angular frequency.

If V(t) is divided by I(t), impedance, Z(ω), is given by:

\[ |Z(\omega)| = \frac{V(t)}{I(t)} \].  \hspace{1cm} (5-4)

The real and imaginary parts of Z(ω) can be represented by:
Re \( (Z) = Z' = |Z| \cdot \cos \theta \) \quad (5-5)

Im \( (Z) = Z'' = |Z| \cdot \sin \theta \), \quad (5-6)

where \( |Z| = [(Z')^2 + (Z'')^2]^{1/2} \) and \( \theta = \tan^{-1}(Z'/Z'') \).

The impedance of solid-state electrolytes is typically measured in the \( 10^{-2}-10^4 \) Hz frequency range. The main factors contributing to an impedance of the solid-state electrolyte in a test cell are the impedance of the solid-state electrolyte and the interfacial impedance between the electrodes and the solid-state electrolyte. Figure 5.1 shows the impedance between an electrode and a solid-state electrolyte. The results fall into one of four cases:

**Case 1. A charge transfer process is very difficult at the interface between an electrode and a solid-state electrolyte, Figure 5.1 (a).**

A double layer capacitance \( (C_{dl}) \) determines the interfacial impedance between an electrode and a solid-state electrolyte. A small leakage current, which is shown as the resistance, \( R_1 \), can flow through a double layer capacitance and make impedance out of a \( 90^\circ \) angle.

**Case 2. A charge transfer process is allowed at the interface between an electrode and a solid-state electrolyte, Figure 5.1 (b).**

Because an interfacial reaction is occurred by thermal activation, impedance is represented as a semi-circle. If the impedance values are measured as a function of temperature, then an activation energy that generates a charge transfer process can be obtained.
Case 3. The reaction between an electrode and a solid-state electrolyte is governed by ion diffusion, Figure 5.1 (c).

Warburg impedance \((Z_W)\) represents ion diffusions at the interface between an electrode and a solid-state electrolyte and forms the 45° phase angle in an impedance plane. It is defined by:

\[
Z_W = D \cdot (j\omega)^{-1/2},
\]

(5-7)

where \(D\) is the diffusion coefficient of chemical species and \(\omega\) is an angular frequency.

Case 4. Impedance does not present a 45° phase angle, Figure 5.1 (d).

When impedance provides neither a 45° nor a 90° phase angle from the real impedance axis, physical interpretation is very complex. If the surface of samples is rough or an electrode forms an imperfect ion-blocking interface, then impedance might have out of 90°. In this case, impedance is given by:

\[
Z_i = K_n \cdot (j\omega)^n
\]

(5-8)

where \(0 < n < 1\) and \(K_n\) and \(n\) do not depend on the angular frequency, \(\omega\).

If Lipon test cells of Au/Lipon/Au are employed to obtain the Lipon resistance \((R_{\text{Lipon}})\) through an EIS measurement, they can be simply modeled by the combination of resistance and capacitance, Figure 5-2. Because gold is an ion-blocking electrode, the interface between the Lipon layer and the Au layer should form a pure capacitance. The geometrical capacitance \((C_g)\) is due to the gold electrodes that are deposited on both top and bottom sides of the Lipon layer. If the total impedance, \(Z(\omega)\), of the circuit is considered, it is given by [80]:
\[
Z(\omega) = R_{Au} + \left( \frac{1}{R_{Lipon} + j \cdot \omega \cdot C_g} \right)^{-1} + \frac{1}{j \cdot \omega \cdot C_{dl}}
\]

\[
= R_{Au} + \frac{R_{Lipon} - j \cdot \omega \cdot C_g \cdot R_{Lipon}}{1 + (\omega \cdot C_g \cdot R_{Lipon})^2} - \frac{j}{\omega \cdot C_{dl}}
\]

\[
= R_{Au} + \frac{R_{Lipon}}{1 + (\omega \cdot C_g \cdot R_{Lipon})^2} - j \left( \frac{\omega \cdot C_g \cdot R_{Lipon}}{1 + (\omega \cdot C_g \cdot R_{Lipon})^2} + \frac{1}{\omega \cdot C_{dl}} \right),
\]

(5-9)

where \( R_{Lipon} \) = Resistance of Lipon film,
\( R_{Au} \) = Resistance of Au,
\( C_g \) = Geometrical capacitance of Lipon cells, and
\( C_{dl} \) = Double layer capacitance between Au and Lipon films.

In equation (5-9), if \( \omega \) goes to infinity, then \( Z(\omega) \) approaches \( R_{Au} \). If \( \omega \) goes to zero, then the real part of \( Z(\omega) \) approaches \( R_{Au} + R_{Lipon} \) and the imaginary part of \( Z(\omega) \) approaches infinity. Thus \( Z(\omega) \) is theoretically plotted as shown in Figure 5.2. However, an experimental \( Z(\omega) \) plot usually has a depressed semicircular arc in a complex \( Z^* \) plane.

When the \( Z(\omega) \) plot forms a depressed semicircular arc, the empirical Cole-Cole equation is generally employed as [82]:

\[
Z(\omega) = R_\infty + \frac{R_o - R_\infty}{1 + (j \omega \tau)^n},
\]

(5-10)

where \( R_o \) = Resistance at low-frequency ranges (\( \Omega \)),
\( R_\infty \) = Resistance at high-frequency ranges (\( \Omega \)),
\( \tau = (R_o \cdot R_\infty) \times C \),
\( C \) = Capacitance (F), and
\( 0 \leq n \leq 1 \).
Because EIS spectra do not have a perfect arc and a $90^\circ$ angle against the $Z_{\text{real}}$ axis in the low-frequency ranges, the ideal circuit model of Figure 5.2 (a) cannot explain the EIS spectra. Thus, the distributed circuit element and the $Z_i$ circuit element have been typically employed together (Figure 5.2 (b)). Since the impedance fitting results determine each component and $R_e-R_\infty$ corresponds to $R_{\text{Lipon}}$, Li-ion conductivities, $\sigma_{\text{ionic}}$, can be calculated by:

$$\sigma_{\text{ionic}} = \frac{d}{R_{\text{Lipon}} \times A}, \quad (5-11)$$

where $d$ is the thickness of the Lipon film, $A$ is the area of the test cell, and $R_{\text{Lipon}}$ is the Lipon resistance deduced by the equation (5-10).
Figure 5.1 Various equivalent circuit impedance models and the complex impedance plane diagrams: (a) Ion blocking at the interface between an electrode and a solid-state electrolyte, i.e., a charge transfer process is very difficult. (b) Non-ion blocking at the interface between an electrode and a solid-state electrolyte, i.e., a charge transfer process is allowed. (c) Ion diffusion, i.e., a reaction between an electrode and a solid-state electrolyte is governed toward or from the interface due to ion diffusion. (d) Impedance forms neither a 45° nor a 90° phase angle.
Figure 5.2 Electrochemical impedance circuit model of Lipon films: (a) Ideal impedance circuit model and (b) Non-ideal impedance circuit model. Each abbreviation represents the following: $R_{\text{Lipon}}$ = Resistance of Lipon layer, $R_{\text{Au}}$ = Resistance of Au, $C_g$ = Geometrical capacitance of Lipon cell, $C_{\text{dl}}$ = Double layer capacitance between the Au layer and the Lipon layer, $D$ = Distributed circuit element for a depressed arc, and $Z_i$ = Impedance in low-frequency ranges.

In this study, either Au-coated silicon or stainless steel substrates were used to prepare the Lipon test cells. The Lipon test cells were prepared as shown in Figure 5.3 and the Au dots were prepared by a DC-diode sputtering method. As shown in Figure 5.3 (right), a nail scratched and made the circles around the Au dots. Because the scratched circles
isolate the Lipon films, during an EIS measurement, Li-ions can only transport through the isolated area of Lipon films. In other words, there is no Li-ion migration all over the Lipon area. Copper wires were attached to the Au dots using a silver paste. After the silver paste was hardened, a vacuum grade epoxy was applied on the Lipon test cells in order to prevent any environmental effects, such as moisture. It should be noted that these steps were performed in ambient environments.

In order to check the EIS measurement procedure, one of the previous Lipon cells was selected. The EIS spectra of the Lipon cell showed a different result at the low-frequency range (Figure 5.4 (a) and (b)), because the Lipon cell had reacted with air in the ambient environment. However, the EIS spectra of the Lipon cell had the same results at the high-frequency range, Figure 5.4 (c) and (d). Thus, if the EIS spectra are considered at the high-frequency range, then Li ions are mostly transported under the Au electrode and the Li-ion movement is negligible out of the Au dot. Furthermore, we checked whether or not EIS spectra come from Lipon films. For the EIS measurement, a vacuum grade epoxy covered the Lipon cell and the EIS spectra of the Lipon cell were measured at DC 0.0 V and DC 0.1 V. As shown in Figure 5.5, the circular data show the EIS spectra at DC 0.0 V and the triangles show the EIS spectra at DC 0.1 V. Since both EIS results were exactly matched, the resistance of the Lipon film did not change with the applied DC biases; otherwise, it changed with the DC biases. Thus, it was certain that they came from the Lipon film in the Lipon cell.
Figure 5.3 Preparation of a Lipon test cell for measuring electrochemical impedance spectroscopy. After a nail scratched the circles around gold dots, copper wires were welded on the gold dots using a silver paste and a vacuum grade epoxy covered the Lipon film, including the gold dots. As a substrate, either a stainless steel substrate or a gold-coated silicon substrate was used.
Figure 5.4 EIS spectra of a Lipon cell. In order to measure the impedance, a 50 mV AC potential was applied across the Lipon cell. The data shown as black dots was initially measured. Five month later, the circular data was measured. At the high-frequency range, the EIS spectra of the Lipon cell had the almost same results (broken circles in Figure (c) and (d)). The EIS spectra of the Lipon cell clearly indicate the different results at the low-frequency range (broken squares in Figure (a) and (b)) where the Lipon cell had a reaction in ambient environments.
Figure 5.5 EIS spectra of a Lipon cell at DC 0.0 V and DC 0.1 V. The EIS spectra were measured by using a 50 mV AC potential. DC 0.0 V and DC 0.1 V tests were performed to check whether or not the EIS signals came from the Lipon film. The black circles show DC 0.0 V and the triangles show DC 0.1 V.
Chapter 6

Effects of Plasma Current on Lithium Phosphorus Oxynitride Thin Films

6.1. Overview

The ion density of a hollow cathode created plasma depends upon the LWEB current (the plasma current). This chapter explores the effects of plasma current upon the properties of PA-DVD Lipon films. It investigates their structure, morphology, composition, and Li-ion conductivity. For a deposition experiment of Lipon films, a Li$_3$PO$_4$ source was evaporated using a high voltage e-beam, and the resulting vapor was entrained in a nitrogen-doped supersonic helium gas jet and deposited on a substrate. A hollow cathode was then used to create an argon plasma that enabled partial ionization of the Li$_3$PO$_4$ vapor and nitrogen just above the substrate surface. These modifications greatly increased the gas phase and surface reactivity and facilitated the synthesis and high-rate deposition of amorphous Lipon films with the N/P ratios between 0.39 and 1.49. Manipulation of the plasma-enhanced process conditions also enabled control of the pore morphology and significantly affected the ionic transport properties of these films. This enabled the synthesis of electrolyte films with Li-ion conductivities of the $10^{-7}$-$10^{-9}$ S/cm.
6.2. Experimental Setup

6.2.1. Film Deposition

Lipon films were synthesized from cold-pressed Li$_3$PO$_4$ source rods obtained by Plasmaterials Inc. USA, Figure 6.1. The source rods were white and were 1.3 cm in diameter and 3.8 cm long. Their densities were typically 60-80% of the theoretical density (2.54 g/cm$^3$). When high electron beam power density was used to melt the Li$_3$PO$_4$ rods, significant melt pool bubbling occurred and molten droplets were ejected from the surface and transported to the substrate. These became entrained in the films and led to pinholes in the Lipon films. To reduce this effect, the cold-pressed Li$_3$PO$_4$ source rods were sintered in air at around 900$^\circ$C for ~10 hours. Their densities were increased to within 95% of 2.54 g/cm$^3$ and their color changed from white to light yellow. An e-beam employed a spiral pattern to uniformly melt the Li$_3$PO$_4$ source rod, Figure 6.2(a). As shown in Figure 6.2(b), the Li$_3$PO$_4$ source rod was uniformly melted by the e-beam with the spiral pattern. A (100) silicon wafer was used as the substrate.

When the plasma was activated, the emitted electrons kept moving from the hollow cathode to the copper anode and then flowed into the current meter of the external power supply, Figure 6.3. In this way, the hollow cathode system forms a closed circuit during the PA-DVD deposition process. The plasma current was controlled by an external power supply and measured by a current meter in the external power supply. Table 6.1 shows the deposition conditions used for growth of Lipon films. These conditions were selected following a series of trial experiments. These began by establishing the base pressure
achievable with the pumping system. Before film deposition experiments were conducted, the initial chamber vacuum pressure was around $1.35 \times 10^{-2}$ Torr. When the He+N$_2$ gas jet was created at the gas flow rate at 2.5 slm, the working chamber pressure increased to around $5.7 \times 10^{-2}$ Torr. This corresponded to a pressure ratio ($P_d/P_u$) of 3.64 across the nozzle opening. However, this supersonic He+N$_2$ gas jet had a flow rate of 2.5 slm and was insufficient to significantly increase the deposition rate. After a series of experiments, Lipon films were finally synthesized with a higher He+N$_2$ gas flow rate of 5.0 slm at a working chamber pressure of around $9.75 \times 10^{-2}$ Torr and a pressure ratio ($P_d/P_u$) of 4.17. Using an e-beam power density of between 110.6 W/cm$^2$ and 165.8 W/cm$^2$, Lipon films were synthesized with the plasma assistance controlling the plasma current between 60 and 150 A, Table 6.1. The substrates were neither heated nor rotated.

![Figure 6.1 As-received Li$_3$PO$_4$ source rod used to synthesize Lipon films. As-received Li$_3$PO$_4$ source rods were sintered at ~900°C for 10 hours.](image)
Figure 6.2 Electron beam pattern and melt pool of a Li$_3$PO$_4$ source rod. In experiments, the spiral electron beam pattern was employed to uniformly melt the Li$_3$PO$_4$ source rod. The electron beam generated the spiral pattern with high beam scanning frequency of 100 kHz and was accelerated by the voltage of 70 kV. The electron beam current used here was in 2-3 mA, which corresponds to a power density range of 110.6-165.8 W/cm$^2$.

Table 6.1 Deposition conditions of Lipon films. The Lipon films were prepared on a (100) silicon substrate. The base chamber pressure was 1.35×10$^{-2}$ Torr. The upstream pressure (the chamber pressure), $P_u$, was 9.75×10$^{-2}$ Torr, and the downstream pressure, $P_d$, was 2.34×10$^{-2}$ Torr.

<table>
<thead>
<tr>
<th>Plasma current (A)</th>
<th>He + N$_2$ (slm)</th>
<th>Pressure ratio ($P_u/P_d$)</th>
<th>Deposition time (min)</th>
<th>Deposition rate (nm/min)</th>
</tr>
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<tbody>
<tr>
<td>0.0</td>
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<tr>
<td>60</td>
<td>5.0</td>
<td>4.17</td>
<td>10</td>
<td>175</td>
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</tbody>
</table>
Figure 6.3 Hollow cathode plasma activation of the PA-DVD approach. The hollow cathode was initially heated by a tungsten-heating coil and, due to thermionic electron emission, finally generated thermal electrons, which are low-voltage electron beams (LVEB) between 3 eV and 25 eV [67-70]. When LVEB was generated, argon gases were simultaneously introduced into the chamber through the hole of the hollow cathode and then ionized by the LVEB.

