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Microstructure And Property Evaluation Of LiFePO4 Thin Films For Application In Microbatteries

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MICROSTRUCTURE AND PROPERTY EVALUATION OF LiFePO$_4$ THIN FILMS FOR APPLICATION IN MICROBATTERIES

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Dean of the Graduate School
Dedicated to my Parents
MICROSTRUCTURE AND PROPERTY EVALUATION OF LiFePO$_4$ THIN FILMS FOR APPLICATION IN MICROBATTERIES

by

JOSE MARCOS MARES

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

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Abstract

The shortage of fossil fuels and the requirements to produce clean, environmental friendly, efficient, and economical energy are the principal problems in the context of energy technology for current and future generations. Therefore, advanced energy storage and conversion capabilities with higher capacity and efficiency are desired. Currently, there is an enormous interest in the development of high energy density rechargeable batteries for use in domestic applications, automotive industries and portable electronic applications. The present research focuses on the development of LiFePO$_4$ thin films for solid-state thin-film microbatteries. The present effort was performed with a specific purpose of understanding the effect of temperature, an important thermodynamic variable, on the microstructure and electronic properties of LiFePO$_4$ films fabricated by radio-frequency (RF) magnetron sputtering. LiFePO$_4$ films were grown under varying deposition temperatures in the range of 25 to 400 °C. In addition, LiFePO$_4$ films were annealed in temperature ranges of 400 to 800 °C for 1 and 2 hours. The effect of growth temperature on the crystal structure, surface morphology, chemical quality and electronic properties is investigated in detail. Characterizations of the films were performed using X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray spectrometry (EDS), optical spectrophotometer, and electrical resistivity measurements. The grain size increased as the annealing temperature increased from 400 to 800 °C. The optical properties of the LiFePO$_4$ films indicate that, as the growth temperature is increased, the transmittance of the films increases.

The band gap increases from 2.75 eV to 3.28 eV with increasing temperature from RT-400 °C. When the films were annealing at 1 hour form 400-800 °C, the band gap increased from 3.12 eV to 3.7 eV. Annealing for 2 hours at temperatures from 400 to 800 °C showed an increase
in band gap 3.12 eV to 3.75 eV showing the maximum value at 600 °C. The electrical capacity indicates that with an increase in substrate temperature, the resistivity of the films also increases.
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Chapter 1: Introduction

Nowadays, there is a scarcity of fossil fuels and environmental concerns across the globe. It is now convinced that the green energy and related industries will become the main stream in the next years to resolve these critical problems. Therefore, there is an immense interest in the development of new energy storage systems with enhanced efficiency and can achieve the best possible energy density. Currently, there is a strong demand of high density rechargeable batteries.

The demand for high energy density rechargeable batteries has been increasing in the previous years and it will increase more in the next years due to portable electronics devices, energy storage systems and new technology. In addition, there will be an urgent need for more automobiles due to world population growth and this is one of the most important issues for the next generations. It is expected that there will be 1.6 billion automobiles in the year 2025 and the total emission of CO₂ will be about 67% higher. To alleviate these problems, various research groups have adopted different strategies to improved energy efficiency in electric vehicles to reduce the global warming. The development of higher performance rechargeable battery systems in technology, automotive industries and portable applications will lead to relieve these problems.

The advance in high density battery technology is critical for advancements in a variety of applications ranging from hybrid electric vehicles to consumer electronics. As mention earlier vehicles, domestic purposes, and industries are significant for this technology. One of the principal investigations is the use of different cathode materials to demonstrate the improvements of the energy efficiency of the rechargeable batteries by increasing its capacity. However, not only the performance of these kinds of batteries is critical for its applications in the future, the
production cost, safety and environmental concern is also important. Several materials as cathode for this type of batteries have been provide high voltages and good capacities but full utilization of these materials for numerous recharging cycles and at high discharge currents continue to be a challenge. To meet the futures needs of electrical energy storage is critically to develop novel battery systems that incorporate revolutionary new materials and chemical processes.

1.1 Batteries

A battery is an electrochemical cell that converts stored chemical energy into electrical energy that was invented by Alessandro Volta in 1800. A battery is composed of an anode, cathode, and an electrolyte that allows for ionic conductivity. The anode and cathode are separated by polymeric materials. The schematic and components of an electrochemical cell are shown in Figure 1. There are two types of batteries: primary batteries, which are designed to be used once and discarded when they are exhausted, and secondary batteries, which are designed to be recharged and used multiple times.

