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## Morphological and Electrochemical Properties of $\text{LiMn}_2\text{O}_4$ Thin Films

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### ABSTRACT

*LiMn<sub>2</sub>O<sub>4</sub> were prepared by pulsed laser deposition technique. Two important deposition parameters such as substrate temperature and oxygen partial pressure during the thin film deposition were controlled. Systematic characterizations like RBS, SEM, TEM and electrochemical studies were performed on to the prepared samples. The SEM data demonstrated that the films exhibited a smooth surface roughness with spherical droplets. The grain size increased with the increase of substrate temperature. The electrochemical measurements were carried out on Li//LiMn<sub>2</sub>O<sub>4</sub> cells with a lithium metal foil as anode and LiMn<sub>2</sub>O<sub>4</sub> film as cathode of 1.5 cm<sup>2</sup> active area. Cyclic voltammetry (CV) measurements have been carried out at sweep rate  $\alpha = 1 \text{ mVs}^{-1}$ . Specific capacity of 133 mC/cm<sup>2</sup>μm was measured for the film grown at 700 °C.*

**Keywords:** LiMn<sub>2</sub>O<sub>4</sub> thin films, PLD, Composition, SEM, TEM and Electrochemical properties.

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### INTRODUCTION

The all solid state thin film lithium ion rechargeable batteries have several attractive features including possible integration of battery fabrication with that of the microelectronic devices such as smart cards [1]. Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices and fuel cells, coatings for the passivation of surfaces against corrosion and as catalysts [2-10]. In the lithium ion batteries, lithium ion insertion/extraction with redox reaction of host is made use of as both cathode and anode reactions. The high performance electrode materials become an important factor for the development of lithium ion batteries. LiMn<sub>2</sub>O<sub>4</sub> is considered to be more attractive cathode material for lithium ion batteries than LiCoO<sub>2</sub> and LiNiO<sub>2</sub> [11]. Lithium ion batteries are the most suitable power supplies for many portable electronic devices, such as cellular phones, digital cameras and notebooks, because of their high energy and power density [12, 13]. LiMn<sub>2</sub>O<sub>4</sub> spinel is an attractive candidate cathode material for Lithium ion rechargeable batteries with a three dimensional framework because it has many advantages, such as low toxicity, cost efficiency, environmental friendliness compared to other lithiated transition metal oxides, such as lithium cobalt oxide or lithium nickel oxide [14, 15]. The structure of spinel LiMn<sub>2</sub>O<sub>4</sub> (space group Fd3m) consists of a cubic close-packing arrangement of oxygen ions at the 32e sites, the Li ions at the tetrahedral 8a sites, and the Mn<sup>3+</sup> and Mn<sup>4+</sup> ions at the octahedral 16d sites.

Lithium manganese oxide is one among the prominent electrode materials for secondary lithium ion battery. Lithium manganese oxide with cubic spinel structure has attracted a great deal of attention due to its advantages like low cost, abundance of manganese in earth crust, environmental harmlessness and high theoretical lithiation capacity (~148mAh/g). Development of the cathode materials for lithium ion battery is vital to meet the demands of portable devices, power tools, e-bikes, future usages of electric vehicles and so on. Among the cathode materials lithium manganese oxides ( $\text{LiMn}_2\text{O}_4$ ) is inexpensive cathode material with a high energy density, environmental acceptability and are more abundant in nature. On the other hand,  $\text{LiMn}_2\text{O}_4$  with spinel-type structure is one of the most attractive candidates to substitute commercial  $\text{LiCoO}_2$  positive electrode, because spinel  $\text{LiMn}_2\text{O}_4$ , which has a theoretical charge storage capacity of 148 mAh/g, has the advantages of low cost, environmental friendliness and high abundance [16].