6.2.2. Film Characterization

Lipon films were characterized by several film analysis methods: X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Fourier Transform Infrared Spectroscopy (FTIR), and Electrochemical Impedance Spectroscopy (EIS). Detailed film analysis methods are described in Chapter 5.
6.2.3. Plasma Analysis

Ions or electrons in plasma can be attracted to a metallic probe depending on an applied voltage and generate ion or electron currents. As shown in Figure 6.4, the plasma current-voltage profile consists of three regions: the electron saturation region \((J_e \gg J_i)\), the electron retardation region \((J_e > J_i)\), and the ion saturation region \((J_i \gg J_e)\), Figure 6.4. Note that \(J_e\) is the electron current density and \(J_i\) is the ion current density. In the electron saturation region \((J_e \gg J_i)\), because a charge-collecting probe is positively biased over the plasma potential \((V_p)\), electrons are mostly attracted to the probe surface and saturated. In the electron retardation region \((J_e > J_i)\), because the probe potential is less than the \(V_p\), the probe attracts a small amount of electrons.

Here, in order to measure the voltage versus the current profile of hollow cathode plasma, a \((2 \times 2\ \text{cm}^2)\) stainless steel substrate was connected in series to an ammeter and a power supply, Figure 6.5. A boron nitride sheet covered the backside of the stainless steel substrate to block the plasma current flow. The voltage versus the current profile of the hollow cathode plasma was then manually measured by recording the power supply voltage and the ammeter indicated current flow.
Figure 6.4 Typical I-V characteristic of plasma. Here, $V_f$ is the floating potential, $V_p$ is the plasma potential, and $V_s$ is the substrate bias.

Figure 6.5 Setup for the measurement of voltage versus plasma current.
The plasma floating potential ($V_f$) is defined as the point where the ion current is equal to an electron current on a substrate. For the hollow cathode plasma used here, the $V_f$ was around -11.0 V, Figure 6.6. Previously, Schiller et al. measured the floating potential in the hollow cathode activated plasma [84]. They obtained -10.0 V, which was quite similar to the floating potential measured here. As shown in Figure 6.6, a substrate bias more positive than -11.0 V attracted more electrons than positive ions to the substrate and created the electron retardation region. On the other hand, a substrate bias of less than -11.0 V attracted more positive ions than electrons to the substrate leading to an ion saturation region. If the electron retardation region is considered, then the electron current exponentially increases with the substrate bias and the slope of the exponential region provides the electron temperature [85]. In the electron retardation region, the electron current density, $J_e$, is simply represented by [85]:

$$J_e = \frac{1}{4} e \cdot n_{es} \cdot \bar{u}_e \cdot e^{\frac{V_s - V_p}{T_e}}, \quad (6-6)$$

where $n_{es} =$ Electron density at plasma sheath edge (cm$^{-3}$),

$\bar{u}_e =$ Electron average velocity $(8eT_e/\pi m_e)^{1/2}$,

$V_s =$ Substrate bias (V),

$V_p =$ Plasma potential (V), and

$T_e =$ Electron temperature (V).

If logarithms are taken of equation (6-6):

$$\ln J_e = \ln \left( \frac{1}{4} e \cdot n_{es} \cdot \bar{u}_e \right) + \frac{V_s - V_p}{T_e} . \quad (6-7)$$

The equation (6-7) can be simply represented by:
\[ \ln J_e = \frac{V_{\text{p}}}{T_e} + C, \]  

(6-8)

where \( C = \ln \left( \frac{1}{4} e \cdot n_{\text{eq}} \cdot \bar{u}_e \right) - \frac{V_{\text{p}}}{T_e} \).

Thus, equation (6-8) shows that if the substrate current density is plotted by the logarithm and is linearly fitted, the slope provides the inverse electron temperature, \( 1/T_e \).

Figure 6.6 shows two slopes in the electron retardation region. The fitted slopes of \( 1/T_e \) were around 0.192 and 0.066, respectively. The electron energies generated by the hollow cathode plasma were around 5.2 eV and 15.2 eV.

Previously, Klagge et al. measured the electron energy created by the hollow cathode plasma [86]. The electron energy distribution range was between 0.0-25.0 eV. Because the hollow cathode plasma consisted of a Maxwellian distribution of the isotropic electrons and a superimposed group of directed electrons (the low-voltage electron beam (LVEB)), electron energy distribution had two peaks one around 3.5 eV and the LVEB peak at around 11.0 eV. The electron energies measured here exist in the range of the electron energy distribution measured by Klagge et al. [86].
Figure 6.6 Voltage versus current characteristics of hollow cathode plasma without carrier gas flow. The plasma floating potential was around -11.0 V. When the substrate was grounded, there was an electron current flow into the substrate.

In the PA-DVD approach, both elastic and inelastic collisions occurs between electrons and the vapor. The vapor can be considered slow moving compared to the velocity of the electrons [87]. If we simply assume that the vapor species are stationary with respect to the moving electron, then an elastic binary collision between the electron and vapor atoms transfers energy that is given by [87]:

\[
\frac{E_a}{E_e} = \frac{1}{2} \frac{M_a u_a^2}{m_e u_e^2} = \frac{4 m_e \cdot M_a}{(m_e + M_a)^2} \cos^2 \theta ,
\]

(6-10)

where \(E_a\) is either vapor or gas atom energy, \(E_e\) is electron energy, \(M_a\) is mass of either vapor or gas atoms (e.g. argon=6.63×10^{-26} kg), \(m_e\) is electron mass (9.1×10^{-31} kg), \(u_a\) is
vapor atom velocity (m/s), $u_e$ is electron velocity (m/s), and $\theta$ is the collision angle between electron and vapor atoms. Because $M_a >> m_e$, equation (6-10) approximately becomes:

$$\frac{E_a}{E_e} \approx \frac{4m_e}{M_a} \cos^2 \theta = \frac{4m_e}{M_a} \quad \text{(for } \cos \theta = 1). \quad (6-11)$$

Thus, because the $m_e/M_a$ mass ratio is usually very small, the electrons transfer very little kinetic energy to the vapor atoms by elastic collisions.

During inelastic collisions between a moving electron and a vapor atom or molecule, the total energy during the collision is conserved but the internal energy, $U$, of vapor atoms can be changed. The maximum fraction of the electron kinetic energy that can be transferred is given by [87]:

$$\frac{\Delta U}{E_e} = \frac{\Delta U}{\frac{1}{2} m_e u_e^2} = \frac{M_a}{m_e + M_a} \cos^2 \theta, \quad (6-12)$$

where $\Delta U$ is internal energy change of the impacted atom or molecule (eV), $M_a$ is mass of either vapor atom (or molecule) or gas (kg), $m_e$ is electron mass ($9.1 \times 10^{-31}$ kg), $u_e$ is electron velocity (m/s), and $\theta$ is the collision angle between the electron and vapor atoms. Again, since $M_a >> m_e$, the equation (6-12) can be approximated and become:

$$\frac{\Delta U}{E_e} \approx \cos^2 \theta = 1, \quad \text{(for } \cos \theta = 1). \quad (6-13)$$

During inelastic collisions, electrons can therefore transfer virtually all of their kinetic energy to the vapor species. In the PA-DVD plasma, the electron energies generated by the hollow cathode were between 5.2 eV and 15.2 eV and those in the LVEB component of the total electron flux could provide sufficient energy to dissociate nitrogen bond (~9.8
eV), ionize nitrogen atom (~14.54 eV) and transfer enough energy into vapor atoms where they can be ionized or dissociated.

When the DVD gas jet is not present, the hollow cathode plasma is formed by ionization of the argon working gas ejected from the cathode. If a floating substrate is placed near plasma, then electrons negatively charge the substrate surface because the velocity of electrons is faster than that of ions [87]. The negatively charged substrate surface attracts ions forming the plasma sheath. Also, plasma pre-sheath between plasma and the plasma sheath is formed. When ions are initially accelerated in the plasma pre-sheath to the plasma sheath edge, the ion velocity \( u_{is} \) at the plasma sheath edge can be estimated by Bohm sheath criterion, which is given by [87]:

\[
u_{is} \geq u_B = \left( \frac{e T_e}{M_i} \right),
\]

(6-14)

where \( u_B \) = Bohm velocity (m/s),

\( T_e = \) Electron temperature (V), and

\( M_i = \) Ion mass.

Equation (6-14) indicates that ions should have at least Bohm velocity, \( u_B \), at the plasma sheath edge. It can be converted into the energy \( E_{is} \) as follows:

\[
E_{is} = \frac{1}{2} M_i u_{is}^2 \geq \frac{1}{2} M_i u_B^2 = \frac{1}{2} e T_e
\]

(6-15)

\[
E_{is} \geq \frac{1}{2} e T_e.
\]

(6-16)

Thus, because the ion energy \( E_{is} \) at the sheath edge becomes half of the electron energy or is greater than half of the electron energy, the ion energy generated by the PA-DVD approach can be approximated to ~2.6 eV and ~7.6 eV.
In order to measure the substrate ion current density \( (J_s) \), a substrate bias of -20 V was applied and the \( J_s \) was monitored by an ammeter along the plasma current of 60-150 A, Figure 6.7. When argon gas only was used to form plasma (i.e., no DVD jet), the \( J_s \) slowly increased with the plasma current indicating a gradual linear increase in plasma density with electron current. When argon and the helium carrier gas jet (using a jet flow rate of 5.0 slm) were used together, the substrate ion-current density \( (J_s) \) increased much more rapidly and reached a value of ~12 mA/cm\(^2\) for a hollow cathode current of 150 A. The increased substrate ion current density indicates that the degree of helium and/or argon ionization increased with the plasma current when the DVD gas jet traversed the plasma.

![Figure 6.7 Substrate ion current density \( (J_s) \) in the plasma current ranges of 60-150 A.](image)

Here, a substrate bias of -20 V was used in order to collect only ions and monitor them along the plasma current.
6.3. Results and Discussion

6.3.1. DVD film Growth without Plasma Assistance

Figure 6.8 shows the surface and fractured cross-section of a Li$_3$PO$_4$ film deposited on a (100) Si substrate. Extensive networks of connected and isolated pores were present. The films were also extensively mud cracked through their entire film thickness. The pore volume fraction of this film was typical of refractory material DVD deposition under low vacuum pressure conditions [83] and arises from flux shadowing under severely restricted surface adatom mobility conditions [60,63].

Figure 6.8 Surface and cross-section of Li$_3$PO$_4$ film deposited without plasma activation. The surface indicated that the Li$_3$PO$_4$ film had “mud cracks,” and on the cross-section, the Li$_3$PO$_4$ film formed highly porous columnar structures.
The XPS results indicated that films grown using a Li$_3$PO$_4$ source and a He+N$_2$ gas jet without plasma assistance did not contain nitrogen, Figure 6.11. This showed that nitrogen was not ionized and did not react with the Li$_3$PO$_4$ vapor without plasma assistance. Also, the XRD pattern indicated that the Li$_3$PO$_4$ film was amorphous, Figure 6.9.

![Figure 6.9](image)

Figure 6.9 X-ray diffraction (XRD) pattern of Li$_3$PO$_4$ film synthesized without plasma assistance. One broad XRD peak indicates that the Li$_3$PO$_4$ films are amorphous.

Additionally, the crystalline properties of the films were conformed by measuring XRD patterns at zero and 45° angles, Figure 6.10. When XRD patterns of the Li$_3$PO$_4$ film were obtained without any tilt, they had just one broad peak in the 17-27° ranges. Also, when the XRD pattern of the Li$_3$PO$_4$ film was obtained with the 45° tilt angle, it had one broad peak in the same 2θ range. These results indicated that the Li$_3$PO$_4$ was isotropic and did not have a texture; thus, the film was amorphous.
Figure 6.10 Comparison of X-ray diffraction (XRD) patterns of Li$_3$PO$_4$ film synthesized without plasma assistance.

6.3.2. Plasma-Assisted Film Growth

a) Film Composition

The use of plasma assistance during the deposition of Li$_3$PO$_4$ resulted in the incorporation of nitrogen in the as-deposited films. Evidence of this can be seen in the appearance of a N$_{1s}$ peak at ~400.0 eV in the XPS spectrum shown in Figure 6.11. The voltage versus current measurements for the hollow cathode plasma used here indicated that electron energies were between 5.2 eV and 15.2 eV; in other words, the electrons generated by the hollow cathode can transfer high energy into vapor atoms and provide enough energy to ionize nitrogen (~14.54 eV). The N/P ratio measured by XPS for the Lipon films increased linearly with the plasma currents, Figure 6.12. The Li/P ratio of
these Lipon films decreased with the increase of plasma currents, Figure 6.13. As shown in later Figure 6.23, if the triply and doubly coordinated bond states of nitrogen are locally incorporated, then they can form a material with a composition of either Li$_2$PO$_3$N$_{0.33}$ or Li$_{2.5}$PO$_3$N$_{0.5}$. In both cases, nitrogen incorporation would then result in lithium deficiencies in the Lipon films. Previously, Rohrbach and Lunk indicated that an increase of plasma currents increases both electron density and electron energy [88]. In general, increased electron energy increases ion energy by inelastic collisions. Since the hollow cathode argon gas working jet has higher energy with an increase of the plasma current and its direction is perpendicular to the direction of the Li$_3$PO$_4$ vapor plume, the lithium deficiencies might also be enhanced by the (lateral) argon gas jet scattering of (light) Li atoms from the Li$_3$PO$_4$ vapor plume.

![XPS spectra](image)

Figure 6.11 XPS spectra of the Lipon films synthesized at a plasma current of (a) 0.0 A and (b) 60 A. The N$_{1s}$ peak shows that the use of plasma enabled doping nitrogen into Li$_3$PO$_4$. 
Figure 6.12 N/P ratio of Lipon films determined by XPS. Note that the error bar is ±10%.

Figure 6.13 Li/P ratio of Lipon films measured by ICP-OES. Note that the error bar represents ±5%.
b) Film Morphologies

Figure 6.14 shows surface images of Lipon films prepared by the PA-DVD approach. The Lipon films deposited using plasma assistance did not show cracks on their surface. These cracks are often associated with differential thermal contraction of the film and substrate. It therefore usually increases with a substrate temperature. This was much higher (190°C ±15°C) during the plasma-assisted depositions, so the disappearance of the cracks is either a result of a much higher in plane coating tensile strength or an effect of the increased ion energy whose impact with the film can reduce intrinsic tensile stresses or make them compressive [89].

Increasing the plasma current also significantly modified the surface morphologies of the Lipon films, Figure 6.14. When a plasma current of 60 A was used, the surface of the Lipon films was composed of intersecting features with a spiral pattern, Figure 6.14(a). Occasional pores were also present near intersections of these features. When the plasma current was increased to 90 A, the Lipon film became denser and smoother. The use of plasma current of 120 A and 150 A resulted in smooth films with no evidence of surface voids.
Figure 6.14 Surface images of the Lipon films deposited using a plasma current of (a) 60 A, (b) 90 A, (c) 120 A, and (d) 150 A. The surface changed from one covered with spiral patterns to a dense spiral-free surface as the plasma current was increased.

Compared to the Li₃PO₄ film, most of the Lipon films formed very dense film structures, Figure 6.15. At a plasma current of 60 A, the Lipon film had a dense columnar structure. A further increase of plasma currents resulted in columnar-free, dense Lipon films. The absence of intercolumnar “crack-like” pore in these films may have significantly improved the in plane tensile strength of the coatings contributing to the absence of mud-cracks.