Currently, batteries have become a common power source for many household and industrial applications and more strict requirements exist both in energy density and power density of energy storage devices. Also, there is a high demand for high performance batteries. The secondary lithium ion battery is a promising option to meet such demands because of its inherent outstanding characteristics. The lithium ion batteries are discussed below.
1.2 Lithium ion Batteries

The lithium ion battery is a rechargeable battery type in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging [2]. The three primary functional components of Li-ion batteries are the anode, cathode and electrolyte. Graphite is the most common anode material. The electrolyte is typically a mixture of organic carbonates. The cathode is significant in determining the capacity of the Li-ion battery, as it is the heaviest component; therefore, it has the greatest potential for the improvement of batteries. Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest energy density for weight. The chemistry, performance, cost, and safety characteristics are the main advantages of this kind of battery among others. Nowadays, lithium ion batteries are the most common in consumer electronics due to the best energy to weight ratios, no memory effect, and a slow loss of charge when not in use. Recently, the popularity of lithium ion batteries has been increasing for military, electric vehicle, and aerospace applications due to their high energy density. New investigation for this battery is yielding a stream of
improvements to traditional Li-ion batteries technology, focusing on energy density, durability, cost, safety, and active cathode materials. The market for Li-ion batteries is driven by the demand of the portable electronic device market, especially the notebook computer and the cellular telephone. This market has had an explosive growth since 1990 and it is still growing. However, one of the challenges for this technology is to improve the performance of lithium ion batteries to meet increasingly demanding requirements for the latest equipment. To overcome this problem, it is necessary to development a suitable cathode material for the next generations of this battery. The charge and discharge process of the lithium ion batteries is shown in Figure 1.2 and 1.3. As described earlier the cathode materials is a very important part of lithium batteries. Most common cathode materials are described below.
1.3 Cathode actives materials for Lithium ion batteries

The successful commercialization of lithium ion batteries for electronics, automobiles, and technology has led to many research groups to invest considerable amount of money in this battery technology that utilizes LiCoO$_2$, LiNiO$_2$, and LiMnO$_2$ cathodes [4]. However, lower cost cathode materials are required for various applications. In addition, these materials limit the applications to small batteries due to the high cost, toxicity, and environmental harmful of the materials. The cathode is particularly critical in determining the capacity of the lithium ion battery, as it is the heaviest component, therefore, it has the greatest potential for the improvement of lithium ion batteries. Cobalt oxide based and materials are dangerous and are
environmentally harmful [5]. Manganese based materials are attractive because of both their low
cost and low toxicity. However, they suffer from important capacity fading during cycling,
especially at high temperatures and poor low temperature character. These characteristics
unfortunately prevent these materials from being used in large scale applications. The
improvement of cathode materials is a challenge for meeting current and future energy storage
requirements. Currently, several materials are testing to replace current cathodes materials. One
of the most promising materials is LiFePO$_4$. The principal properties and benefits of LiFePO$_4$ are
described below.

1.4 LiFePO$_4$ for Lithium ion batteries

LiFePO$_4$ has many advantages compared with conventional cathode materials described
earlier and it is considered as a promising cathode material because of its theoretical energy
density for lithium ion batteries for the next generations of electronic devices [6]. Lithium iron
phosphate cell has a discharger potential around 3.4 V vs. lithium [7]. It has received attention as
a cathode for Li-ion batteries during the past years, due to the exceptional stability of LiFePO$_4$ at
elevated temperatures enables safe, large lithium ion batteries for large scale applications such as
electric vehicles or space applications [8]. LiFePO$_4$ can be prepared from different sources, in
recent years new synthetic methods are used to reduce the energy consumption, cost, and
processing time. In addition, the excellent cycling performance of LiFePO4 in lithium ion
batteries at high temperature has been confirmed [9]. However, the main issue of the LiFePO$_4$ is
its low conductivity, therefore, many efforts have been devoted to increase and optimize the
conductivity of LiFePO$_4$. Currently, there are a lot of different methods to improve the poor
conductivity of this material but more investigation is necessary to achieve the ideals results.
Finally, all the materials are inexpensive and with good operability, therefore, it is possible to reach industrial production of LiFePO$_4$ for lithium ion batteries. In Table 1.1 there is a comparison data among various lithium ion batteries.

Table 1.1: Cathode material comparison for Lithium batteries

<table>
<thead>
<tr>
<th>Battery</th>
<th>LiFePO$_4$</th>
<th>LiCoO$_2$</th>
<th>LiMnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>Safest</td>
<td>Not Stable</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Environmental</td>
<td>Not Dangerous</td>
<td>Dangerous</td>
<td>Dangerous</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>Best</td>
<td>Good</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Power Density</td>
<td>Acceptable</td>
<td>Good</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>Excellent (-20°C to 70°C)</td>
<td>Decay (-20°C to 55°C)</td>
<td>Decay Fast over 50°C</td>
</tr>
<tr>
<td>Cost</td>
<td>Economic</td>
<td>High</td>
<td>Acceptable</td>
</tr>
</tbody>
</table>

1.5 Problems Encountered for LiFePO$_4$

The commercial implementation of LiFePO$_4$ material has been facing problems due to the poor rate capability resulting from its inherent low electronic conductivity ($10^{-9}$ S cm$^{-1}$) and low Li$^{+}$ ions diffusion rate [12]. This limitation is its principal drawback and has hindered its wide application in the commercial market. The poor conductivity is because during the lithium insertion and extraction, the resulting phases, LiFePO$_4$ and FePO$_4$ are both poor electronic conductor because they contain Fe cations with only one oxidation state $2^+$ and $3^+$ respectively [13]. Efforts to optimize the electrical and ionic conductivity of LiFePO$_4$ have focused largely on doping the compound. Chiang and co-worker from MIT increased the conductivity by aliovalent doping. However, doping may have harmful impact if it occurs on the lithium sites.
1.6 History of LiFePO$_4$