Preparations of  $\text{LiMn}_2\text{O}_4$  with improved properties have been developed.  $\text{LiMn}_2\text{O}_4$  thin films can be obtained by various techniques such as radio frequency (rf) sputtering [17], pulsed laser deposition (PLD) [18-20], electrostatic spray deposition [21] and chemical vapour deposition [22]. Many efforts have been devoted to investigate the crystal structure and electrochemical properties of  $\text{LiMn}_2\text{O}_4$ . Even though the technology is rather expensive and the material is highly toxic, lithium cobaltate is still the most widely used cathode material in lithium-ion batteries. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [23]. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as Reactive Pulsed Laser Deposition (RPLD)), the flux of the laser ablated material interacts with the gas molecules all along the transit from the target to the collector surface. The resulting deposited layer was found to have a chemical composition substantially the same as the base or starting material. In thin film deposition, the substrate temperature plays the important role of determining the morphology of films. Besides these battery materials we have studied other materials like CdTe, ZnSe and CdSe nanopolymers are of great industrial interest for developing photoluminescence based biomedical labeling reagents [24-27]. Quantum dots have applications in both organic and inorganic light emitter devices such as electroluminescence devices. They are dispersed within or between phosphor layers and emit a specific color of light [28-30]. In this study, we have deposited  $\text{LiMn}_2\text{O}_4$  thin films on silicon substrates and investigated the morphological and electrochemical properties of these thin films.

## MATERIALS AND METHODS

$\text{LiMn}_2\text{O}_4$  thin films were grown by pulsed laser deposition technique on silicon substrates maintained. PLD target was prepared by sintering a mixture of high purity  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{O}$  powders (Cerac products) with excess of lithium i.e.  $\text{Li}/\text{Mn} > 1.0$  by adding  $\text{Li}_2\text{O}$  to compensate the loss of lithium during the deposition. The mixture was crushed, pressed and sintered at 800 °C to get quite robust targets and used for the growth of films. The typical substrates i.e. Si wafers were cleaned using HF solution. The target was rotated at 10 rotations per minute with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248 nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1x3 mm and the energy 300 mJ. The power density at the target surface was 10  $\text{Jcm}^{-2}$ . The target substrate distance was 4 cm [31-55]. The deposition temperature was maintained with thermocouple and temperature controller. During the deposition pure oxygen was introduced into the deposition chamber and desired pressure was maintained with a flow controller.

The composition of the  $\text{LiMn}_2\text{O}_4$  thin films were analyzed using Rutherford backscattering spectroscopy. The surface topography was investigated by scanning electron microscopy (SEM) using Philips XL 30. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Electrochemical measurements were carried out on  $\text{Li}/\text{LiMn}_2\text{O}_4$  cells with lithium metal foil as anode and a  $\text{LiMn}_2\text{O}_4$  film as cathode of 1.5  $\text{cm}^2$  active area using a Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and covered by insulating epoxy leaving only the PLD film as active area. The electrolyte consisted of 1 M  $\text{LiClO}_4$  dissolved in propylene carbonate. Cyclic voltammetry measurements have been carried out at sweep rate  $\alpha = 1 \text{ mVs}^{-1}$ . Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile system in the potential range between 2.0 and 4.2 V. Quasi open-circuit voltage profiles were recorded using current pulses of 5  $\mu\text{Acm}^{-2}$  supplied for 1 h followed by a relaxation period of 0.5 h. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps.

## RESULTS AND DISCUSSION

Pulsed laser deposited  $\text{LiMn}_2\text{O}_4$  films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of  $\text{LiMn}_2\text{O}_4$  films are 250 nm. The influence of oxygen partial pressure ( $p\text{O}_2$ ) and deposition temperature ( $T_s$ ) on the microstructural properties were systematically studied. The chemical compositional studies made on  $\text{LiMn}_2\text{O}_4$  films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

### *Composition*

Composition of the  $\text{LiMn}_2\text{O}_4$  thin films deposited on silicon wafers was determined from the Rutherford backscattering spectroscopic analysis. The Li/Mn ratio has been studied as a function of the substrate temperature. The films prepared in the substrate temperature range 300-700 °C were found to be nearly stoichiometric.

### *Surface Morphology*

The surface morphology and texture as well as particle sizes were observed by scanning electron microscopy. The scanning electron micrographs of pulsed laser deposited  $\text{LiMn}_2\text{O}_4$  film grown in oxygen partial pressure  $p\text{O}_2 = 100$  mTorr on silicon wafers maintained at 700 °C is shown in Figure 1. The SEM micrograph of film grown at 700 °C exhibits a smooth surface roughness with spherical droplets related to the ejection of liquid material from the molten zone of the irradiated targets. The grain size of the films is found to be small at lower temperatures. The crystallite sizes tend to increase as the deposition temperature increased, suggesting the formation of submicron sized particles with uniform grain size distribution. The grain size of the films formed at 700 °C is 175 nm. The particle size increases with increasing substrate temperature as expected due to grain growth. It has been known that the particle size influences directly battery performance and it has reported that decrease of particle size improves the cyclability and discharge capacity [56, 57]. TEM measurements were performed to confirm the crystalline nature of the samples and to study the morphology of the particles. The TEM images of  $\text{LiMn}_2\text{O}_4$  thin films are depicted in Figure 2. The particles are more or less uniformed in size and of irregular shape.