The increase of plasma currents increased the probability of vapor and working gas
ionization. These ionized species can be accelerated across the plasma sheath and so increased the average kinetic and internal energies of the depositing species. The resulting densification of the film observed above might therefore be a consequence of enhanced atomic reassembly on the growth surface that increased as the plasma current was increased. When the plasma current was increased to 150 A, some pores were present at the interface between the silicon substrate and the Lipon film. These pores are highly undesirable since they can facilitate electrical shorting of a thin-film battery during the recharging cycle. It suggests the existence of an optimum plasma current for electrolyte film deposition.

Figure 6.15 Cross-sectional images of Lipon films deposited by a plasma current of (a) 60 A, (b) 90 A, (c) 120 A, and (d) 150 A. The Lipon films were changed from porous to dense along the plasma current; however, at 150 A, the pores were generated.
Furthermore, when the substrate was rotated with 5 rpm, Lipon films formed very smooth surface morphologies and did not have columnar structures, Figure 6.16. This result indicates that substrate rotation can significantly reduce geometrical vapor shadow effects during film growth and effectively remove the spiral morphologies of Lipon films.

![Image](a) Surface (5.0 rpm)  ![Image](b) Cross-section (5.0 rpm)

Figure 6.16 Surface and cross-section of Lipon film synthesized by substrate rotation. The Lipon film deposition was performed with the following conditions: plasma current of 60 A, nitrogen flux of $2.13 \times 10^{18}$ molecules/cm$^2$·s, and substrate rotation of 5.0 rpm.

c) Deposition Rates

When Li$_3$PO$_4$ film was deposited without the plasma assistance, its deposition rate was 175 nm/min. The Lipon films deposited with the plasma assistance had deposition rates of 9-128 nm/min, Table 6.2. This plasma assistance greatly reduced the deposition rates of Lipon films. However, these deposition rates of Lipon films are 4.5-64 times higher than those achieved by the RF-magnetron sputtering approach (~2 nm/min).
During film deposition, argon gases pass through the hole of the hollow cathode and then will be expanded into a sonic gas jet because of the pressure difference between the process chamber and the hollow cathode tube. Before vapor atoms arrive on the substrate surface, the argon gas jet disturbed vapor atoms out of the substrate, thereby reducing the deposition rate. Previously, Ferreira et al. calculated gas pressures in a hollow cathode tube [90]. The gas pressure, $P_c$, was represented by:

$$P_c = \frac{Q_M}{\pi \cdot R^2} \left( \frac{k \cdot T}{\gamma \cdot M_{\text{molecule}}} \right)^{1/2},$$  

(6-16)

where $Q_M$ is the mass flow rate through the hollow cathode, $R$ is the radius of the hollow cathode, $T$ is the gas temperature (K), $k$ is the specific gas constant (8.314 J-K$^{-1}$-mole$^{-1}$), $\gamma$ is the ratio of specific heats (5/3 for argon), and $M_{\text{molecule}}$ is the mass of the gas molecules.

If the argon gas flow rate through the hollow cathode was 0.1 slm, the argon mass flow rate ($Q_M$) become around 2.96×10$^{-6}$ kg/s. It should be noted that the mass of argon gas is 0.004 kg/mole and the radius of the hollow cathode is 0.002 m. Thus, equation (6-16) indicates that the plasma working gas pressure, $P_c$, in the hollow cathode tube is approximately 45.46 Pa. Since the chamber pressure, $P_d$, was 13 Pa, the pressure ratio, $P_c/P_d$, becomes 3.5. Using this pressure ratio and the equation (4-1), the Mach number, $M$, becomes 1.4. Thus, the speed of the hollow cathode argon gas jet as it exits the hollow cathode ($U_{Ar}$) is around 450.94 m/s, Equation (4-2). During the PA-DVD deposition experiment, the pressure ratio, $P_u/P_d$, was 4.17. The pressure ratio corresponds to a Mach number of 1.53 and equation (4-2) indicates that the speed of the carrier gas jet is around 1549 m/s. However, because the speed of the carrier gas jet is the speed at the nozzle exit and the carrier gas jet has multiple collisions with background gases, their speed will be
reduced near the plasma gas jet. Hass et al. simulated the speed of the carrier gas jet with Direct Simulation Monte Carlo (DSMC) method [91]. When the pressure ratio, \( P_u/P_d \), was 4.5, the speed of the carrier gas jet was in the range of 350-450 m/s. Thus, because the speed of the hollow cathode argon gas jet (450.94 m/s) was comparable to that of the carrier gas jet and also the argon gas jet transferred high momentum to helium gas jet (i.e., argon mass \( 6.63 \times 10^{-26} \) kg) is much higher than helium mass \( 6.64 \times 10^{-27} \) kg), the hollow cathode argon gas jet disturbed the helium carrier gas jet. This added a lateral component of flux scattering out vapor entraining of the DVD jet and reduced both the fraction of vapor deposited on the substrate and the deposition rates of the Lipon films grown with plasma assistance.

d) Film Structures

The XRD patterns of Lipon films grown with plasma assistance contained broad peaks, Figure 6.17, and are indicative of the Lipon films that were entirely amorphous. This is beneficial for applications of thin-film Li/Li-ion batteries because the ionic conductivity of amorphous films is generally more isotropic and higher than that of crystalline films [3,44]. In order to check further the crystalline property of the Lipon film, XRD patterns were measured with zero and 45° tilt angles, Figure 6.18. When XRD patterns of the Lipon film were obtained with the zero and 45° tilt angles, they also had just one broad peak, indicating that the Lipon film was amorphous.
Figure 6.17 X-ray diffraction (XRD) patterns of Lipon films synthesized along plasma currents of (a) 60 A, (b) 90 A, (c) 120 A, and (d) 150 A. In these XRD patterns, the Lipon films all had broad peaks, which are amorphous.

Figure 6.18 Comparison of X-ray diffraction (XRD) patterns of Lipon film synthesized with a plasma assistance of 60 A.
Fourier Transform Infrared Spectroscopy (FTIR) can provide information about the local bond structure of the films. \( \text{Li}_3\text{PO}_4 \) contains phosphorus and oxygen distributed in a tetrahedral framework that has four normal modes of vibration, Figure 6.19 [93,94]. Modes \( \nu_1 \) and \( \nu_3 \) represent symmetric and asymmetric stretches, respectively. Modes designated \( \nu_2 \) and \( \nu_4 \) represent bending (T\(_2\)) motions of the PO\(_4^{3-}\) tetrahedra. Molecular symmetry considerations indicate that only the T\(_2\) modes would be IR active and are triply degenerate. The vibrational modes and frequencies of the PO\(_4^{3-}\) tetrahedron are summarized in Table 6.2 [92-96].

![Diagram](image)

Figure 6.19 Vibrational modes of a tetrahedral molecule of the XY\(_4\) type. A\(_1\), E, and T\(_2\) represent molecular symmetry groups that can be found in the reference [79].
Table 6.2 Vibrational modes of $\text{PO}_4^{3-}$ observed by Raman and IR spectra of Li$_3$PO$_4$. The $\beta$ and $\gamma$ in front of Li$_3$PO$_4$ represents their crystal phases.

<table>
<thead>
<tr>
<th>PO$_4^{3-}$ vibrational mode</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$-Li$_3$PO$_4$</td>
</tr>
<tr>
<td></td>
<td>$\beta$-Li$_3$PO$_4$</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-Li$_3$PO$_4$</td>
</tr>
<tr>
<td>$\nu_1$(A$_1$)</td>
<td>925</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$\nu_2$(E)</td>
<td>490, 509, 519, 560</td>
</tr>
<tr>
<td></td>
<td>490, 521</td>
</tr>
<tr>
<td></td>
<td>496</td>
</tr>
<tr>
<td>$\nu_3$(T$_2$)</td>
<td>1024, 1035, 1049, 1063</td>
</tr>
<tr>
<td></td>
<td>1045</td>
</tr>
<tr>
<td></td>
<td>1036, 1071, 1153</td>
</tr>
<tr>
<td>$\nu_4$(T$_2$)</td>
<td>604, 609, 623, 629,</td>
</tr>
<tr>
<td></td>
<td>636, 666</td>
</tr>
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<td>592</td>
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<td>591, 605</td>
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<td>[95]</td>
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<tr>
<td></td>
<td>[96]</td>
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<td></td>
<td>[96]</td>
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</table>

Figure 6.20 shows the FTIR spectra of Lipon films synthesized by the PA-DVD approach. These studies provided that four IR peaks were mainly observed in Li$_3$PO$_4$ films: 1150 cm$^{-1}$, 1044 cm$^{-1}$, 929 cm$^{-1}$, and 580 cm$^{-1}$. When nitrogen was incorporated into Li$_3$PO$_4$, the vibrational mode of 1150 cm$^{-1}$ became broad and then disappeared. Also, the vibrational mode ($\nu_4$) of 580 cm$^{-1}$ became weak and disappeared because nitrogen created -N= or -N< linkages between the PO$_4^{3-}$ tetrahedral, which made the bending motions of PO$_4^{3-}$ difficult. The vibrational mode of $\sim$928 cm$^{-1}$ formed a weak shoulder as the plasma currents was increased. The FTIR spectra of the films all included the $\nu_3$ mode at the wavenumber of 1044 cm$^{-1}$. Because this mode is the dominant vibration mode in Li$_3$PO$_4$, the Lipon films form PO$_4^{3-}$ bonds in a short-range order.
Figure 6.20 FTIR transmittance spectra of the Lipon films deposited by a plasma current of (a) 0.0 A, (b) 60 A, (c) 90 A, (d) 120 A, and (e) 150 A.

The P-N peak position was calculated in phosphoramidates: ~738 cm\(^{-1}\) [93]. If a P-N stretch mode is considered as a diatomic oscillator, then its vibrational frequency (\(f\)) is given by:

\[
f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},
\]

where \(\mu\) is the reduced mass of phosphorus and nitrogen, and \(k\) is the force constant.

Here, the force constant (\(k\)) can be approximated by [97]:

\[
k \approx 1.67 \cdot n \cdot \left(\frac{x_P \cdot x_N}{d^3}\right)^{3/4} + 0.30,
\]

where \(x_P\) and \(x_N\) are the electronegativities (P=2.1, N=3.0, respectively), \(n\) is the bond order and \(d\) is the interatomic distance. The wavenumber, \(\nu\), is given by:

\[
\nu = \frac{f}{c}.
\]
where c is the light velocity \((3.0 \times 10^{10} \text{ cm/s})\). In a model-based study, Hassan Rabaa et al. calculated the P-N bond distance that was 1.53 Å in a crystalline Lipon [98]. This P-N bond distance corresponds to \(v=801.6 \text{ cm}^{-1}\), Equation (6-17)-(6-19). Experimentally, its peak position was inconsistent because it was observed between 789 cm\(^{-1}\) and 1102 cm\(^{-1}\) [92]. These experimental results may generate a peak overlap with phosphate materials and this peak overlaps have led to a difficulty in assigning the P-N vibrational mode.

Reidmeyer et al. suggested a possible way for nitrogen atoms to substitute for phosphorus atoms in NaPO\(_3\) [56]. As shown in Figure 6.21, when NaPO\(_3\) reacts with HN\(_3\), nitrogen atoms can possibly substitute for phosphorus atoms and form NO\(_3\) in NaPO\(_3\)\(_{x}\)N\(_x\). Similarly, if nitrogen atoms substitute for phosphorus atoms in Li\(_3\)PO\(_4\), then a strong N-O stretch of NO\(_3\) should appear at \(\sim 950 \text{ cm}^{-1}\) in the infrared absorption spectrum [99]. Figure 6.21 indicates that the IR spectra of the Lipon films did not have any N-O stretching vibration of NO\(_3\). Therefore, when the Lipon films were deposited, nitrogen did not substitute for phosphorus in Li\(_3\)PO\(_4\) films.
XPS spectra can be used to investigate how nitrogen was incorporated into Lipon films. The XPS $P_{2p}$ peaks of Lipon films were shifted from 134.1 eV to 132.8 eV as the plasma current was increased, Figure 6.22. Simple charged-shell models have been used to explain a binding energy chemical shift such as this. They indicate that the shift is approximately proportional to the change of charge on the atom of interest (i.e. phosphorus here) [100-102]. The binding energy chemical shift, $\Delta(BE_i)$, can be written:

$$\Delta(BE_i) = k \cdot \Delta q_i,$$

where $\Delta q_i$ is the change in the i-th atom’s charge and k is a proportionality constant. Brow and Pantano investigated silicon oxynitride thin films using XPS and found that nitrogen incorporation resulted in a binding energy chemical shift of phosphorus in the silicon oxynitride thin films [102]. Brow et al. also investigated sodium phosphorus oxynitride glasses, $\text{NaPO}_x\text{N}_y$ [103]. In their experiments, $P_{2p}$ XPS peaks were shifted from 134.8 eV to 133.9 eV with an increased nitrogen concentration. They attributed the XPS $P_{2p}$ chemical shift to the replacement of P-O bonds by P-N bonds, which changes
the charge distribution around phosphorus in their films. The same effect is believed to be responsible for the shift seen in the Lipon films here.

Figure 6.22 XPS $P_{2p}$ peak shifts of Lipon films. The vertical line shows the phosphorus binding energy of a Li$_3$PO$_4$ film (134.1 eV). The increase of plasma currents lowers the phosphorus binding energy of Lipon films.

Previously, Veprek et al. conducted XPS measurements and suggested that nitrogen was incorporated as both a doubly and triply coordinated state in amorphous phosphorus nitride [104]. Wang et al. investigated nitrided bulk Li$_3$PO$_4$ materials [59]. They also found strong evidence that two types of nitrogen bonds were incorporated into Li$_3$PO$_4$, as shown in Figure 6.23.
Figure 6.23 Illustration of nitrogen incorporations in a Lipon film.

Figure 6.24 indicates that the N$_{1s}$ XPS peak can be decomposed into two peaks: triply coordinated nitrogen (−N=(N$_t$)) and doubly coordinated nitrogen (−N<(N$_d$)). Similarly, other nitrogen XPS peaks were decomposed into the two nitrogen peaks. We observed that the average binding energy of the triply coordinated form was $\sim$397.3 eV, while that of the doubly coordinated structure was $\sim$398.5 eV. These results agree well with the binding energies observed by Veprek et al. [104]. Table 6.3 shows the ratio N$_t$/N$_d$ deduced from each of the films grown using plasma assistance. Increasing plasma currents reduced the N$_t$/N$_d$ ratio and was correlated with an increase of the N/P ratio of the films. It also should be noted that because the effective ionic radius of N$^{3-}$ (1.32 Å) is larger than that of O$^{2-}$ (1.24 Å), nitrogen substitution for oxygen is likely to induce a structural distortion of Li$_3$PO$_4$. Bates et al. suggested that increasing the triply bonded nitrogen concentration results in a higher Li-ion conductivity in Lipon films, because these triply coordinated nitrogen atoms induce larger structural distortions compared
with the doubly coordinated nitrogen atoms [105]. However, they did not provide any further supporting experimental data. In their experiments, nitrogen incorporation of \( \text{Li}_3\text{PO}_4 \) improved two properties; that is, Lipon films were not decomposed over 5.5 V in contact with a lithium anode and nitrogen incorporation increased the Li-ion conductivity up to \( \sim 10^6 \) S/cm [8,10]. These properties resulted in significant cyclic life extension (>10,000 discharge cycles) of their rechargeable thin-film lithium batteries [106].

Figure 6.24 Deconvolution of \( \text{N}_{1s} \) XPS spectra of a Lipon film prepared at a plasma current of 60 A.
Table 6.3 Ratio of nitrogen bonds in the Lipon films along the plasma currents.