John Goodenough discovered LiFePO$_4$ with his research group at the University of Texas at Austin in 1996, as a cathode material for rechargeable lithium batteries [15]. It is a very stable material due to the covalent P-O bonding which stabilize the fully charged cathode versus O$_2$ release [31]. The theoretical energy density of LiFePO$_4$ is 170 mAh g$^{-1}$ is higher compared with iron based compounds [40]. LiFePO$_4$ which has an ordered olivine type structure has received particular attention during the past years to replace the current cathode material for lithium ion batteries. The main characteristics of LiFePO$_4$ for cathode material are its low cost, non-toxicity, high abundance of iron, its excellent thermal stability, outstanding electrochemical performance, and high specific capacity [47]. The structure of LiFePO$_4$ can be seen in Figure 1.4
Figure 1.4: The crystal structure of LiFePO$_4$. Purple-Phosphorous, Blue-Li, Grey-Fe, Red-O.
1.7 Objectives

It is clear that LiFePO$_4$ is a viable candidate as cathode active material for Li-ion batteries. The results are wished to be valuable in the further design of the structure of the LiFePO$_4$ cathode materials for lithium batteries of other applications. The following are the specific objectives of the work:

1. Fabricated LiFePO$_4$ thin films using RF magnetron sputtering under varying growth conditions.

2. Study the effect of growth temperature on the structure and electronic properties of LiFePO$_4$.

3. Study the annealing temperature effects on the microstructure and electronic properties of LiFePO$_4$ thin films.

4. Optimized the conditions to high-quality LiFePO$_4$ thin films.
Chapter 2: Experimental

2.1 LiFePO$_4$ Target

LiFePO$_4$ powder was obtained using the solid state route. The obtained powder was mixing with polyvinyl alcohol (PVA) and pressed at 7300 psi for 15 minutes to obtained a pellet. The pellet obtained has a 2 inches in diameter and .25 inches of thickness. The formed pellet was sintered during 24 hours at 700°C under normal atmosphere.

2.2 Substrate Cleaning

Silicon wafers and quartz were using in all the experiments. The silicon used were p-type Si (100) wafers. The quartz used were 25mm by 25 mm. To avoid contamination, all the substrates were cleaning before deposition. The silicon wafer were cleaning using the RCA clean procedure to remove all the contaminants. These are the steps for the process:

1. First the silicon wafers were soaked during 5 minutes in methanol, then it was dried by nitrogen.

2. Then, it was soaked in acetone during 5 minutes and rinse with DI water for 5 minutes.

3. Finally it was treated with Buffered Oxide Etch (BOE) to remove any oxide on it. Then it was rinsed in DI water for 5 minutes and dried with nitrogen.

The quartz used were cleaning using an ultrasonic bath of methanol and acetone. The quartz were soaked in methanol during 5 minutes and dried with nitrogen. Then they were soaked in acetone for another 10 minutes and dried with acetone.
2.3 Thin Films

The LiFePO$_4$ thin films were grown using a radio-frequency (RF) sputtering system. Sputter deposition, commonly called sputtering, removes the atoms from the target surface, projecting them into the gas phase from which they condense on another surface. Usually Ar flows into the chamber, the chamber is evacuated to high vacuum usually $10^{-6}$ Torr. The Ar gas will be ionized to create Ar$^+$ plasma. Ar$^+$ ions accelerate towards cathode, under the influence of cathode voltage, and bombard the target ejecting a target atom. These target atoms will be deposited on to the substrate placed above the target to form the film. The sputtering process is shown in Figure 2.1.

The deposition system used for all the depositions was Kurt J Lesker sputter machine (Figure 2.1). During R.F. magnetron sputtering, the distance between the target and the substrate was 8 cm. As described earlier the substrates used were silicon wafers and quartz. The sputtering gas was high purity Ar with 99.999% purity, the gas total flow was set at 50 sccm. An R.F magnetron sputtering power of 40 Watts was applied to the target. Before deposition of the films, the target was pres-puttered for 10 minutes in order to remove any contaminant atoms from the chamber and target. During deposition, the substrates were grown at various temperatures, from RT to 500 °C. To increase the temperature of the substrates halogen lamps were used, and they were controlled by Athena X25 system until they reached the desired temperature. The prepared LiFePO$_4$ thin films were annealed at 400°C, 500°C, 600°C, 700°C, and 800°C for 1 and 2 hours using a furnace. The deposition and annealing conditions are described in Table 2.1 and 2.2 respectively.
Figure 2.1: Kurt J Lesker sputter system.