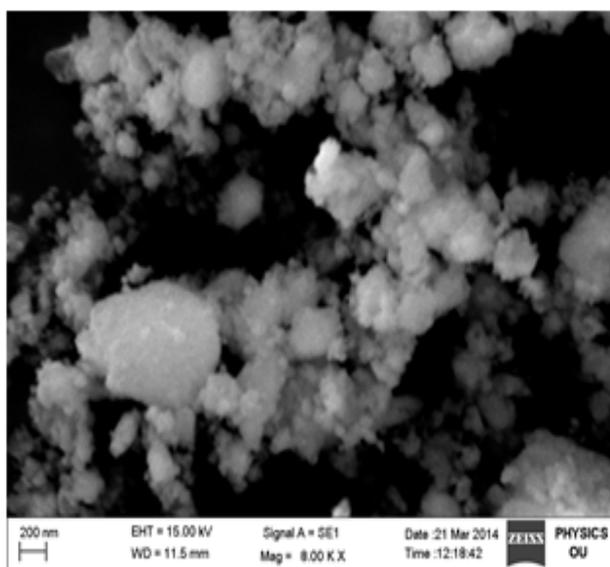


Figure 1: SEM image of  $\text{LiMn}_2\text{O}_4$  thin film deposited at 700 °C in  $p\text{O}_2 = 100$  m Torr

The morphological changes, grain size enhancement and their distribution characteristics as a result of increase in growth temperature can be explained on the basis of the difference in the mobility of ablated species on the substrate surface as follows. When the laser beam hits the target the ions or molecules or atoms of the target material are liberated. The ablated atomic or molecular or ionic species impinging on the substrate surface (which is at higher temperature) acquire a large thermal energy and hence a large mobility. This enhances the diffusion density of the ablated species. As a result, the collision process initiates the nucleation and enhances the island formation in order to grow a continuous film with larger grains. These results are suitable for the further utilization of PLD films

because a fundamental role in terms of charge transfer capability and cycle life is played by the morphology of the films used as cathodes in lithium microbatteries.

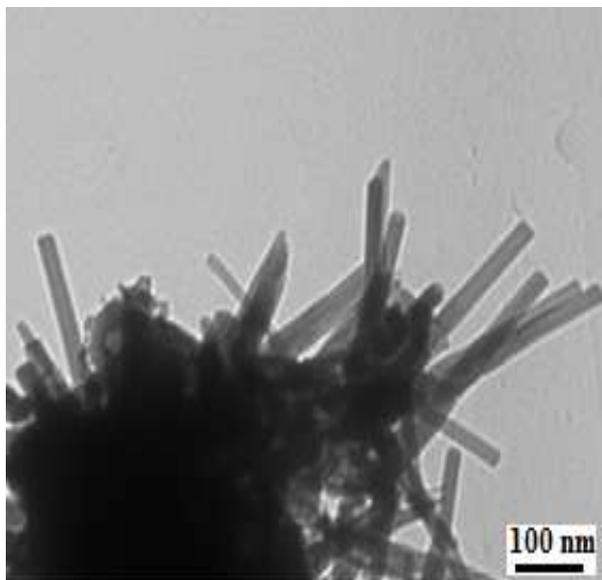


Figure 2: TEM image of  $\text{LiMn}_2\text{O}_4$  thin film deposited at  $700\text{ }^\circ\text{C}$  in  $p\text{O}_2 = 100\text{ m Torr}$

#### *Electrochemical properties*

Figure 3 shows the cyclic voltammogram for a  $\text{Li}/\text{LiMn}_2\text{O}_4$  cell with a film grown at temperature  $700\text{ }^\circ\text{C}$  in an oxygen partial pressure of 100 mTorr. There are two sets of well defined current peaks observed in the CV diagram corresponding to the oxidation and reduction reaction: they are located at 3.70 and 3.60 V for the  $\text{LiMn}_2\text{O}_4$  film. These CV features are associated with the redox process of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and vice-versa, when lithium is extracted from, and inserted into the  $\text{Li}_x\text{Mn}_2\text{O}_4$  phase. The redox couple with a mid peak potential of about 3.65 V is considered to be a single phase insertion/deinsertion reaction of lithium ions in  $\text{LiMn}_2\text{O}_4$ .