<table>
<thead>
<tr>
<th>Plasma current (A)</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>−N&lt;−N=</td>
<td>1.65</td>
<td>1.57</td>
<td>0.73</td>
<td>0.72</td>
</tr>
<tr>
<td>N/P</td>
<td>0.39</td>
<td>0.92</td>
<td>0.99</td>
<td>1.49</td>
</tr>
</tbody>
</table>

The PA-DVD approach described above resulted in Lipon films with an N/P ratio range of 0.39-1.49. Yu et al. achieved an N/P ratio of 0.16-0.46 by RF-magnetron sputtering approach [10]. Dudney et al. used a cosputtering technique with Li₃PO₄ and Li₃N targets and achieved an N/P ratio of 1.2 [107]. Choi et al. also conducted RF-magnetron sputtering with a Li₃PO₄ target under a pure N₂ atmosphere and achieved an N/P ratio of 0.4-1.25 [108]. More recently, Harmon et al. were able to achieve an N/P ratio of 0.7-1.4 by the RF-magnetron sputtering approach [109]. The PA-DVD approach therefore appears capable of achieving nitrogen concentrations in Lipon films that are similar to those present in RF-sputtered material.

Day proposed that alkali metaphosphates (RPO₃, R=Li or Na) may contain a high nitrogen concentration [110]. As shown in Figure 6.25, a large amount of nitrogen can be incorporated into alkali metaphosphates: i.e., RPON₁₃₃ = 30.72 atomic percent of nitrogen. Similarly, if nitrogen atoms are incorporated into Li₃PO₄, then a large amount of nitrogen atoms can be incorporated into Li₃PO₄. In the PA-DVD approach, because the supersonic He+N₂ gas jet could entrain ionized nitrogen atoms and focus them towards a substrate, the reaction rate between evaporants and nitrogen increased in both a
vapor phase and on the substrate surface [60,111]. In this manner, it is possible to incorporate a large amount of nitrogen into Lipon films.

![Figure 6.25](image-url) Maximum nitrogen incorporation in alkali metaphosphates (RPO$_3$, R=Li, or Na). The alkali metaphosphorus oxynitrde has the composition of RPON$_{1.33}$ that includes the nitrogen atomic percent of 30.72 [110].

**e) Li-ion Conductivity**

The Li-ion conductivity of Lipon films has been deduced by electrochemical impedance spectroscopy (EIS) technique. Figure 6.26 shows the EIS spectra of Lipon films prepared by the PA-DVD approach. Table 6.4 shows the fitting parameters of the EIS spectra that were used to calculate Li-ion conductivities via the impedance circuit model. These conductivities are shown in Table 6.5. Li-ion conductivities of the Lipon films synthesized by the PA-DVD approach were in the range of 10$^{-7}$-10$^{-9}$ S/cm. The Lipon test cell prepared at the plasma current of 150 A had an electrical short because
either the Lipon film was not thick enough or the Lipon film had the pores, Figure 6.14 (d). The Li$_3$PO$_4$ films also generated an electrical short because they had a cracked porous structure. The Li-ion conductivities achieved using the PA-DVD approach were comparable to the values reported for films grown by the e-beam evaporation technique [13]. However, they were still lower than that of Lipon films prepared by the RF-magnetron sputtering approach [8,10].

Choi et al. reported that when Lipon films had a high nitrogen incorporation (that is, a composition near Li$_{2.971}$PO$_{1.875}$N$_{1.25}$), their Li-ion conductivities were the highest value of $\sigma_{\text{ionc}}=1.67\times10^{-6}$ S/cm [108]. However, Bates et al. reported that the Li-ion conductivity of their Lipon films was highest ($3.3\times10^{-6}$ S/cm) with a moderate nitrogen incorporation corresponding to an overall composition near Li$_{2.9}$PO$_{3.3}$N$_{0.36}$ [8,10]. Hamon et al. argued that the Li-ion conductivity of Lipon films depended upon the deposition parameters and deposition process equipment [109]. This may be connected to variations in the fraction of doubly and triply coordinated nitrogen in the Lipon films. The experimental relationship between nitrogen incorporation and Li-ion conductivity has yet to be resolved, in part because of the difficult of precisely determining the composition and coordination state. The work studied here indicates that the Li-ion conductivity achieved by the PA-DVD approach decreased with an increase of the plasma current even though the N/P ratio increased. This may be attributed to the decrease of Li/P ratio in the Lipon films, which increased with the plasma current, Figure 6.13.

Motivated by rechargeable thin-film battery applications, Park et al. synthesized Lipon
films with a reactive RF-magnetron sputtering approach and obtained Li-ion conductivities of $9.1 \times 10^{-7} - 7.2 \times 10^{-9}$ S/cm [112]. Using the Lipon films with these different Li-ion conductivities, they fabricated rechargeable thin-film lithium batteries. As shown in Figure 6.27, the Lipon films that had Li-ion conductivities of $9.1 \times 10^{-7}$ S/cm showed good charge-discharge properties required for rechargeable thin-film lithium batteries. The Lipon films that had Li-ion conductivities of $1.2 \times 10^{-8}$ S/cm also showed acceptable charge-discharge properties. However, the use of Lipon films with Li-ion conductivities of $7.2 \times 10^{-9}$ S/cm, resulted in rechargeable thin-film lithium batteries that suffered serious capacity losses. In the work reported here, Lipon films synthesized at the plasma current of 60-90 A had Li-ion conductivities between $10^{-7}$ S/cm and $10^{-8}$ S/cm and therefore appear well suited for applications as the electrolyte of rechargeable thin-film lithium batteries. Because of its high deposition rate capability, the PA-DVD approach might also potentially provide an economical deposition route for synthesizing Lipon films.
Figure 6.26 EIS spectra of Lipon films prepared by a plasma current of (a) 60 A, (b) 75 A, (c) 90 A, and (d) 120 A. The EIS spectra were measured in the 1-10^5 Hz range. In the impedance spectra, black solid dots are experimental data and black lines show a graph fitted by the impedance circuit model. Li-ion conductivities are determined by fitting results of the EIS spectra.
Table 6.4 Fitting parameters used to calculate the Li-ion conductivities of Lipon films prepared on stainless steel or gold-coated silicon substrates. Here, subscript letters are represented by: hf=high frequency, el=electrolyte, dl=double layer, and g=geometrical.

<table>
<thead>
<tr>
<th>Plasma current (A)</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>120</th>
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<td>R_hf (Ω)</td>
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<td>1300</td>
<td>600</td>
<td>500</td>
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<tr>
<td>n_el</td>
<td>0.76</td>
<td>0.8</td>
<td>0.7</td>
<td>0.65</td>
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<tr>
<td>Z_el (Ω)</td>
<td>3.7×10³</td>
<td>1.99×10⁴</td>
<td>2.5×10⁵</td>
<td>1.42×10⁵</td>
</tr>
<tr>
<td>C_g (F)</td>
<td>3.8×10⁻⁹</td>
<td>1.3×10⁻⁹</td>
<td>8.3×10⁻⁹</td>
<td>3.4×10⁻⁹</td>
</tr>
<tr>
<td>n_dl</td>
<td>0.87</td>
<td>0.78</td>
<td>0.62</td>
<td>0.65</td>
</tr>
<tr>
<td>C_dl (F)</td>
<td>2.5×10⁻⁸</td>
<td>2.8×10⁻⁸</td>
<td>3.0×10⁻⁷</td>
<td>1.2×10⁻⁷</td>
</tr>
</tbody>
</table>

Table 6.5 Li-ion conductivities of the Lipon films. Note that the thickness of the Lipon layers was measured by a thickness profiler meter.

<table>
<thead>
<tr>
<th>Plasma current (A)</th>
<th>σ_ionic (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>5.23×10⁻⁷</td>
</tr>
<tr>
<td>75</td>
<td>1.21×10⁻⁷</td>
</tr>
<tr>
<td>90</td>
<td>1.22×10⁻⁸</td>
</tr>
<tr>
<td>120</td>
<td>4.66×10⁻⁹</td>
</tr>
</tbody>
</table>
Figure 6.27 Charge-discharge curves of rechargeable thin-film lithium batteries. The rechargeable thin-film lithium batteries used the LiCoO$_2$ cathode and the lithium anode. As a solid-state electrolyte, Lipon films were used and their Li-ion conductivities were (a) $8.8-9.1 \times 10^{-7}$ S/cm, (b) $1.7-2.0 \times 10^{-8}$ S/cm, and (c) $7.2-7.5 \times 10^{-9}$ S/cm [112].
6.6 Summary

A plasma-assisted directed vapor deposition (PA-DVD) approach has been successfully used to synthesize lithium phosphorus oxynitride (Lipon) films. Using this PA-DVD approach, it has been possible to deposit Lipon films at rates of up to 60 times those reported for reactive RF-magnetron sputtering processes. The use of plasma during deposition facilitated significant microstructure control enabling the growth of porous, amorphous columnar, or dense amorphous Lipon structures with no detectable porosity or cracking. Modification of the plasma current could control the level of nitrogen incorporation into the Lipon films. However, it was accompanied by a reduction in lithium content as the N/P ratio approached 1.5. XPS P$_{2p}$ peak shift measurements indicated that nitrogen atoms substituted for oxygen atoms in Li$_3$PO$_4$. Analysis of the XPS nitrogen peaks indicates the existence of both triply and doubly coordinated nitrogen. The PA-DVD approach resulted in Lipon films with Li-ion conductivities in the 10$^{-7}$-10$^{-9}$ S/cm range at room temperature. The Li-ion conductivities decreased with an increase of plasma current, because the increase of plasma current resulted in lithium losses in the Lipon films.
Chapter 7

Effects of Nitrogen Gas Flux on Lithium Phosphorus Oxynitride Thin Films

7.1 Overview

Chapter 6 has shown that significant changes to the composition and properties of lithium phosphorus oxynitride (Lipon) films occur when the DVD process is plasma activated. During the PA-DVD process, the plasma current significantly effected the film composition and ionic conductivity. Here, the effects of varying a partially ionized, incident nitrogen flux upon the composition, structure and ionic conductivity of Lipon films has been investigated. The films were grown from a lithium phosphate source using the same plasma-assisted directed vapor deposition (PA-DVD) approach described earlier. A high-voltage electron beam is used to vaporize a Li$_3$PO$_4$ source, and a supersonic He+\text{N}_2$ mixture gas jet transported the vapor to a substrate. A hollow cathode technique was used here to then create an argon plasma just above the substrate. This sufficiently ionized the nitrogen to allow its incorporation into the Li$_3$PO$_4$ film, forming a lithium phosphorus oxynitride film. The experimental results reported here indicate that the nitrogen concentration significantly affects the deposition rates of the films as well as
their surface morphology, pore distribution, nitrogen concentration and Li-ion conductivity.

7.2 Experimental Setup

7.2.1 Film Deposition Procedures

The PA-DVD approach utilizes an electron beam evaporation process to create a Li$_3$PO$_4$ evaporant. For the experiments conducted here, a 1.3 cm in diameter cold-pressed Li$_3$PO$_4$ source rod (PLASMATERIALS, INC. (CA, USA)) was used for evaporation. An e-beam power density of ~110.6 W/cm$^2$ was used to create Li$_3$PO$_4$ vapor atoms. The Li$_3$PO$_4$ evaporation rate was estimated by weighing the Li$_3$PO$_4$ source material before and after a timed evaporation run. For the incident power density used here, the fixed Li$_3$PO$_4$ source evaporation rate was ~2.05×10$^{-4}$ g/s for all of the experiments reported here. The circular area over which the Li$_3$PO$_4$ vapor deposition occurred (at a source to substrate distance of 22 cm) was approximately 104 cm$^2$. If the source evaporation rate is divided by the formula mass of Li$_3$PO$_4$ (~115.77 g/mole) and the circular area, then the average incident Li$_3$PO$_4$ molecular flux was approximately 1.02×10$^{16}$ molecules/cm$^2$⋅s for the source-substrate position used here. The Lipon films were grown using the nitrogen fraction in the supersonic helium gas jet that varied from 0.0 to 0.25. The total He+N$_2$ gas flux was held constant at ~2.14×10$^{19}$ molecules/cm$^2$⋅s. The nitrogen molecular flux component in the jet therefore varied from 0-4.28×10$^{18}$ molecules/cm$^2$⋅s.
Prior to each growth experiment, the deposition chamber was evacuated to a base pressure of $1.35 \times 10^{-2}$ Torr. During the deposition process, this rose to $9.0-9.75 \times 10^{-2}$ Torr. When the nitrogen fraction in the supersonic helium gas jet was increased, the density of the nitrogen-doped helium gas increased in the compartment under the nozzle, which resulted in an increase in the upstream pressure ($P_u$). This increased the $P_d/P_u$ ratio from 3.33 to 4.42. The Lipon films were all grown at a substrate temperature of $\sim 180 \pm 20^\circ$C. A silicon wafer and a stainless steel were used as the substrate.

When a hollow cathode source is heated, its emitted thermionic electrons can be accelerated forming a low-voltage electron beam (LVEB). Previous study indicated that the use of a hollow cathode electron beam with an energy in the range of 5-15 eV is sufficient to ionize both molecules of the evaporant and the nitrogen and enhance their reactivity [67]. For the experiments conducted here, the hollow cathode utilized an argon working gas (i.e., 0.1 slm) to form the initial plasma, Figure 4.2. The plasma forming gas jet and coaxial LVEB were perpendicular to the nitrogen-doped helium gas jet just below the substrate. The nitrogen flux was controlled in the range of $0.0-4.28 \times 10^{18}$ molecules/cm$^2$/s, while keeping the total 5.0 slm for He+N$_2$ gas constant. A substrate bias of $-20$ V was applied so that only positive ions were attracted towards the substrate. The substrate ion current density ($J_s$) was roughly estimated from the substrate ion current. It should be noted that numerous ionized species contributed to ion currents. The detailed measurements of the substrate ion currents are given in Chapter 6. As shown in Figure 7.1, the substrate ion current density increased linearly from $3.89 \times 10^{-4}$ A/cm$^2$ to $5.41 \times 10^{-}$
4 A/cm² as the nitrogen flux in the gas jet was increased. This corresponded to an ion flux (that is, ions/cm²-s). This experiment shows that the nitrogen addition generated more ionized nitrogen atoms colliding with Li₃PO₄ vapor more frequently and transferring more kinetic energy to them.

7.2.2 Film Characterizations

The Lipon films were characterized using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and Electrochemical Impedance Spectroscopy (EIS). Further detailed film analysis methods are explained in Chapter 5. Scanning Electron Microscopy (SEM) was used to determine the deposition rates of Lipon films and then deposition rates of all the films (by dividing the Lipon film thickness by the film deposition time).

7.2.3 Film Deposition Rates

The deposition rate was initially decreased and then gradually increased from 112.7 nm/min to 177.7 nm/min with the increase of nitrogen flux (Table 7.2). During the plasma-assisted deposition process, the direction of vapor transport was geometrically perpendicular to that of the argon plasma jet created by the hollow cathode technique. The initial decrease in deposition rate appears to be consequence of lateral deflection of the light vapor molecules by the argon jet used to create the plasma [60]. The increase of the deposition rate is attributed to the increase of the nitrogen flux in the supersonic helium gas jet. Since the increase of nitrogen in the supersonic helium gas jet increased
the $P_u/P_d$ ratio, it reduced the lateral spreading of the Li$_3$PO$_4$ vapor plume and, subsequently, more Li$_3$PO$_4$ vapor was focused towards the substrate (Table 7.1). The highest deposition rate was over 60 times higher than that reported for the RF-magnetron sputtering ($\sim$2 nm/min).

Table 7.1 Deposition conditions of Lipon films prepared by a total He+N$_2$ gas flow of 5.0 slm. Chamber vacuum pressure was $1.35 \times 10^{-2}$ Torr. Note that $P_d$ is the downstream pressure, $P_u$ is the upstream pressure, and source-plasma distance was 12 cm.