Figure 2.2: Sputtering Process
Table 2.1: Deposition Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Name</th>
<th>Total Pressure (Torr)</th>
<th>Argon Flow (sccm)</th>
<th>Temperature (°C)</th>
<th>Power (Watts)</th>
<th>Deposition Time (hr)</th>
<th>Distance Target to Substrate (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiFEPO4-SQ1</td>
<td>2.1X10E-3</td>
<td>50</td>
<td>RT</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>LiFEPO4-SQ2</td>
<td>2.2X10E-3</td>
<td>50</td>
<td>100</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>LiFEPO4-SQ3</td>
<td>2.4X10E-3</td>
<td>50</td>
<td>200</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>LiFEPO4-SQ4</td>
<td>2.1X10E-3</td>
<td>50</td>
<td>300</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>LiFEPO4-SQ5</td>
<td>2.3X10E-3</td>
<td>50</td>
<td>400</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>LiFEPO4-SQ6</td>
<td>2.1X10E-3</td>
<td>50</td>
<td>500</td>
<td>40</td>
<td>1</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2.2: Annealing Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Name</th>
<th>Temperature (°C)</th>
<th>Deposition Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiFEPO4-SQ1</td>
<td>400</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>LiFEPO4-SQ1</td>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>LiFEPO4-SQ1</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>LiFEPO4-SQ1</td>
<td>700</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>LiFEPO4-SQ1</td>
<td>800</td>
<td>1</td>
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<tr>
<td>6</td>
<td>LiFEPO4-SQ2</td>
<td>400</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>LiFEPO4-SQ2</td>
<td>400</td>
<td>2</td>
</tr>
<tr>
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<td>LiFEPO4-SQ2</td>
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<td>LiFEPO4-SQ2</td>
<td>600</td>
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<tr>
<td>10</td>
<td>LiFEPO4-SQ2</td>
<td>700</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>LiFEPO4-SQ2</td>
<td>800</td>
<td>2</td>
</tr>
</tbody>
</table>

2.4 Surface Morphology

The surface morphology of LiFePO₄ thin films was obtained using a HRSEM. The information about the microstructure of the thin films was found using the surface morphology. In addition, the information about the thin film and substrate interaction was obtained using the
interface analysis. The HRSEM used in this work was a Hitachi S-4800 electron microscope (Figure 2.3).

Figure 2.3: Hitachi S-4800 electron microscope

The SEM electron beam is produced via an electron gun or filament. A voltage is applied to the filament which acts like a cathode, causing it to heat up. When the filament gets hot enough, electrons are emitted thermionically. A strong electric force is present between the electrons emanating from the filament and the anode plate. This force causes the electrons to be accelerated towards the anode plate. In fact, some of the thermionic electrons are accelerated in such a manner as to stream right by the anode plate and down the column of the microscope to the sample. This electron beam is scanned back and forth over the surface of the specimen using electromagnetic lenses and the electrons that are reflected from the specimen are used to resolve an image on the computer monitor. SEM must be carried out under a high vacuum such as 10⁻
In Figure 2.2 one can see the schematic sketch of an (SEM) showing its major components.

Analysis software is used to determine the grain size and thickness of the thin film. To acquire the image of the surface the sample is placed on a flat stage with its film surface facing the beam. For the interface image or cross section, the sample is placed in a way that both the film and the substrate are facing the beam.

Figure 2.4: Schematic of Scanning Electron Microscopy (SEM)
2.5 Structural Characterization

The XRD pattern of the sample was obtained using a Bruker D8 advance x-ray diffractometer (Figure 2.5) employing Cu Kα radiation (1.54 Å). The crystal structure, crystallite size, and the phases of the thin films were determined from XRD patterns. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions such as lattice parameter, d-spacing, film orientation. The XRD operates based in the Bragg’s Law [57].

\[ \lambda = 2d\sin\theta \]

where \( \lambda \) is the wavelength, \( d \) is the inter planar distance, and \( \Theta \) is the angle.

Figure 2.5: Bruker D8 advance x-ray diffractometer
2.6 Optical Characterization

The samples obtained have been characterized using a Cary 5000 UV-VIS-NIR optical spectrophotometer. The transmittance of a sample is the ratio of the intensity of the light that has passed through the sample to the intensity of the light when it entered the sample. The transmittance data obtained for the samples is used for calculating the band gap. First, the absorption coefficient has to be determined. The absorption coefficient determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. It is determined using the thickness of the film (t) and transmittance data (T) from the formula [50].

\[
\alpha = \frac{-\ln(T)}{t} \quad \text{(2)}
\]

The energy of the photons (hv) is calculated at every wavelength of light using the following equation

\[
hv = \frac{1240}{\lambda} \quad \text{(3)}
\]

Finally, the optical band gap energy was estimated from transmittance spectra by assuming that the absorption coefficient \(\alpha\) is given by the following equation [51]

\[
\alpha hv = B(hv - E_g)^2 \quad \text{(4)}
\]
Chapter 3: Literature Review

Padhi et al. [15] have demonstrated in 1996 that LiFePO₄ could be used as an active cathode material in lithium ion rechargeable batteries. The advantages of this LiFePO₄ compared to other ion based compounds for high density batteries such as, cost, toxicity, theoretical capacity and electrochemical performance were discussed. The pioneering work of this research group at University of Texas at Austin attracted the attention of electromechanical and energy research community worldwide and generated a strong interest in this material.