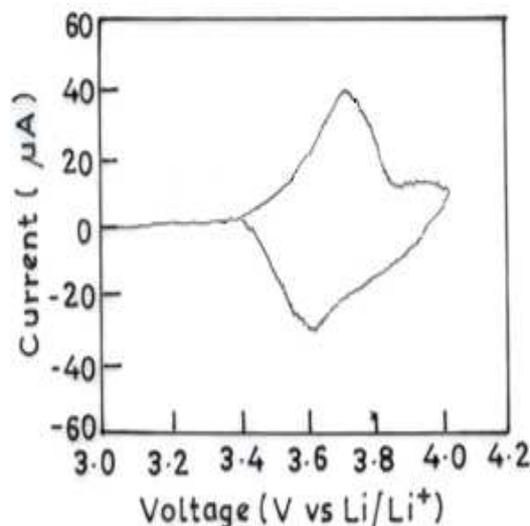


Figure 3: Cyclic Voltammogram of  $\text{Li}/\text{LiMn}_2\text{O}_4$  cell deposited at  $700\text{ }^\circ\text{C}$  in  $p\text{O}_2 = 100\text{ m Torr}$

Figure 4 shows the typical charge – discharge curves of  $\text{Li}/\text{LiMn}_2\text{O}_4$  cells using pulsed laser deposited film grown at temperature  $700\text{ }^\circ\text{C}$  in an oxygen partial pressure of 100 mTorr. The electrochemical measurements were carried out on  $\text{Li}/\text{LiMn}_2\text{O}_4$  cells with a lithium metal foil as anode and a polycrystalline film as cathode of  $1.5\text{ cm}^2$  active area using a Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and

covered by insulating epoxy leaving only the PLD film as active area. The electrolyte consisted of 1 M LiClO<sub>4</sub> dissolved in propylene carbonate. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile system at a rate of C/100 in the potential range between 2.7 and 4.0 V, as such, the voltage profile should provide a close approximation to the open-circuit voltage (OCV) [58]. The initial open circuit voltage of the film is 2.7 V and it is cycled between 4.0 and 2.7 V. The LiMn<sub>2</sub>O<sub>4</sub> film grown at 700 °C has interesting electrochemical properties for the microbattery application. In the high voltage region, such a cell delivered a specific capacity of 133 mC/μm cm<sup>2</sup>.

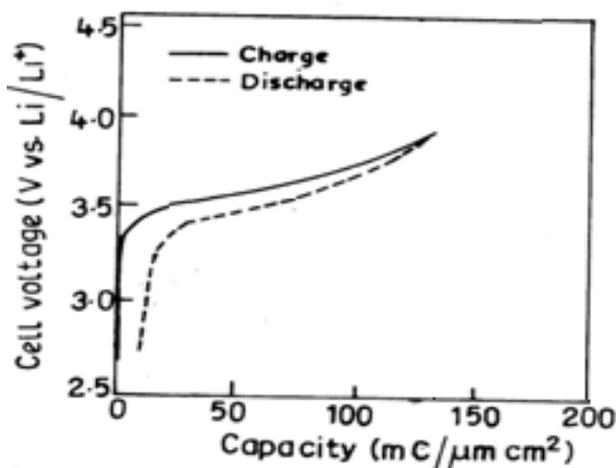


Figure 4: Charge - discharge profile of Li/LiMn<sub>2</sub>O<sub>4</sub> cell

### CONCLUSION

LiMn<sub>2</sub>O<sub>4</sub> thin films were grown using the pulsed laser deposition technique, in which the control of the deposition parameters promotes the film stoichiometry. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. The microstructural properties of the films have been investigated as a function of deposition conditions, which play important roles in the physical and chemical characteristics of the material. Cyclic voltammetry measurements have been carried out at sweep rate  $\alpha = 1 \text{ mVs}^{-1}$ . Electrochemical titration was made by charging and discharging the cells in the potential range between 2.5 and 4.0 V. Specific capacity as high as 133 mC/cm<sup>2</sup>μm was measured for the film grown at 700 °C. This performance is due to the good crystallinity of the LiMn<sub>2</sub>O<sub>4</sub> films grown by PLD technique. These results suggest that the open and porous structured LiMn<sub>2</sub>O<sub>4</sub> PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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