<table>
<thead>
<tr>
<th>Nitrogen (slm)</th>
<th>Plasma current (A)</th>
<th>Nitrogen (molecules/cm$^2$-s)</th>
<th>Pressure ratio ($P_u/P_d$)</th>
<th>Deposition time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>3.33</td>
<td>10</td>
</tr>
<tr>
<td>0.25</td>
<td></td>
<td>1.07×10$^{18}$</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>60</td>
<td>2.13×10$^{18}$</td>
<td>4.17</td>
<td>30</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>4.28×10$^{18}$</td>
<td>4.42</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2 Deposition rates of Lipon films. Here, the argon plasma was not activated without the nitrogen flux.

<table>
<thead>
<tr>
<th>Nitrogen (molecules/cm$^2$-s)</th>
<th>Film thickness (µm)</th>
<th>Deposition rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.75</td>
<td>175.0</td>
</tr>
<tr>
<td>1.07×10$^{18}$</td>
<td>3.38</td>
<td>112.7</td>
</tr>
<tr>
<td>2.13×10$^{18}$</td>
<td>3.84</td>
<td>128.0</td>
</tr>
<tr>
<td>4.28×10$^{18}$</td>
<td>5.33</td>
<td>177.7</td>
</tr>
</tbody>
</table>
Figure 7.1 Substrate current density ($J_s$) as a function of nitrogen flux transported by the gas jet. The hollow cathode current was 60 A and the total He+N$_2$ gas flux was held constant at $2.14 \times 10^{19}$ molecules/cm$^2$-s.

7.3 Results and Discussion

7.3.1. Film Morphologies

Figures 7.2 (a) shows the surface morphology and figure 7.3 (a) the cross-section of a Li$_3$PO$_4$ film evaporated on a silicon substrate without plasma assistance. It contained no detectable nitrogen. The Li$_3$PO$_4$ film surface contained intercolumnar porosity, and the cross-section of the film contained many pores some of which traversed almost the entire film’s thickness, Figure 7.3 (a). Using a Kinetic Monte Carlo (KMC) simulation approach, Yang et al. also showed that highly porous, columnar structures such as this are
formed when vapor atoms have a low incident energy of ~0.1 eV and the substrate temperature is low [113]. These conditions were present here and the pore structures are typical of films deposited under low surface atomic mobility conditions from fluxes that are subjected to self-shadowing by a rough growth surface [60,114,115].

When the plasma was activated with a plasma current ($I_{HC}$) of 60 A, nitrogen was incorporated in the Li$_3$PO$_4$ and Lipon films were formed. Figure 7.1 (b) and (c) show that the growth surface had a spiral surface morphology when the nitrogen flux was in the range of $1.0-2.1 \times 10^{18}$ molecules/cm$^2$-$s$. However, this spiral morphology disappeared as the nitrogen flux was increased to $4.3 \times 10^{18}$ molecules/cm$^2$-$s$. None of the Lipon films contained surface-breaking cracks.

As shown in Figure 7.2 (b), (c) and (d), the cross-sectional microstructures of the Lipon films changed from a porous columnar to a dense columnar structure as the nitrogen flux was increased. For a nitrogen flux of $1.1 \times 10^{18}$ molecules/cm$^2$-$s$, pores were located at intercolumnar boundaries. It was well known that pores of films are usually generated by a limited atomic mobility, a shadowing effect, and the incident angle of vapors [114,115]. As shown in Figure 7.3, because more ionized nitrogen atoms were generated by the nitrogen addition, they collided with Li$_3$PO$_4$ vapor more frequently and transferred more kinetic energy to them. Increasing the nitrogen flux therefore reduced the pore fraction in these Lipon films.
Figure 7.2 Surface morphologies of the Lipon films synthesized using various nitrogen fluxes in the gas jet. Figure 7.1 (a) was deposited without plasma assistance or nitrogen doping. Figure 7.1 (b)-(d) show deposited using a plasma current of 60 A.
Figure 7.3 Cross-sections of Lipon films synthesized by a nitrogen flux of (a) 0.0 molecules/cm\(^2\)⋅s, (b) \(1.07\times10^{18}\) molecules/cm\(^2\)⋅s (c) \(2.13\times10^{18}\) molecules/cm\(^2\)⋅s, and d) \(4.28\times10^{18}\) molecules/cm\(^2\)⋅s.

7.3.2. Film Compositions

Figure 7.4 shows XPS spectra for both Li\(_3\)PO\(_4\) and a Lipon film. The appearance of a nitrogen peak was clearly evident at an energy of \(~400\) eV when plasma assistance was used, Figure 7.4 (b). The electron energies generated by the hollow cathode were in the range of 5-15 eV, which is sufficient to dissociate nitrogen bonds (\(~9.8\) eV) and ionize nitrogen (14.53 eV). This activation clearly led to the nitrogen incorporation into a Li\(_3\)PO\(_4\) films.

As the nitrogen flux increased, the N/P ratio increased to a value of 0.75, Figure 7.5. This arose because ionized nitrogen increased with nitrogen flux, Figure 7.3. The Li/P ratio initially increased with increasing nitrogen flux but then decreased above a flux of \(2.1\times10^{18}\) molecules/cm\(^2\)⋅s, Figure 7.6. The initial rise is thought to be a consequence of an increase in \(P_d\) (and this the \(P_d/P_d\) ratio) as nitrogen was added to the supersonic helium
gas jet. The jet speed then increases (with the pressure ratio) and this enhances entrainment of Li$_3$PO$_4$ vapor atoms in the jet plume (see Equations (4-1) and (4-2)). This effect was eventually compensated by the increase in activated nitrogen in the gas jet. This led to an increase in the N/P ratio and therefore reduced the Li/P ratio in the Lipon films [104].

![XPS spectra of Lipon films prepared by plasma assistance](image)

Figure 7.4 XPS spectra of Lipon films prepared by plasma assistance, *i.e.* (a) No plasma, (b) 60 A, N$_2$: 4.28×10$^{18}$ molecule/cm$^2$·s.
Figure 7.5 N/P ratio of Lipon films as a function of the gas jet. The N/P ratio was obtained by XPS and the error bars were ±10% of the N/P ratio.

Figure 7.6 Li/P ratio of Lipon films as a function of the nitrogen flux in the helium gas jet. The Li/P ratio was determined by ICP-OES. The error bar shows ±5% of the Li/P ratio.
7.3.3. Film Structures

Amorphous films are generally preferred as thin-film electrolytes because they have a more isotropic and higher ionic conductivity than equivalent composition crystalline films [3,44]. They are also preferred because they do not require an annealing (crystallization) step, which can be problematic for multi-layer structures. The structures of the films deposited here were investigated by XRD patterns for each film as shown in Figure 7.7. The XRD data for most films contained no sharp diffraction peaks. They are therefore indicative of an amorphous structure. However, as the nitrogen flux was increased to $4.28 \times 10^{18}$ molecules/cm$^2$·s, weak crystalline peaks began to be observed in addition to the diffuse scattering associated with amorphous structures. The positions of these weak crystalline peaks are consistent with the presence of the $\gamma$-Li$_3$PO$_4$ crystalline phase [116, 117]. They suggest the existence of local crystalline phases that may have been formed by an increased growth surface mobility associated with a high incident energetic ion flux.

Figure 7.8 shows FTIR spectra of Lipon films. In literature, Li$_3$PO$_4$ had four vibrational modes of PO$_4^{3-}$: that is, $\nu_1$ (925 cm$^{-1}$), $\nu_2$ (496 cm$^{-1}$), $\nu_3$ (1036 cm$^{-1}$, 1071 cm$^{-1$} and 1153 cm$^{-1}$), and $\nu_4$ (591 cm$^{-1}$) [92-96]. The $\nu_1$ and $\nu_3$ modes are symmetric and asymmetric stretching modes, respectively. The $\nu_2$ and $\nu_4$ modes represent molecular bending motions. As shown in Figure 7.8, Li$_3$PO$_4$ had three vibrational modes: that is, $\nu_1$ (925 cm$^{-1}$), $\nu_3$ (1044 cm$^{-1}$ and 1150 cm$^{-1}$), and $\nu_4$ (590 cm$^{-1}$). By adding nitrogen, one of $\nu_3$ modes, 1150 cm$^{-1}$, disappeared and the $\nu_1$ mode decreased to a weak shoulder. Because the $\nu_3$ mode of 1040 cm$^{-1}$ was the main vibrational mode of PO$_4^{3-}$ and existed
regardless of the nitrogen incorporation, it indicated that Lipon films formed the chemical bond structure of Li$_3$PO$_4$. A theoretical calculation indicated that the P-N stretch mode was $\sim$736 cm$^{-1}$ [93]. However, because its vibrational peak position was experimentally found in the 789-1102 cm$^{-1}$ range, the P-N stretch mode resulted in a peak overlap with phosphate materials, which caused a difficulty in assigning the P-N stretch mode [92].

Figure 7.7 X-ray diffraction patterns of Lipon films synthesized using gas jets with the different nitrogen fluxes. The curve marked (a) used a pure He jet and no plasma assistance. The other curves show the effect of increasing the N$_2$ flux within the gas jet from 1.07 molecules/cm$^2$·s to $4.28 \times 10^{18}$ molecules/cm$^2$·s at $I_{HC} = 60$ A. The XRD patterns indicate that Lipon films grown using low N$_2$ flux were amorphous. However, the film grown using the highest N$_2$ flux contained regions of crystalline material.
Figure 7.8 FTIR transmission spectra of the Lipon films prepared by a nitrogen gas flux of (a) 0.0 molecules/cm$^2$⋅s, (b) 1.07×10$^{18}$ molecules/cm$^2$⋅s, (c) 2.13×10$^{18}$ molecules/cm$^2$⋅s, and (d) 4.28×10$^{18}$ molecules/cm$^2$⋅s.

When nitrogen substitutes for oxygen in Li$_3$PO$_4$, the charge on the phosphorus ions changes [100]. Consequently, there will be a shift in binding energy (BE), which is approximately proportional to the charge change on anion [100-102]. The binding energy chemical shift, $\Delta$(BE$_i$), is given by:

$$\Delta$(BE$_i$) = k \cdot \Delta q_i,$$

(7-1)

where $\Delta q_i$ is the change in the atom’s charge and k is a proportionality constant. XPS technique can therefore be used to determine the nitrogen coordination state in an as-deposited film and enable an investigation of the inter-atomic structure.
Brow and Pantano investigated silicon oxynitride thin films with XPS and found that the nitrogen incorporation resulted in the binding energy chemical shift of phosphorus in the silicon oxynitride thin films [102]. Brow et al. investigated sodium phosphorus oxynitride glasses, NaPO$_x$N$_y$ type compound [103]. They observed that P$_{2p}$ XPS peaks were shifted from 134.8 eV to 133.9 eV with the nitrogen incorporation. This reduction in the P$_{2p}$ binding energy arises because P-O bonds are replaced by P-N bonds. Figure 7.9 shows that when nitrogen was added to the helium gas jet, the XPS P$_{2p}$ peaks of Lipon films were similarly shifted from 134.1 eV to 133.34 eV. This result is consistent with nitrogen replacing oxygen in the Li$_3$PO$_4$ film and consistent with the increase of the N/P ratio in the films, Figure 7.5.

It is well known that nitrogen could be incorporated into Li$_3$PO$_4$ in either a doubly or triply coordinated manner [57,59,104]. When nitrogen atoms of either the doubly (N$_d$) or triply (N$_t$) coordinated states are incorporated into Li$_3$PO$_4$ films, they link PO$_4$ tetrahedra in the Li$_3$PO$_4$ structure [57]. Also, because the atomic radius of nitrogen atoms (1.32 Å) is larger than that of oxygen atoms (1.24 Å), nitrogen atoms caused a structural distortion of Li$_3$PO$_4$. When the nitrogen XPS peaks of the films were decomposed, components arising from both doubly and triply coordinated nitrogen could be identified, Figure 7.10. It was found that the average binding energies of the triply coordinate structure was ~397.3 eV while that of the doubly coordinated structure was ~398.5 eV, Figure 7.10. As shown in Table 7.3, as the ratio of the number of triply to doubly coordinated nitrogen states (N$_t$/N$_d$) increased, the N/P ratio increased (i.e., the fraction of triply coordinated nitrogen in the films increased with the increase in N/P ratio).
Figure 7.9 XPS P$_{2p}$ peak shift for a lithium phosphate film (a) and Lipon films synthesized using gas jets containing a nitrogen dimmer flux of (b) $1.07 \times 10^{18}$ molecules/cm$^2$·s, (c) $2.13 \times 10^{18}$ molecules/cm$^2$·s, and (d) $4.28 \times 10^{18}$ molecules/cm$^2$·s. The vertical line shows the phosphorus binding energy of the Li$_3$PO$_4$ film (134.1 eV). Increasing the nitrogen flux in the helium gas jet lowers the phosphorus binding energy of Lipon films.
Figure 7.10 Components of the N\textsubscript{1s} XPS spectrum for a Lipon film synthesized using a gas jet with a nitrogen flux of $4.28 \times 10^{18}$ molecules/cm\textsuperscript{2}\cdot s. The asymmetric nitrogen peak can be decomposed into two peaks: one corresponds with triply coordinated nitrogen ($N_t$) and the other a doubly coordinated form of nitrogen ($N_d$).

<table>
<thead>
<tr>
<th>Nitrogen flux (molecules/cm\textsuperscript{2}\cdot s)</th>
<th>Ratio of bond states</th>
<th>N/P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.07 \times 10^{18}$</td>
<td>0.525</td>
<td>0.13</td>
</tr>
<tr>
<td>$2.13 \times 10^{18}$</td>
<td>1.706</td>
<td>0.39</td>
</tr>
<tr>
<td>$4.28 \times 10^{18}$</td>
<td>1.205</td>
<td>0.75</td>
</tr>
</tbody>
</table>
7.3.4. Li-ion Conductivity

Using stainless steel/Lipon/Au cells, Li-ion conductivities of Lipon films were determined by electrochemical impedance spectroscopy (EIS). The complex impedance was measured over the 1-10^5 Hz frequency range at 0.1 logarithmic increments. The real and imaginary components are plotted in Figure 7.11. The data were fitted to the Cole-Cole equation to deduce the film resistance, R_{Lipon} [82]. Because the interface between the Au layer and Lipon film was neither a perfect ion-blocking electrode nor ideally smooth, EIS spectra usually do not exhibit a pure capacitive response at low frequency (the EIS spectra do not meet the real impedance axis at a 90°) [80]. In view of this, an interfacial impedance, \( Z_i = C_{dl} \cdot (j \cdot \omega)^{-n} \), was introduced into the Cole analysis to characterize the low frequency response. The Li-ion resistance was then used to find the conductivity, \( \sigma_{\text{ionic}} \), using the relation:

\[
\sigma_{\text{ionic}} = \frac{d}{R_{\text{Lipon}} \times A}, \tag{7-2}
\]

where \( d \) is the thickness of the Lipon film, \( A \) is the overlapped area of the Au layers, and \( R_{\text{Lipon}} \) is the Lipon film resistance deduced by fitting to the modified Cole-Cole model. These data are summarized in Table 7.4. A detailed description of this analysis is given in Chapter 5.

The Li-ion conductivities of the Lipon films are summarized in Table 7.5. The films were all prepared with plasma assistance since those grown without plasma assistance suffered from electrical shorts due to their porous and cracked film structure, Figure 7.2 (a). The \( \text{Li}_3\text{PO}_4 \) film made in this way had a Li-ion conductivity of \( 3.65 \times 10^{-9} \) S/cm. When nitrogen was incorporated in the films, Li-ion conductivities increased into \( 10^{-7} \)-
$10^{-8}$ S/cm range, Table 7.5. These results indicate that the nitrogen incorporation into Li$_3$PO$_4$ makes 10-100 times higher Li-ion conductivities than those of Li$_3$PO$_4$ films. The highest Li-ion conductivities in Table 7.5 are comparable to those reported for Lipon films synthesized by the e-beam evaporation approach [15].