Takahashi et al. [5] discussed the effect of operating temperature of LiFePO₄ used as cathode material. It was showed that the cell capacity increases as the cell operating temperature is raised because the lithium ion diffusion in the LiFePO₄ particles is enhanced. They found that electrochemical lithiation and delithiation occurs as a two-phase reaction and the structure of the delithiated product is similar to heterosite, the same as that of chemically delithiated product. Good reversibility is expected from the small structural change between LiFePO₄ and FePO₄, which coexist during lithium insertion and extraction.

Prosini et al. [6] suggested that the capacity of LiFePO₄ can be greatly improved by the addition of fine particles of carbon black during its synthesis. Improvements in the rate capability have also been achieved by synthesizing small particles and by the addition of silver or copper. It was reported that a specific capacity of 120 mAh g⁻¹ can be obtained at a high rate.

Ravet et al. [11] improved significantly the electrochemical performance of LiFePO₄ by applying carbon coating. Yamada et al. [14] reported that increase in the specific surface area resulting from very fine and uniform particles gives good electrochemical cycle performance. He also obtained capacities as high as 165 mAh/g.
Xia et al. [17] discussed the effect of surface area. It was found that the rate capability of LiFePO$_4$ is mainly controlled by its specific surface area and it is an effective way to improve the rate capability of the sample by increasing its specific surface area. LiFePO$_4$ prepared with a high specific surface area of 24.1 m$^2$ g$^{-1}$ has an excellent rate capability and can deliver 115 mAh g$^{-1}$ and 145 mAh g$^{-1}$ of reversible capacity even at the 1C and 5C rates respectively. The results showed that by increasing the specific surface area, the electrochemical performance can be improved.

Kim et al. [19] prepared LiFePO$_4$ powder at 700 °C. It showed a higher capacity compared with powders prepared at 600 and 800 °C. This is because it has a well-developed crystalline structure and optimum particle size. At high operating temperatures, the capacity of a LiFePO$_4$ cell is increased, however, there is a low conductivity of the powder. This problem can be solved by increasing the conductivity of the powders by using a more suitable conductive additive.

Sang et al. [23] prepared LiFePO$_4$ by mechanical alloying (MA). It showed a maximum discharge capacity of 135 mAh g$^{-1}$ at the C/20 rate (8.5 mAg$^{-1}$) when fired at a relatively low temperature of 600 °C. The composite also displays a better rate capability, a higher charge and discharge capacity and a more stable cycle-life than when produced by the conventional solid-state method. The improved electrode performance of MA samples originates mainly from very fine particles of sub-micron size and with a rough surface morphology. These powder characteristics increase the surface area of LiFePO$_4$ particles and maximize the contact area with the conductor additive, which results in enhanced electronic conductivity. It is concluded that fine particle size and uniformly dispersed carbon black between the particles achieved with the MA process increases the electronic conductivity.
Ceder et al. [34] based on phase diagram reported that a fast Li$^+$ ion conductivity phase prepared by a controlled off stoichiometry method on the surfaces of LiFePO$_4$ particles less than 500nm to display rate capability equivalent to full battery discharge.

Li et al. [35] used the pressure pulsed chemical vapor infiltration (PCVI) technique, to deposited pyrolytic carbon films on the surface of LiFePO$_4$ particles for cathode material of lithium-ion batteries. All the PCVIed samples exhibited excellent rate performance. The specific capacities of the samples were maintained at 117, 124 and 132 mAh g$^{-1}$, respectively, which were 120.8, 264.7 and 29.47% larger than those of corresponding original LiFePO$_4$, respectively, at a 5C rate at 55 °C. The electrochemical performance of LiFePO$_4$ electrodes is improved significantly for the PCVIed samples.

Rousse et al. [36] reported neutron diffraction results from polycrystalline samples, confirming the collinear structure below $T_N=52$ K. Santoro et al. [12] studied the magnetic properties of LiFePO$_4$ and showed that its space group is Pnma. The magnetic results showed a paramagnetic-antiferromagnetic phase transition. Denis et al. [32] also discussed the magnetic properties of this compound. His results showed that the ground state of LiFePO$_4$ is a collinear antiferromagnet and very robust against crystal imperfections.