The data in Table 7.5 indicate that the Li-ion conductivity increased monotonically from $3.65 \times 10^{-9}$ S/cm to $5.24 \times 10^{-7}$ S/cm as the nitrogen concentration increased in the gas jet. This can be understood by recalling the relationships between structural change and nitrogen incorporation. Because the atomic radius of nitrogen atoms (1.32 Å) is larger than that of oxygen atoms (1.24 Å), incorporation of nitrogen atoms causes a structural distortion. Wang et al. investigated the structure of bulk polycrystalline Lipon by X-ray diffraction and neutron diffraction [59]. They observed that nitrogen incorporation in Li$_3$PO$_4$ increased the average Li-O bond distances. Because the binding energy between lithium and oxygen is inversely proportional to the Li-O bond distance, this increase of the average Li-O bond length reduces the Li-O binding energy and enhances lithium ion mobility in the Li$_3$PO$_4$ structure. Furthermore, since a lithium ion is located within a LiO$_4$ tetrahedron, it should pass through one of the triangular faces of the tetrahedron for diffusion to occur. Because the increase of the average Li-O bond length increases the area of a triangular face in the LiO$_4$ tetrahedron, it enables lithium ions to more easily diffuse through them as the nitrogen content increases. Thus, as nitrogen atoms become incorporated in the Li$_3$PO$_4$ system, Li-ion conductivities are expected to increase.
However, the data in Table 7.5 indicate that when a Lipon film was synthesized using very high nitrogen fluxes, the Li-ion conductivity began to decrease (to $1.65 \times 10^{-7}$ S/cm, Table 7.5). This appears to be result of lithium losses and partial crystallizations in the Lipon films (see Figures 7.6 and 7.7). This observation appears to be consistent with the previous study of Chapter 6, which indicated that increases of the N/P ratio decreased the Li/P ratio and reduced the Li-ion conductivity.

Furthermore, literature studies indicate that the relationship between nitrogen concentration and the Li-ion conductivity of Lipon films is not clear. Choi et al. indicated that the highest Li-ion conductivity of Lipon films was $\sim 1.67 \times 10^{-6}$ S/cm where Lipon films had the largest amount of nitrogen (i.e., $\text{Li}_{2.971}\text{PO}_{1.875}\text{N}_{1.25}$) [108]. However, Bates et al. reported that the highest Li-ion conductivity of Lipon films was $\sim 3.3 \times 10^{-6}$ S/cm with a moderate nitrogen incorporation, $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.36}$ [8,10]. Recently, Hamon et al. suggested that the Li-ion conductivity of Lipon films depended on the deposition process method [109]. Likewise, the relationship between compositions and Li-ion conductivities was not clear, because no one could accurately measure the composition of Lipon films. Nevertheless, it is clear that the nitrogen incorporation increases the Li-ion conductivity of Lipon films.
Figure 7.11 Electrochemical impedance spectroscopy (EIS) data for (a) lithium phosphate film and (b)-(d) Lipon films synthesized using gas jets containing nitrogen dimmer flux up to $4.28 \times 10^{18}$ molecules/cm$^2$·s. The impedance was measured between 1 and $10^5$ Hz. The dots correspond to experimental data while the solid lines are a best fit to the impedance circuit model. The deduced ionic conductivity for each film is also shown.
Table 7.4 Fitting parameters of EIS spectra of Lipon test cells. The $Z_{el}$ was used to calculate Li-ion conductivities of the Lipon films. Here, subscript letters represent as follows: hf=high frequency, el=electrolyte, dl=double layer, and g=geometrical.

<table>
<thead>
<tr>
<th>Nitrogen flux (molecules/cm²·s)</th>
<th>0.0</th>
<th>$1.07 \times 10^{18}$</th>
<th>$2.13 \times 10^{18}$</th>
<th>$4.28 \times 10^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{hf}$ ($\Omega$)</td>
<td>3000</td>
<td>2000</td>
<td>900</td>
<td>1300</td>
</tr>
<tr>
<td>$n_{el}$</td>
<td>0.7</td>
<td>0.92</td>
<td>0.76</td>
<td>0.81</td>
</tr>
<tr>
<td>$Z_{el}$ ($\Omega$)</td>
<td>$1.17 \times 10^5$</td>
<td>$1.58 \times 10^5$</td>
<td>$3.7 \times 10^3$</td>
<td>$2.47 \times 10^4$</td>
</tr>
<tr>
<td>$C_g$ (F)</td>
<td>$2.3 \times 10^{-9}$</td>
<td>$1.8 \times 10^{-10}$</td>
<td>$3.8 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>$n_{dl}$</td>
<td>0.695</td>
<td>0.68</td>
<td>0.87</td>
<td>0.8</td>
</tr>
<tr>
<td>$C_{dl}$ (F)</td>
<td>$8.0 \times 10^{-7}$</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$2.5 \times 10^{-8}$</td>
<td>$2.3 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Table 7.5 Li-ion conductivities of Lipon films.

<table>
<thead>
<tr>
<th>Nitrogen flux (molecules/cm²·s)</th>
<th>$\sigma_{ionic}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$3.65 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1.07 \times 10^{18}$</td>
<td>$1.45 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2.13 \times 10^{18}$</td>
<td>$5.24 \times 10^{-7}$</td>
</tr>
<tr>
<td>$4.28 \times 10^{18}$</td>
<td>$1.65 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
7.4 Summary

In this chapter, the effects of varying the activated nitrogen flux incident upon the growth surface of Lipon films grown from lithium phosphate have been explored using a PA-DVD film synthesis approach. As the nitrogen flux and nitrogen content of the films was increased, the atomic structure of the films changed from an amorphous structure to a partially-crystallized amorphous structure. This was accompanied by a change in surface morphology from spiral growth rings to a spiral-free smooth surface. The cross-sections also changed from a porous columnar structure to a structure consisting of dense tightly packed columns. These changes appear to be a consequence of an increase in the reaction rate of high-energy nitrogen ions with the evaporated lithium phosphate on the substrate surface. As the nitrogen flux incident on the growth was increased, the N/P ratio of Lipon film increased up to 0.75. The XPS P$_{2p}$ binding energy shifts indicated that the nitrogen replaced oxygen in the Li$_3$PO$_4$ structure. As the nitrogen flux was increased to 2.13×10$^{18}$ molecules/cm$^2$·s, the Li-ion conductivities of the films increased from 3.56×10$^{-9}$ S/cm to reach a maximum of 5.24×10$^{-7}$ S/cm. This increased Li-ion conductivity was attributed to an increase of nitrogen concentration in the film as the nitrogen flux in the jet increased. However, further increase of the nitrogen flux decreased the Li-ion conductivity because of lithium losses and partial crystallization in the Lipon films. The Li-ion conductivities of the Lipon films grown using a nitrogen flux were comparable to those reported by other using the e-beam evaporation approach. The use of a nitrogen-doped helium gas jet concentrated the vapor onto the substrate resulting in a deposition rate that was over 60 times that reported for other deposition approaches.
Chapter 8

Substrate Bias-Assisted Deposition of Lithium Phosphorus Oxynitride Thin Films

8.1 Overview

When a negative substrate bias is used with plasma assistance, it will repulse electrons and attract positive ions near the substrate. The positive ions form a plasma sheath that holds a constant plasma sheath potential [85]. If positive ions arrive at the plasma sheath edge, they will be accelerated towards a substrate by the plasma sheath potential. If positive ions are accelerated in the plasma sheath and have energy over sputtering threshold energy (E_{th}) of materials, then they will begin to sputter a growing film and modify properties of films. Previously, ion plating has been used during the film deposition process because it can modify the properties of films such as density, composition, and adhesion [71]. Ion plating performs the film deposition and sputtering of deposited films because it attracts ionized vapor atoms and energetic gas ions toward the biased substrate. The attraction of the energetic ions induces ion bombardment on the film growth surface, which generates film sputtering. Because film sputtering selectively removes a component of the film, it modifies the composition of films. Also, film
sputtering will reduce the deposition rate. The energetic ions affect the nucleation and growth mechanism of films, because they will heat a substrate and enhance the lateral adatom diffusion and the chemical reactions. Mattox et al. used the planar dc-diode sputtering technique to deposit the tantalum [72]. They found that the ion plating modified structures of films from columnar structures to dense structures and also increased film densities with an increase of the negative substrate bias. The negative substrate bias increased film stresses. So far, the substrate bias effect in a plasma-assisted directed vapor deposition (PA-DVD) approach has not been investigated for synthesizing lithium phosphorus oxynitride (Lipon) films.

In this chapter, the substrate bias effects upon the growth of Lipon films have been explored. Lipon films have been synthesized by the PA-DVD approach. For their synthesis, a hollow cathode technique was used to create an argon plasma and a nitrogen-doped helium gas jet rapidly transported an e-beam generated Li$_3$PO$_4$ vapor towards a negatively biased substrate. The resulting Lipon films showed that the substrate bias-assisted deposition technique manipulated the properties of the films and reduced their deposition rate.

8.2 Experimental Setup

8.2.1. Film Deposition Procedures

Cold pressed 1.3 diameter Li$_3$PO$_4$ evaporation source rods were manufactured from a
powder source (Plasmaterials Inc. CA). The Li$_3$PO$_4$ vapor was reactively deposited with plasma activated nitrogen to form Lipon. These Lipon films were grown using hollow cathode plasma generation technique with variable substrate bias, Figure 4.1. A bias wire was connected to a metallic substrate holder where a silicon substrate is attached and provided a negative substrate bias, which is controlled by an external power supply. The resistivity of silicon wafer was around 18±4 $\Omega\cdot$cm. After the vacuum chamber was pumped down to around 10$^{-2}$ Torr, the He+N$_2$ gas mixtures of 5.0 slm were introduced around the Li$_3$PO$_4$ source rod. It increased the downstream pressure ($P_d$) to 2.34×10$^{-2}$ Torr while increasing the upstream pressure ($P_u$) to 9.75×10$^{-2}$ Torr. This makes the pressure ratio ($P_u/P_d$) of 4.17, which generates a speed of 2,355 m/s. An argon plasma was activated by electrons, which were generated from the heated hollow cathode. The plasma current of 60 A kept this argon plasma and a negative bias was applied to a substrate. Using an e-beam power density of ~110.6 W/cm$^2$, the deposition experiments of Lipon films were preformed on silicon wafers for 20-40 minutes at 180±20$^\circ$C. Table 8.1 gives deposition conditions of Lipon films.

<table>
<thead>
<tr>
<th>Substrate bias (V)</th>
<th>He (slm)</th>
<th>N$_2$ (slm)</th>
<th>$P_u/P_d$</th>
<th>U (m/s)</th>
<th>Plasma current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.5</td>
<td>0.5</td>
<td>4.17</td>
<td>2,355</td>
<td>60</td>
</tr>
<tr>
<td>-10</td>
<td>4.5</td>
<td>0.5</td>
<td>4.17</td>
<td>2,355</td>
<td></td>
</tr>
<tr>
<td>-20</td>
<td>4.5</td>
<td>0.5</td>
<td>4.17</td>
<td>2,355</td>
<td></td>
</tr>
<tr>
<td>-30</td>
<td>4.5</td>
<td>0.5</td>
<td>4.17</td>
<td>2,355</td>
<td></td>
</tr>
<tr>
<td>-50</td>
<td>4.5</td>
<td>0.5</td>
<td>4.17</td>
<td>2,355</td>
<td></td>
</tr>
</tbody>
</table>
8.2.2. Film Characterizations

The Lipon films were characterized by various methods: Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Fourier Transform Infrared Spectroscopy (FTIR), and Electrochemical Impedance Spectroscopy (EIS). Details of each experimental method are given in Chapter 5.

8.2.3 Ion Fluxes on the Substrate

When a substrate is floated in plasma, electrons negatively charge its surface because they move into the substrate much faster than ions. In this manner, the substrate has a floating potential where the substrate has the equal flux of both electrons and ions. This floating potential forms a plasma pre-sheath and plasma sheath near the substrate. Because ions are initially accelerated through the plasma pre-sheath, their energy can be estimated at the plasma sheath edge by ion velocity \( u_{is} \), which is provided by Bohm sheath criterion condition. This Bohm sheath criterion condition is given by [85]:

\[
  u_{is} \geq u_B = \left( \frac{T_e}{M_i} \right),
\]  

(8-1)

where \( u_B \) is the Bohm velocity (m/s), \( T_e \) is the electron temperature (eV), and \( M_i \) is the ion mass (kg). Equation (8-1) indicates that ions have the Bohm velocity \( u_B \) at the plasma sheath edge. The ion velocity can be converted into the ion energy \( E_{is} \) as follows [85]:

\[
  E_{is} = \frac{1}{2} M_i u_{is}^2 \geq \frac{1}{2} M_i u_B^2 = \frac{1}{2} T_e.
\]  

(8-2)

At the plasma sheath edge, the ion energy becomes half of the electron energy or greater.
If ions arrive at the plasma pre-sheath edge, then they will be accelerated to the plasma sheath edge with the Bohm velocity and then accelerated through the plasma sheath by the plasma sheath potential. When the accelerated ions hit the floating substrate surface, their energy, \( E_{if} \), is approximately proportional to a floating potential as follows [85]:

\[
E_{if} = E_{is} + e \cdot V_f
\]

\[
= \frac{1}{2} T_e + T_e \ln \left( \frac{M_i}{2\pi m_e} \right)^{1/2},
\]

(8-3)

where \( V_f \) is the floating potential (V), \( T_e \) is the electron temperature (eV), \( M_i \) is the ion mass (e.g., Ar=6.64x10^{-26} kg), and \( m_e \) is the electron mass (9.11x10^{-31} kg).

If a substrate bias is negatively applied, then ions will be attracted into the substrate by a plasma sheath potential (\( V_{ps} \)) and the ion current (\( j_i \)) is represented by [85]:

\[
\frac{4}{9} \varepsilon_0 \left( \frac{2e}{m_i} \right)^{1/2} \frac{(V_{ps})^{3/2}}{d_{ps}^2},
\]

(8-5)

where \( V_{ps} = V_p - V_{sb} \), \( V_p \) is the plasma potential (V), \( V_{sb} \) is the substrate bias (V), \( m_i \) is the ion mass (argon = 6.671x10^{-26} kg), \( \varepsilon_0 \) is the dielectric constant (8.84x10^{-14} F/cm), and \( d_{ps} \) is the plasma sheath thickness (mm). In this case, the ion kinetic energy (\( E_i \)) at a substrate surface is approximately proportional to the applied negative bias (\( V_{sb} \)) [85]:

\[
E_i \approx \frac{1}{2} T_e + e \cdot |V_{sb}|.
\]

(8-6)

As shown in the equation (8-5) and (8-6), if a negative bias is applied to the substrate, then it will increase the substrate ion current and the ion energy. This substrate bias will increase ion bombardments onto the substrate, which can modify a surface morphology and a composition. In these aspects, ion plating has been used to modify the properties of
films such as film density, film adhesion, and film composition [71-73].

Before synthesizing Lipon films, ion flux was measured by using a current meter and a power supply; more detailed measurement steps are given in Chapter 6. As shown in Figure 8.1, the plasma floating potential was around −11 V. If the substrate bias is positively increased more than −11 V, then electrons are attracted toward the substrate. If the substrate bias is negatively increased over −11 V, then positive ions will be attracted toward the substrate. As shown in Equation (8-3), their energy can be approximated to $0.5T_e + eV_f$. For an electron energy range in the 5-15 eV range, the substrate floating potential measured here was around −11 V. This result indicates that ion energy ranges can be approximated to 14-19 eV. Mean free paths of vapor can be usually approximated by [118]:

$$\lambda_{mfp} = \frac{5 \times 10^{-3}}{P},$$

where $\lambda_{mfp}$ is the vapor mean free path (cm) and $P$ is the chamber pressure (Torr). When Lipon films were synthesized, the pressure of working chamber was $2.3 \times 10^{-2}$ Torr. This pressure provides that during Lipon film growth, the vapor mean free path was approximately 2.0 mm. Also, the plasma sheath thickness, $d_{ps}$, can be approximated by [118]:

$$d_{ps} \approx \left[ \frac{e \cdot (V_P - V_s)}{T_e} \right]^a \cdot \lambda_D$$

where $\lambda_D$ is the plasma Debye length ($\mu$m), $V_P$ is the plasma potential (V), $V_s$ is the substrate bias (V), $T_e$ is the electron temperature (eV), and a is between 2/3 at high pressures and 3/4 at low pressures.
When plasma potential ($V_p$) was assumed in the ranges of 40-100 V, the equation (2) indicates that the plasma sheath thickness was 10 times smaller than the vapor mean free path. Thus, when the substrate bias was negatively greater than –11 V, ions start arriving at the substrate, Figure 8.1 and their energy will linearly increase as a function of the negative substrate bias, Equation (8-6).

Figure 8.1 Ion flux versus substrate bias potential. Hollow cathode plasma generation process used argon as the working gas with a flow rate of 0.1 slm. A nitrogen-doped helium gas jet with a flow rate of 5.0 slm was used to reactively synthesize lithium phosphorus oxynitride from Li$_3$PO$_4$ vapor.
8.3 Results and Discussion

8.3.1. Film Morphologies

When the Li$_3$PO$_4$ films were synthesized without plasma assistance, they included cracks and pores because the low vacuum pressure ($7.5 \times 10^{-3}$-0.75 Torr) of the DVD approach highly thermalized vapor [60,63]. Figure 8.2 shows the surface morphologies of Lipon films synthesized using plasma assistance with a variable substrate bias. When the substrate was grounded with the plasma activation, Lipon films included spiral surfaces, Figure 8-2 (a). As the substrate bias was increased, the surface morphologies evolved to very smooth flat profile. Recent molecular dynamics simulations of the flux dependence of low energy ions on film growth indicate that the surface roughness depends on ion flux and highly becomes smooth as a function of argon ion flux [119]. Figure 8.1 shows that the ion fluxes linearly increased as a function of the negative substrate bias. This indicates that increases of the negative substrate bias accelerated more ions towards the film growth surface and increased the number of energetic ions bombarding the substrate surface, thus, the negative substrate bias modified the surface morphologies of the films.

Previously, Stuart et al. investigated sputtering yields of materials by argon ions. They indicated that sputtering threshold energies ($E_{th}$) of many materials were in the 20-40 eV ranges [120]. In general, sputtering yields are inversely proportional to the surface binding energy of materials [121]. This indicates that during film growth, if energetic ions bombard surface adatoms that do not form a complete bond, films can be
resputtered with lower ion energies than the sputtering threshold energies of materials. In the PA-DVD approach, the increase of the negative substrate bias reduced the deposition rates of the Lipon films, Table 2. If film resputtering does not occur at the negatively biased substrate, then deposition rates of the film usually increase [122]. As shown in Figure 8.1, when the nitrogen-doped helium gas jet of 5.0 slm was used, ion surface bombardment increased with the increase of a negative substrate bias. Equation (8-6) also indicates that ion energies increased with an increase in the negative substrate bias. Film resputtering therefore occurred during Lipon film growth.

<table>
<thead>
<tr>
<th>Substrate bias (V)</th>
<th>Film thickness (µm)</th>
<th>Deposition time (min)</th>
<th>Deposition rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.84</td>
<td>30</td>
<td>128.0</td>
</tr>
<tr>
<td>-10</td>
<td>1.81</td>
<td>30</td>
<td>60.3</td>
</tr>
<tr>
<td>-20</td>
<td>1.26</td>
<td>30</td>
<td>42.1</td>
</tr>
<tr>
<td>-30</td>
<td>1.61</td>
<td>40</td>
<td>40.3</td>
</tr>
<tr>
<td>-50</td>
<td>0.27</td>
<td>20</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Figure 8.2 Surface morphologies of the Lipon films synthesized using the negative substrate bias assistance.
8.3.2. Film Compositions

The Li/P ratio in Lipon films was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), Figure 8.3. The Li/P ratio in Lipon films increased as a function of the negative substrate bias. The P/N ratio of the films was determined by XPS, Figure 8.4. As the negative substrate bias was increased, the P/N ratio decreased. The XPS and ICP-OES results indicate that during film growth, phosphorus concentration in the Lipon films decreased.

Because the preferential sputtering of elements is inversely proportional to their mass and surface binding energy, light elements are more preferentially sputtered than heavy elements [121]. In this study, as the negative substrate bias increased, the Li/P ratio increased, and the P/N ratio deceased. These results generated a difficulty to be understood by the preferential sputtering of elements. Previously, Dudney et al. sputtered a Li$_3$PO$_4$ target by argon ions in a RF-magnetron sputtering system and the resulting films were near in the target composition [11]. This result shows that the preferential sputtering did not occur in the Li$_3$PO$_4$ target bombarded by energetic argon ions. In the PA-DVD approach used here, when the negative substrate bias was applied, ions will be accelerated towards the biased substrate surface and their velocity in the plasma sheath can be approximated by [85]:

$$u_i = \left( \frac{2qV_{ps}}{M_i} \right)^{1/2},$$

(8-9)

where $q$ is the ion charge, $V_{ps}$ is the plasma sheath potential ($V_{ps}=V_p-V_{sb}$), $V_p$ is the plasma potential (V), $V_{sb}$ is the substrate bias (V), and $M_i$ is the ion mass (kg).
If a constant negative substrate bias is considered and ions have the same charge, an ion velocity in the plasma sheath is inversely proportional to their mass, Equation (8-9). Thus, light ions have higher velocity than heavy ions. Because lithium mass is $1.15 \times 10^{-26}$ kg and phosphorus mass is $5.14 \times 10^{-26}$ kg, the equation (8-9) indicates that lithium ion velocity is approximately 2.1 times higher than phosphorus ion velocity. Thus, when the negative substrate bias was used, lithium ions might be accelerated with a higher velocity in the plasma sheath than phosphorus ions. Increasing the negative substrate bias accelerated more lithium ions towards the substrate than phosphorus ions. Resulting films therefore included more lithium than phosphorus.

Figure 8.3 Li/P ratio of Lipon films synthesized using a substrate bias assistance. The Li/P ratio was determined by ICP-OES. The error bars are $\pm 5\%$ of the Li/P ratio.
Figure 8.4 P/N ratio in Lipon films deposited using a negative substrate bias. The P/N ratio was obtained by XPS. The error bars represent ±10% of the P/N ratio.

8.3.3. Film Structures

X-ray diffraction (XRD) was used to analyze structures of the Lipon films, Figure 8.5. When the substrate bias was zero, the Lipon film had a broad peak without a local crystallinity. This indicates that the Lipon film was amorphous. However, when the substrate bias was used from –10 V to –50 V, the Lipon films formed a broad peak and weak local crystalline peaks at (120), (220) and (002), which correspond to peaks of a Li₃PO₄ phase. Both the broad peaks and the local crystalline peaks indicate that Lipon films included a local crystallinity in an amorphous phase. Martin et al. synthesized ZrO₂ films by an electron-beam evaporation while bombarding the growing film surface by
argon ions [123]. ZrO$_2$ films bombarded by the argon ions had crystalline properties while e-beam evaporated ZrO$_2$ films were amorphous without a substrate heating. Because the negative substrate bias increased a surface atomic mobility of vapor by accelerating ionized vapor, it generated the local crystalline peaks in Lipon films.

As shown in Figure 8.6, the FTIR spectra of Li$_3$PO$_4$ and Lipon showed four absorption bands: the asymmetric stretches of PO$_4^{3-}$ (1044 cm$^{-1}$, 1150 cm$^{-1}$), the symmetric stretch of PO$_4^{3-}$ (929 cm$^{-1}$) and the bending vibration of PO$_4^{3-}$ (597 cm$^{-1}$) [92-96]. As the negative substrate bias increased, one of the asymmetric PO$_4^{3-}$ stretches, 1150 cm$^{-1}$, disappeared and the symmetric PO$_4^{3-}$ stretch gradually decreased. However, at the substrate bias of –50 V, the asymmetric PO$_4^{3-}$ stretch was weak; thus, the FTIR spectra indicated that the increase of the negative substrate bias disrupted the Li$_3$PO$_4$ structure. Previously, P-N vibrations were assigned at ~743 cm$^{-1}$ [93]. However, because the P-N vibrations have been experimentally observed in the 789-1102 cm$^{-1}$ ranges, they resulted in a peak overlap with phosphate materials [92]. The peak overlaps caused a difficulty in assigning the P-N vibrations.
Figure 8.5 X-ray diffraction patterns of Lipon films prepared using a substrate bias.

There is a peak shift at the substrate bias of –30 V. The weak peaks marked as “*” are unknown.
Figure 8.6 FTIR transmittance spectra of Lipon films. Each peak shows the asymmetric stretches of $\text{PO}_4^{3-}$ ($1044 \text{ cm}^{-1}$, $1150 \text{ cm}^{-1}$), the symmetric stretch of $\text{PO}_4^{3-}$ ($929 \text{ cm}^{-1}$), and the bending motion of $\text{PO}_4^{3-}$ ($597 \text{ cm}^{-1}$) [92-96].

8.3.4. Li-ion Conductivity

Figure 8.7 shows the EIS spectra of the Lipon films measured by the same method described in Chapter 5. The Li-ion conductivities of these Lipon films are shown in Table 8.4. It can be seen that they decreased from $10^{-7}$ S/cm to $10^{-10}$ S/cm as the substrate bias was increased. Bates et al. observed that when nitrogen atoms were incorporated into $\text{Li}_3\text{PO}_4$ structure, Li-ion conductivities of amorphous Lipon films increased from $10^{-8}$ S/cm to $10^{-6}$ S/cm [8]. In polycrystalline Lipon, the nitrogen incorporation increased average Li-O atomic distances [57]. Because these weakened the Li-O bond energy and also increased a triangular face of tetrahedra where lithium ions stay, the incorporation of
nitrogen reduced the activation energy from 0.67 eV to 0.54 eV in Lipon films. Lithium ions can therefore easily move in Lipon films and the resulting Li-ion conductivity increases with the nitrogen incorporation. In this experiment, Li-ion conductivities gradually decreased because the negative substrate bias created local crystalline peaks in Lipon films, Figure 8.5. Even though Lipon films included the local crystallinities at the substrate bias of –20 and –30 V, their Li-ion conductivities were in the range of \(~10^{-7}\) S/cm. As indicated by Park et al., these Li-ion conductivities of Lipon films synthesized here were still in acceptable ranges for fabricating rechargeable thin-film Li/Li-ion batteries [112].
Figure 8.7 EIS spectra of the Lipon films synthesized using a substrate bias of (a) –10 V, (b) –20 V, (c) –30 V and (d) –50 V. The frequency was scanned in the range of 1-10^5 Hz with 0.1 logarithmic increments and decreased along the direction of the arrow.
Table 8.3 Fitting parameters used to calculate Li-ion conductivities of the Lipon test cells. Here, subscript letters represents as follows: hf=high frequency, el=electrolyte, dl=double layer, and g=geometrical.

<table>
<thead>
<tr>
<th>Substrate bias (V)</th>
<th>-10</th>
<th>-20</th>
<th>-30</th>
<th>-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{hf}$ (Ω)</td>
<td>1500</td>
<td>1100</td>
<td>1000</td>
<td>600</td>
</tr>
<tr>
<td>$n_{el}$</td>
<td>0.8</td>
<td>0.75</td>
<td>0.72</td>
<td>0.69</td>
</tr>
<tr>
<td>$Z_{el}$ (Ω)</td>
<td>1.25×10^4</td>
<td>4657</td>
<td>6.7×10^3</td>
<td>2.7×10^6</td>
</tr>
<tr>
<td>$C_{g}$ (F)</td>
<td>8.5×10^{-10}</td>
<td>1.8×10^{-9}</td>
<td>2.0×10^{-9}</td>
<td>1.1×10^{-9}</td>
</tr>
<tr>
<td>$n_{dl}$</td>
<td>0.9</td>
<td>0.88</td>
<td>0.76</td>
<td>0.53</td>
</tr>
<tr>
<td>$C_{dl}$ (F)</td>
<td>8.5×10^{-9}</td>
<td>1.2×10^{-8}</td>
<td>7.3×10^{-8}</td>
<td>1.1×10^{-7}</td>
</tr>
</tbody>
</table>

Table 8.4 Li-ion conductivities of Lipon films prepared by the substrate bias.

<table>
<thead>
<tr>
<th>Substrate bias (V)</th>
<th>$\sigma_{ion}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>1.27×10^{-7}</td>
</tr>
<tr>
<td>-20</td>
<td>1.35×10^{-7}</td>
</tr>
<tr>
<td>-30</td>
<td>8.82×10^{-8}</td>
</tr>
<tr>
<td>-50</td>
<td>3.12×10^{-10}</td>
</tr>
</tbody>
</table>
8.4 Summary

In this chapter, the effects of the substrate bias have been explored for synthesizing lithium phosphorus oxynitride (Lipon) electrolyte films for rechargeable thin-film Li/Li-ion batteries. The bias-assisted deposition created a local crystallinity in amorphous Lipon films and modified surface morphologies of the films from spiral surfaces to spiral-free smooth surfaces. During film deposition, the negative substrate bias increased the surface atomic mobility by accelerating either ionized vapor or gas ions towards a substrate and this effected the crystallinity and morphology of the films. However, the increase of the negative substrate bias increased ion bombardments at the film growth surface, which led to a decreased deposition rate for the Lipon films. The negative substrate bias accelerated more lithium ions than phosphorus ions, which increased the Li/P ratio in the films. The increase of the substrate bias also lowered the Li-ion conductivities because it promoted a crystallization of the Lipon films. Li-ion conductivities of Lipon films were in the range of $10^{-7}$-$10^{-10}$ S/cm, with those in the $10^{-7}$ S/cm range acceptable for fabricating rechargeable thin-film batteries.
Chapter 9

Discussion

9.1 Overview

Lithium phosphorus oxynitride (Lipon) film electrolytes have been synthesized by the Plasma-Assisted Directed Vapor Deposition (PA-DVD) approach and their composition, structure and ionic conductivity explored using various experimental methods. The properties of Lipon films have been investigated as dependent upon the several film deposition conditions: the plasma current, the nitrogen flux, and the negative substrate bias. Using the PA-DVD approach, the deposition rate of Lipon films was increased up to 60 times higher than that of the RF-magnetron sputtering approach. This deposition rate is sufficient to create ~2 µm thick Lipon films within ~20 minutes. Current sputter based methods require around 17 hours to create a similar film. Thus, the use of this approach will greatly reduce the processing time for fabricating rechargeable thin-film Li/Li-ion batteries.

The use of a DVD approach using a Li$_3$PO$_4$ source and no plasma assistance made it difficult to synthesize dense film structures because the energy of vapor atoms was much
lower than 0.2 eV [45]. It was also unable to incorporate nitrogen at detectable levels in the films. The plasma assistance method enabled the film morphologies to be modified and facilitated fully dense structures to be made. It also enabled the incorporation of significant nitrogen level in the films. Variation of the plasma current and the substrate bias provided sensitive control of the deposition process and facilitated manipulation of the film morphology, composition, structure, conductivity, and deposition rate. The best Lipon films synthesized by the PA-DVD approach had Li-ion conductivities in the $10^{-7}$ S/cm range and could be deposited at rates 60 times those of currently utilized sputtering methods. This Li-ion conductivity is acceptable as a thin-film electrolyte for rechargeable thin-film Li/Li-ion batteries.