Xian-Juan et al. [45] prepared thin films by radio frequency magnetron sputtering. It was found that when the temperature increased, the thin film structure change form amorphous to crystalline. However, at high temperatures an impurity phase can be developed. Chiu et al. [46] showed that thin films of carbon mixed with LiFePO$_4$ prepared with inductively coupled plasma (ICV) exhibited higher specific capacity that can be related to the film structure and surface morphologies.
Sauvage et al. [48] prepared free carbon LiFePO$_4$ thin films using the Pulsed Laser Deposition (PLD) technique. It clearly showed that once again the main limitation of this compound is its low conductivity with the main limitation being the ionic conductivity. The results demonstrated that thin film approach is very valuable to understand electrode material limitations. Tang et al. [49] also discussed LiFePO$_4$ thin films prepared using (PLD) technique. He showed that the influence of deposition parameters, e.g. substrate temperature, argon pressure, and annealing modify the crystalline, surface morphology, and the electrochemical properties of the compound.

Numerous studies have been devoted to understand and establish the relation between the deintercalation and intercalation process in LiFePO$_4$. Islam et al. [54] have shown that the lithium ions can move easily in the tunnels parallel to the b direction. However, Maier et al [52] showed that the electronic conductivity, ionic conductivity, and chemical diffusion of lithium ions are essentially two dimensional b-c plane in the LiFePO$_4$ single crystal.
Chapter 4: Results and Discussion

The purpose of the research work is to perform fabrication, microstructure analysis, and electronic property measurement of LiFePO$_4$ thin films for application in high-energy density microbatteries. This chapter discusses the results obtained in the following sequence. X-ray diffraction (XRD) measurements are first discussed to establish the effect of substrate temperature on the crystal structure and phase formation. Subsequently, the scanning electron microscopy (SEM) data are presented to discuss the grain structure and surface morphology evolution. Energy dispersive x-ray spectrometry (EDS) data are presented following the SEM analyses to establish the chemical composition or phase of LiFePO$_4$ films. After that, the optical properties are discussed to show the electronic structure of LiFePO$_4$ films as a function of growth temperature. The electrical properties are presented and explained following optical properties. An emphasis is made to establish a correlation between growth conditions and electronic properties of LiFePO$_4$ thin films. This is very important since most of the applications of LiFePO$_4$ depend on its microstructure and electronic properties. Also, the ability to tailor the microstructure and properties so as to optimize electrochemical performance requires a detailed fundamental understanding of LiFePO$_4$ thin films.

4.1 Crystal Structure

The XRD patterns of LiFePO$_4$ thin films are shown in Figures 4.1 and 4.2. The XRD patterns of bulk LiFePO$_4$ are shown in Figure 4.1. LiFePO$_4$ was found to form in the Pnma space group with olivine-type structure without any impurity phase. The calculated values of the lattice constant is $a=10.4093\,\text{Å}$, $b=6.0500\,\text{Å}$ and $c=4.7315\,\text{Å}$ [6], which are slightly higher than that of the reported values. Figure 4.2 shows the XRD spectra of the LiFePO$_4$ thin films post-fabrication.
annealed at different temperatures. LiFePO$_4$ thin films grown or annealed at temperatures T ≤ 500 °C did not show any features and are completely amorphous. Onset of crystallization is noticed in the LiFePO$_4$ thin films when annealing was performed at 600 °C. It can be seen that the XRD spectra show crystalline features for LiFePO$_4$ thin films annealed at 600 °C. The peak at 2θ=21.5° corresponds to the diffraction from (111) planes. The intensity of this peak increases with further increase in the annealing temperature. It is evident (Fig. 4.2) that for the films post annealed at 600–800 °C, the (111) peak shows the highest intensity.

The results indicate that annealing at 600 °C promotes the crystallinity and development of (111) orientated structure of LiFePO$_4$ thin films. The (101) plane is parallel to the a and b axis in the LiFePO$_4$ olivine structure, which is more stretchable as observed during the Li$^+$ intercalation and de-intercalation process [45]. As a consequence, grains with (101) plane parallel to the substrate are slightly more favorable.

![Figure 4.1: XRD pattern of LiFePO$_4$ bulk](image-url)
4.2 Surface Morphology

The scanning electron microscopy (SEM) images of LiFePO$_4$ thin films as a function of substrate temperature $T_s$ are shown in Figures 4.3 and 4.4. The effect of temperature on the surface morphology of the thin films is significant. The images show no features for LiFePO$_4$ films grown at $T_s \leq 500$ °C even at very high magnifications. The thin films were grown from RT to 500°C. The images are in agreement with the XRD results indicating the complete amorphous nature of the samples. However, as seen in SEM images, some micro-cracks develop on the film
surfaces. It can be attributed to severe ion bombardment induced plasma damage. It has been reported that the finer grain size shortened transport length of lithium ions and therefore improved electrochemical performance of LiFePO₄ [39]. Preliminary studies on the sputtered thin films show that the substrate temperature has a strong effect on the morphology and the electrochemical characteristics of LiFePO₄ thin films. The texture of LiFePO₄ thin films has a significant effect on the electrochemical properties [47].

Figure 4.3: SEM images of LiFePO₄ thin films
The results from XRD and SEM suggest that a further increase in temperature beyond 600 °C results in changes in the crystal structure and morphology. LiFePO$_4$ films continue to show preferred growth along with an increase in average particle size with increasing temperature. These results suggest that an optimum substrate temperature is essential to obtain well crystallized LiFePO$_4$ thin film.