9.2 Film Morphologies

The PA-DVD approach modified the morphologies of Lipon films from a very porous film structure to a very dense film structure. The deposition conditions of the plasma current, the nitrogen flux, and the substrate bias all affected the surface morphologies and cross-sectional microstructures of Lipon films. By controlling the deposition conditions, dense Lipon films could be generated. The Li$_3$PO$_4$ films synthesized without plasma assistance formed porous film structures because the vapor generated from the Li$_3$PO$_4$ source was highly thermalized in the low-pressure environment of the PA-DVD approach [60,63]. These film structures are undesirable in applications of rechargeable thin-film Li/Li-ion batteries because they can cause an electrical short. When the plasma assistance
was used, the morphology of Lipon films could be controlled from dense columnar structures to fully dense columnar-free structures. The fully dense columnar-free structures are desirable in applications of rechargeable thin-film Li/Li-ion batteries, because they are mechanically strong and prevent an electrical short. When a plasma current of 60 A was used, Lipon films formed the spiral surface morphologies and these surface morphologies might generate a rough surface and some pores. This film growth condition provided the highest Li-ion conductivity (i.e., $5.24 \times 10^{-7}$ S/cm) of Lipon films. During the film growth, the use of the substrate rotation could provide dense, smooth surface morphologies of Lipon films by reducing geometrical shadow effects and thus effectively remove the spiral morphologies of Lipon films.

### 9.3 Film Compositions

Increasing nitrogen concentration has increased Li-ion conductivities of Lipon films, Figure 2.4. When N/P ratio is in range of 0.3-1.4, and Li/P ratio is in the range of 2.4-3.6, Li-ion conductivities of Lipon films were higher than $1 \times 10^{-7}$ S/cm range [10,108,109,112]. Compositions of Lipon films synthesized by the PA-DVD approach here were investigated by ICP-OES and XPS. The Li/P ratio was determined by ICP-OES and the N/P ratio was determined by XPS. The Li/P and N/P ratios were all affected by the deposition conditions: plasma current, nitrogen flux, and substrate bias. The Li/P ratio decreased with the increase of the plasma current, while it increased with the increase of the negative substrate bias. The N/P ratio increased with the plasma current
and the nitrogen flux. Because the Li$_3$PO$_4$ vapor fluxes were entrained in the nitrogen-doped helium gas jet and carried toward the substrate, they had multiple collisions with the nitrogen-doped helium gas jet. This deposition process condition of the PA-DVD approach could provide very reactive environments to the Lipon vapor and achieve the high N/P ratio up to 1.49. When the negative substrate bias was used, it accelerated more lithium ions in the plasma sheath than phosphorus ions. This increased the Li/P ratio in the films. However, the negative substrate bias reduced the deposition rate of the films. This result indicated that the films were resputtered by ion bombardments.

### 9.4 Film Structures

Crystallinity of Lipon films was investigated using X-ray diffraction measurements. When the Li$_3$PO$_4$ films were evaporated without plasma assistance, they were amorphous. When the plasma assistance was used to synthesize Lipon films and nitrogen flux was less than $4.28 \times 10^{18}$ molecules/cm$^2$-s, Lipon films were amorphous. These results can be attributed to vapor thermalization that occurred in the low-pressure environment ($9.75 \times 10^{-2}$ Torr) of the PA-DVD approach [60,63]. However, the use of the negative substrate bias created a local crystallinity in amorphous Lipon films because it accelerated ionized vapor towards a substrate and increased their atomic energy on the substrate. Also, when the nitrogen flux was $4.28 \times 10^{18}$ molecules/cm$^2$-s, Lipon films included a local crystallinity in amorphous phase.
In addition, the crystalline properties of the films were conformed by measuring XRD patterns at zero and 45° tilt angles. As shown in Figure 6.10 and 6.17, when XRD patterns of both the Li$_3$PO$_4$ and Lipon film were obtained without tilting a sample, they had just one broad peak. XRD patterns of both the Li$_3$PO$_4$ and Lipon film measured with the 45° tilt angle also had one broad peak in the same 2θ range. These results indicated that both the Li$_3$PO$_4$ and Lipon films were isotropic and did not include a preferred texture; thus, the films were amorphous.

In FTIR spectra, Lipon films all had the asymmetric stretch of PO$_4^{3-}$. The asymmetric stretch indicated that the Lipon films all formed their PO$_4^{3-}$ tetrahedral structure in a short-range order. Also, XPS spectra showed that the P$_{2p}$ binding energies were shifted to a lower binding energy with the increase of nitrogen concentrations because the nitrogen incorporation changed the charge distribution of phosphorus. This result indicated that nitrogen atoms substitute for oxygen atoms near phosphorus atoms.

9.5 Li-ion Conductivity

The Li-ion conductivities of Lipon films were determined by electrochemical impedance spectroscopy (EIS). The Li$_3$PO$_4$ films evaporated without plasma assistance had very porous film structures. The porous film structures frequently caused electrical shorts of Li$_3$PO$_4$ test cells. When the Li$_3$PO$_4$ films were synthesized with a plasma assistance of 60 A, they had the low Li-ion conductivity of \( \sim 3.65 \times 10^{-9} \) S/cm. When
nitrogen was incorporated into Li$_3$PO$_4$, the Li-ion conductivities of Lipon films depended on the film deposition conditions of the PA-DVD approach: the plasma current, the nitrogen flux, and the negative substrate bias. These Li-ion conductivities of Lipon films are compared along the film deposition conditions used here, Figure 9.1. During the synthesis of Lipon films, changing the plasma currents created the Li-ion conductivity of $10^{-7}$-$10^{-9}$ S/cm. Increasing the plasma current resulted in lithium losses in Lipon films and decreased their Li-ion conductivities. When Lipon films were synthesized as a function of the nitrogen flux, they possessed the Li-ion conductivity of $10^{-7}$-$10^{-8}$ S/cm. In this experiment, an increase in the nitrogen flux generated lithium losses and local crystallinities in amorphous Lipon films and these reduced the Li-ion conductivities. When Lipon films were synthesized with a negative substrate bias, their Li-ion conductivities were in the range of $10^{-7}$-$10^{-10}$ S/cm. Because the negative substrate bias created the local crystallinity in Lipon films, it decreased Li-ion conductivities of Lipon films. The results observed here indicate that the nitrogen incorporation increased the Li-ion conductivity up to $5.24 \times 10^{-7}$ S/cm that is around 100 times higher than that of Li$_3$PO$_4$ film. This increase of Li-ion conductivities is attributed to an expansion of the average Li-O bond length by doping nitrogen into Li$_3$PO$_4$ [59]. These Li-ion conductivities were comparable to those of Lipon films prepared by plasma-assisted e-beam evaporation [13]. However, their highest Li-ion conductivities were lower than those of Lipon films prepared by RF-magnetron sputtering approach [7,8].

Recently, Park et al. synthesized Lipon films by the RF-magnetron sputtering approach and obtained Li-ion conductivities of $9.1 \times 10^{-7}$-$7.2 \times 10^{-9}$ S/cm [111]. They
showed that Lipon films with different Li-ion conductivities affected the charge-discharge properties of rechargeable thin-film lithium batteries, Figure 6.27. When the Lipon films had Li-ion conductivities of $9.1 \times 10^{-7}$ S/cm, they showed the symmetric charge-discharge profile. Also, the use of Lipon films, which had Li-ion conductivities of $1.2 \times 10^{-8}$ S/cm, showed a small internal IR loss in the charge-discharge curve. However, when the Lipon films had Li-ion conductivities of $7.2 \times 10^{-9}$ S/cm, they caused a serious internal IR loss in rechargeable thin-film lithium batteries. Those results indicated that Li-conductivities of $10^{-7}$-$10^{-8}$ S/cm range were sufficiently acceptable as a solid electrolyte in rechargeable thin-film lithium batteries. Therefore, the Lipon films synthesized by the PA-DVD approach can be used as an electrolyte in rechargeable thin-film lithium batteries.
Figure 9.1 Li-ion conductivity comparison of Lipon films along the process conditions: plasma current, nitrogen flux, and substrate bias.
9.6 Film Deposition Rates

The deposition rates of Lipon films all were effected by deposition conditions: plasma current, nitrogen flux, and negative substrate bias. The plasma activation greatly decreased the deposition rates. When argon gas passed through the hole of the hollow cathode, they were expanded as a sonic gas jet. The pressure \( P_c \) generated by the argon gas flow was approximately 45.46 Pa, which was expanded into the process chamber with the speed of \( \sim 450.94 \) m/s, Equation (4-1). Because the speed of the supersonic gas jet indicated by Hass et al. was in the range of 350-450 m/s, the argon gas jet sufficiently disturbed vapor impinging on the substrate [91].

When Lipon films were synthesized along the dependence of plasma currents, their deposition rates were in the range of 9-128 nm/min. When Lipon films were synthesized as a function of nitrogen gas flux, their deposition rates increased from 112.7 nm/min to 177.7 nm/min. This result can be attributed to the increased vapor focusing by increasing the nitrogen flux in the supersonic helium gas jet. The use of the negative substrate bias achieved the deposition rates of 13.5-60.3 nm/min. The increase of the negative substrate bias decreased the deposition rates by film resputtering. When Lipon films were synthesized with the deposition condition including the plasma current of 60 A, the nitrogen flux of \( 2.13 \times 10^{18} \) molecules/cm\(^2\)-s and the zero substrate bias, they have the highest Li-ion conductivity \( (5.24 \times 10^{-7} \) S/cm). This film growth condition indicates that the PA-DVD approach can synthesize Lipon films at over 60 times higher deposition rates than that reported by RF-magnetron sputtering approach [11]. Up to now, low
deposition rates of Lipon films have been a problem in fabricating rechargeable thin-film Li/Li-ion batteries because of a long processing time [11,15]. The high deposition rates where the PA-DVD approach achieved can potentially provide a short processing time for synthesizing Lipon films. Because the Lipon films synthesized by the PA-DVD approach have Li-ion conductivities of \( \sim 10^{-7} \) S/cm range, the PA-DVD approach is a promising rapid deposition route for synthesizing Lipon films.

In addition, if a substrate is positioned to near the hollow cathode that generates the argon plasma gas jet, it will include more impinging vapor, which is less deflected from the source-substrate axis. This can increase film deposition rates. Also, if an ion gun is employed in the PA-DVD approach, then it can direct ions towards a substrate surface with the same direction of gas jet. Thus, the use of an ion gun enables to increase film deposition rates without disturbing the axial jet propagation in the PA-DVD approach.
Chapter 10

Conclusions

In this dissertation, the plasma-assisted directed vapor deposition (PA-DVD) approach has been explored as a means for synthesizing lithium phosphorus oxynitride (Lipon) films. The Lipon films have been extensively used as an electrolyte of rechargeable thin-film Li/Li-ion batteries [9,18,23]. Unlike conventional e-beam evaporation techniques, the PA-DVD approach employed a supersonic gas jet for the rapid transport of vapor and much higher chamber pressures (7.5×10^{-3}-0.75 Torr) than conventional e-beam evaporation techniques (~7.5×10^{-7} Torr) [15]. An extensive study of the effects of deposition conditions on properties of Lipon films has been performed using various experimental methods. The results of this study indicate that Lipon films can be rapidly synthesized by deposition rates over 60 times higher than those deposited by the RF-magnetron sputtering approach and possessed Li-ion conductivities of ~10^{-7} S/cm range. As Park et al. indicated, the Lipon films possessing a Li-ion conductivity of ~10^{-7} S/cm can be sufficiently integrated into rechargeable thin-film Li/Li-ion batteries without a significant internal IR loss [111]. As a result, it appears that the PA-DVD approach is a promising rapid deposition route for synthesizing dense amorphous Lipon films.
Here, the effects of deposition conditions on the properties of Lipon films have been extensively investigated. As a result of the work conducted for this dissertation, specific conclusions can be drawn:

- The PA-DVD approach achieved a high deposition rate of Lipon films. When the hollow cathode plasma was used for the film growth, the hollow cathode generated an argon gas jet, which impeded the vapor flow direction. This greatly reduced the deposition rates of Lipon films. When the nitrogen was mixed in the helium gas jet, the deposition rates of Lipon films increased up to 177.7 nm/min. However, the use of the negative substrate bias decreased deposition rates of Lipon films by film resputtering. Overall, Lipon films can be synthesized at over 60 times higher deposition rates than those of the RF-magnetron sputtering approach.

- The morphologies of Lipon films were effected by the deposition conditions: plasma current, nitrogen flux, and substrate bias. The increase of the plasma currents modified microstructures of Lipon films from dense columnar structures to fully dense structures. By increasing nitrogen in the helium gas jet, Lipon films formed porous columnar structures to very dense fibrous structures. Increase of the negative substrate bias increased ion bombardments on the growth film surface and this modified surface, morphologies of the films from spiral surface to spiral-free smooth surface.

- The compositions of Lipon films were effected by the film deposition conditions. The increase of plasma currents increased the N/P ratio in Lipon films while it decreased the Li/P ratio. The reduction of Li/P ratio can be linked to the doubly and triply coordinated bond states of nitrogen, which substituted for oxygen in Li$_3$PO$_4$. 
and removed lithium. When the nitrogen flux was increased in the helium gas jet, it increased the N/P ratio in Lipon films. However, the increase of nitrogen flux initially increased Li/P ratio of Lipon films and then ultimately decreased it. This initial increase of Li/P ratio was attributed to the increase of nitrogen flux in the helium gas jet, which focused more lithium than phosphorus. When the negative substrate bias was increased, it increased the Li/P ratio of Lipon films by accelerating more lithium ions in the plasma sheath than phosphorus ions.

- The atomic structures of Lipon films were affected by the deposition conditions. When the Li$_3$PO$_4$ films were synthesized without plasma assistance, they were amorphous. When the plasma assistance was used, the Lipon films were amorphous. However, increasing the nitrogen flux in the helium gas jet created a local crystallinity in amorphous Lipon films. The use of the negative substrate bias also created a local crystallinity in amorphous Lipon films.

- In the FTIR spectra, Lipon films synthesized by the PA-DVD approach all contained asymmetric PO$_4^{3-}$ stretch bands. These results indicated that the Lipon films formed their tetrahedral bond structures in a short-range order.

- XPS spectra indicate that nitrogen in Lipon films formed two nitrogen bonds: doubly coordinated nitrogen and triply coordinated nitrogen. Also, XPS P$_{2p}$ peaks were shifted to a low binding energy with the increase of the N/P ratio in Lipon films. These results indicate that nitrogen substituted for oxygen near phosphorus.

- The EIS measurement indicates that Li$_3$PO$_4$ films had a Li-ion conductivity range of $\sim 10^{-9}$ S/cm. When nitrogen is incorporated into Li$_3$PO$_4$ films, Lipon films synthesized by the PA-DVD approach had Li-ion conductivities of between $10^{-7}$-
$10^{-8}$ S/cm. These results show that the nitrogen incorporation increases Li-ion conductivities of Lipon films up to 100 times higher than those of Li$_3$PO$_4$ films. The Li-ion conductivities of Lipon films achieved by the PA-DVD approach are comparable to those of Lipon films obtained by the conventional e-beam evaporation technique. Lipon films, including the Li-ion conductivity of $\sim 10^{-7}$ S/cm, can be integrated as a thin-film electrolyte in rechargeable thin-film Li/Li-ion batteries.
References


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