Figure 4.4: SEM image of LiFePO$_4$
4.3 Chemical Composition

The energy-dispersive X-ray (EDS) spectra of representative LiFePO$_4$ films as a function of annealing temperature are shown in Figure 4.5. The spectra indicate the characteristic x-ray peaks corresponding to O, P, and Fe atoms present in the sample. The absence of Li is because the materials cannot be detected by the EDS. No other elements were detected, which is a sign of high purity LiFePO$_4$ and without any elemental impurities incorporated from chemical processing or post-annealed.

![EDS spectra of LiFePO$_4$ films](image)

Figure 4.5: LiFePO$_4$ films EDS spectra at various temperatures

4.4 Optical Properties

The optical transmittance spectra of LiFePO$_4$ films are shown in Figure 4.6 to 4.8. The spectral transmittance characteristics of LiFePO$_4$ films as a function of substrate temperature ($T_s$)
exhibit interesting features. The spectral transmittance in general increases with increasing $T_s$. In the visible to near infrared regions of the spectrum, the transmittance of these films is found to be generally high. The on-set of a sharp decrease in the spectral transmittance towards ultraviolet regions of the spectrum is due to fundamental absorption of the incident energy across the band gap of the material. It can be seen that this absorption edge is shifting towards shorter wavelength side with increasing $T_s$. This feature is an indicative of the electronic structure changes in the LiFePO$_4$ films with increasing $T_s$.

![Figure 4.6: Optical transmittance spectra of LiFePO$_4$ films. Inset the visible spectrum.](image)
Figure 4.7: Optical transmittance spectra of LiFePO$_4$ films. Annealing 1 hour. Inset the visible spectrum.

4.8: Optical transmittance spectra of LiFePO$_4$ films. Annealing 2 hours. Inset the visible spectrum.
The optical band gap energy was estimated from transmittance spectra. It is known that the optical absorption below $E_g$ follows an exponential behavior. The absorption, therefore, is exponentially dependent on the energy ($hv$) of incident photon in that region. For LiFePO$_4$, in the $E_g$ region or above the fundamental absorption edge, the absorption follows a power law of the form [50, 51]:

$$\alpha hv = A(hv - E_g)^{2}$$

where $A$, $hv$, and $E_g$ are a constant of proportionality, photon energy and optical band gap energy, respectively. The optical band gap values were calculated for the films with different thickness. The optical absorption coefficient ($\alpha$) was determined using the relation [48];

$$\alpha = 2.303 \frac{\log_{10}[(1 - R)^2 / T]}{d}$$

where $R$ is the reflectance, $T$ is the transmittance and $d$ is the thickness of the film. The optical energy gap of a given film is found by plotting $(\alpha hv)^{1/2}$ versus $E$ and extrapolating linear portion of the curve to $\alpha=0$.

The absorption data and the plots obtained for LiFePO$_4$ films are shown in Figures 4.9, 4.10, and 4.11. The $E_g$ values were determined by extrapolating the linear region of the plot to $hv = 0$. From RT- 500 °C $E_g$ increases from 2.5 to 3.25 eV with increasing $T_s$. The same results occur with the annealing samples. The $T_s$ and $E_g$ relation is shown in Figure 4.11. The highest values were obtained with the annealing samples. The maximum value 3.75eV was obtained when $T_s$ was annealing at 600°C for 2 hours.
Figure 4.9: \((\alpha \nu)^{1/2}\) vs. \(\nu\) plots for LiFePO\(_4\) films. Linear fits of the absorption data indicate the indirect band gap of LiFePO\(_4\) films. The \(E_g\) values determined by extrapolating the linear region of the plot to \(\nu = 0\)

Figure 4.10: \((\alpha \nu)^{1/2}\) vs. \(\nu\) plots for LiFePO\(_4\) films. Annealing 1 hour
The results indicate that the microstructure has significant effect on the optical properties of LiFePO4 films. The films annealed from 600-800 °C show higher band gap energy. The film annealed at 600 °C for 2 hours has the highest band gap.
4.5 Electrical Properties

The room temperature electrical conductivity variation of LiFePO$_4$ films with Ts is shown in Figure 4.13. It can be seen that the electrical conductivity decreases with increasing Ts. Therefore, the conductivity will be decrease if T$_s$ is increasing. The electrical resistivity of pure LiFePO$_4$ is $10^7$ Ω-m [40]. The electrical resistivity of RF sputter deposited LiFePO$_4$/C thin film is at the order of $10^2$ Ω-m [45]. Our results are in good agreement with these works. The difference in the results it is due to that the films were sputtered from a pure LiFePO$_4$ target without any conducting media such as carbon or metals imbedded [48].

Figure 4.13: Changes of electrical resistivity of LiFePO$_4$ samples with growth temperature
The frequency dependence of the electrical conductivity ($\sigma_{ac}$) of LiFePO$_4$ films grown from RT-500 °C is shown in Figure 4.14. The total conductivity of the films can be expressed by the relationship:

$$\sigma_{tot} = \sigma_0(T) + \sigma_0(\omega, T)$$ (7)

Figure 4.14: Frequency dependence of the electrical conductivity

The first term at R.H.S. is the dc conductivity due to the band conduction, which is frequency independent. On the other hand, second term of the equation is purely a representation of the ac conductivity due to the electron hoping between the Fe$^{2+}$/Fe$^{3+}$ ions.

LiFePO$_4$ has an ordered olivine structure (space group Pnma). The oxygen atoms are arranged in a slightly distorted, hexagonal close-packed arrangement. The FeO$_6$ octahedra share
common corners in the bc plane, and the LiO$_6$ octahedra form an edge-sharing chain in the b-direction. The separation of the FeO$_6$ octahedra by PO$_4$ polyanions significantly reduces the electrical conductivity of the material. The electronic conductivity in this material is determined by the mobile electrons in Fe$^{2+}$/Fe$^{3+}$ redox couple. In addition to that, the hoping mechanism in LiFePO$_4$ films can be attributed to the presence of oxygen vacancies. Based on the LiFePO$_4$ bulk electronic structure, the valence band is formed by the filled O 2p orbital and the conduction band is formed by the Metal (Fe) 3d orbital. The vacancy level forms below the conduction band and it can also trap one or two electrons. Conductivity increases (by three orders of magnitude) with increasing frequency from 20 Hz to 1 MHz is attributed due to the hoping mechanism in LiFePO$_4$ films.

The observed dispersion in the resistivity is due to the contribution from the O$^{2-}$, Li$^+$ and Fe$^{2+}$/Fe$^{3+}$ ions to the relaxation. At low frequency regime, hopping of electron between the localized Fe ions increases subsequently the resistivity decreases. The frequency variation of electrical resistivity data was fit to the following equation:

\[
\rho - \rho_\infty = \frac{(\rho_0 - \rho_\infty)}{1 + (\omega \tau)^{2(1-\alpha)}} \tag{4}
\]

Where $\rho_\infty$ is the resistivity value at 1 MHz, $\rho_0$ is the resistivity value at 20 Hz, $\tau$ is the mean relaxation time (3.4, 3.3, 3.1, 2.8, 2.5 and 2.2 µs for the films grown from $T_s$=RT to 500 °C) and $\alpha$ is the spreading factor (about the Figure 4.16) mean relaxation time (0.62, 0.60, 0.57, 0.53 and 0.51 for the films grown from $T_s$=RT to 500 °C). The calculated mean relaxation time values are found to decrease from 3.4 µs to 2.5 µs with increasing $T_s$ from RT to 500 °C due to the increase in conductivity. Figure 4.15 shows the variation of the mean relaxation time with increasing $T_s$. $\tau$ is seen to decrease with increasing $T_s$. Increasing grain size with increasing $T_s$
subsequently the decreasing grain boundary scattering leads to decreasing resistivity and the mean relaxation time.

Figure 4.15: Relaxation Time

Figure 4.16: Spreading Factor
Chapter 5: Conclusions

LiFePO$_4$ thin films were fabricated using Si wafers (100) and quartz substrates and a RF magnetron sputtering system. The effect of growth temperature (RT-500 °C) and annealing temperature (400-800 °C) on the structure, surface/interface morphology, chemical quality, and optical and electrical properties of LiFePO$_4$ films was investigated. XRD and HRSEM results indicate that the effect of growth temperature on the LiFePO$_4$ films is significant. Samples grown from RT-500 °C are amorphous while those annealed from 600-800 °C are crystalline. The grain size increase as the temperature is increased. Therefore, it is concluded that the crystal-size can be obtained by carefully controlling the growth temperature. The effect of $T_s$ was significant on the optical characteristics of LiFePO$_4$ films. The microstructure effects were remarkably evident in the optical spectra and band gap analysis. The transmittance of the films decreased with the increase in $T_s$. The decrease in band gap of LiFePO$_4$ films (2.75-3.75 eV; RT-800 °C) is due to the oxygen vacancies. The highest band gap 3.75 eV was obtained by annealed the sample at 600 °C for 2 hours. The corresponding electrical resistivity of the samples increases with increase in $T_s$ which is due to improvement in the crystal structure. The $T_s$-$E_g$ and $T_a$-$E_g$ relationships found for LiFePO$_4$ films suggest that the electronic structure can be tuned by achieving control over the growth temperature or post-deposition annealing conditions. A direct correlation between growth conditions, microstructure and electronic properties as noted in this work is useful to design LiFePO$_4$ thin films for microbattery applications.
Chapter 6: Future Work

The scope for the future work and some directions are as listed below.

1. The LiFePO$_4$ films grown can be tested for electrochemical performance.
2. The optimized conditions from this work can be used to construct a microbattery.
3. Doping with some carbon can be considered to improve its low conductivity.
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