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Research Article

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Microstructural and Electrochemical Studies on Laser Ablated $LiNiO_2$ Thin Films

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ABSTRACT

Thin films of $LiNiO_2$ were prepared by pulsed laser deposition technique and the properties were studied in relation to the deposition parameters. 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 Li/Ni ratio has been studied as a function of the substrate temperature. The films prepared in the substrate temperature range 300-700 ^{0}C were found to be nearly stoichiometric. The electrochemical measurements were carried out on Li//$LiNiO_2$ cells with a lithium metal foil as anode and $LiNiO_2$ film as cathode of 1.5 cm^2 active area using a Teflon home-made cell hardware. The Li//$LiNiO_2$ cells were tested in the potential range 2.6 – 4.0 V. Specific capacity as high as 200 $mC/cm^2\mu m$ was measured for the film grown at 700 ^{0}C. The growth of $LiNiO_2$ films were studied in relation to the deposition parameters for their effective utilization as cathode materials in solid state microbattery application.

Keywords: $LiNiO_2$ thin films, PLD, Composition, SEM, TEM and Electrochemical properties.

INTRODUCTION

Rechargeable lithium batteries are widely used in portable electronic devices, such as cell phones and computer notebooks, and their usage promises to increase even further as new applications for them develop [1, 2]. Both the lightest of all metals and the one with the highest standard reduction potential, lithium promises high energy density when used as the anode material in rechargeable battery architecture. Lithium batteries can typically be made small-sized, are low-maintenance and can be made to function without memory effects or the requirement for scheduled cycling to prolong battery life. Layered lithium metal oxides such as $LiCoO_2$ and $LiNiO_2$ have been of great interest as cathode materials for secondary lithium batteries. Presently $LiNiO_2$ has been intensely investigated because of its comparatively low cost, less toxicity, lower price, large reversible capacity and environmental advantages over $LiCoO_2$ [3, 4]. However, it still has problems, i.e., irreversible phase transformation, difficulty in synthesis and safety concerns, which need to be settled for the wider usage in practical lithium batteries. The discharge capacity of $LiNiO_2$ measured experimentally was certified to have about 140 -150 mAh g^{-1} due to the synthesis of non-stoichiometric $LiNiO_2$ [5]. In the fully charging state, Li_xNiO_2 with low lithium content ($x < 0.3$) is unstable and might generate oxygen, which would trigger the exothermic oxidation reaction of electrolyte, resulting in safety problem and particle fracture. Lithium ions may be inserted or extracted with accompanying reduction or oxidation of nickel. Electrochromic switching in LiNiO materials involves the Ni^{3+} (dark)/Ni^{2+} (transparent) redox couple. Thus, the nickel ions must be at or near an average oxidation state of '2' when the films are bleached. Assuming the absence of oxide ion vacancies, this requires insertion of more lithium ions than there are vacancies in the nickel sites. The additional lithium ions presumably occupy tetrahedral sites, which may give them lower mobility. This may take place during the formatting process, which involves some irreversible insertion of lithium.

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 [6]. 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 [7-15]. 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 [16, 17].

The nickel containing lithium metal oxides, however, are more problematic. Formally, nickel is Ni^{3+} in stoichiometric $LiNiO_2$. However, an octahedrally coordinated Ni^{3+} presents a d^7cation that is not particularly stable in the solid state [18]. Two different descriptions of the nickel cation in $LiNiO_2$ have emerged in response to this. In one, the cation is assumed to be Ni^{3+}, a d^7 species that undergoes Jahn-Teller distortion somewhat ameliorating the poor stability of a d^7 octahedral cation. The lattice oxygen should formally remain O_2 − for this system, although depending upon the amount of the distortion, the charge transfer overlap between Ni 3d and O 2p could be affected, which should manifest itself by a change in the Ni 2p satellite structure.

The second model creates a localized Ni^{2+}- O^{1-} charge-transfer pair, producing a “NiO” like octahedral Ni^{2+} and relatively electron-poor lattice oxygen. Similar to $LiCoO_2$, $LiNi_xCo_yMn_{1-x-y}O_2$ generally exhibits a well defined α-$NaFeO_2$ layered structure (Figure 1), which is hexagonal crystalline and indexed as R-3m space group.

PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [19]. 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. Figure 2 shows the schematic diagram of the pulsed laser deposition chamber.

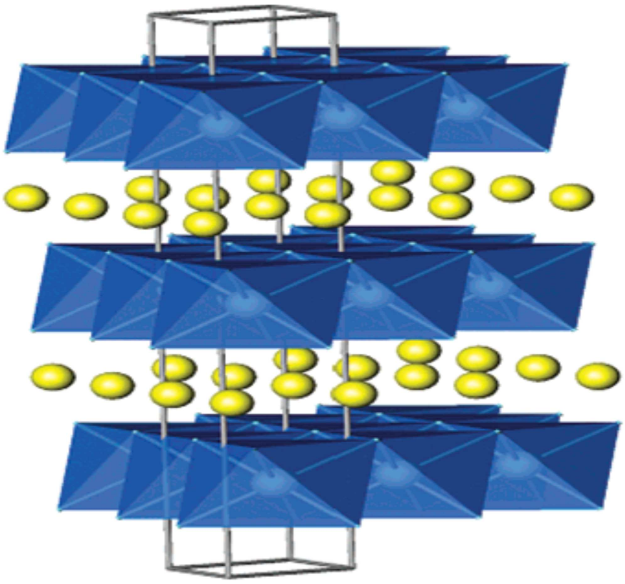

Figure 1: Layered structure of $LiNiO_2$ showing the lithium ions between the transition- metal oxide

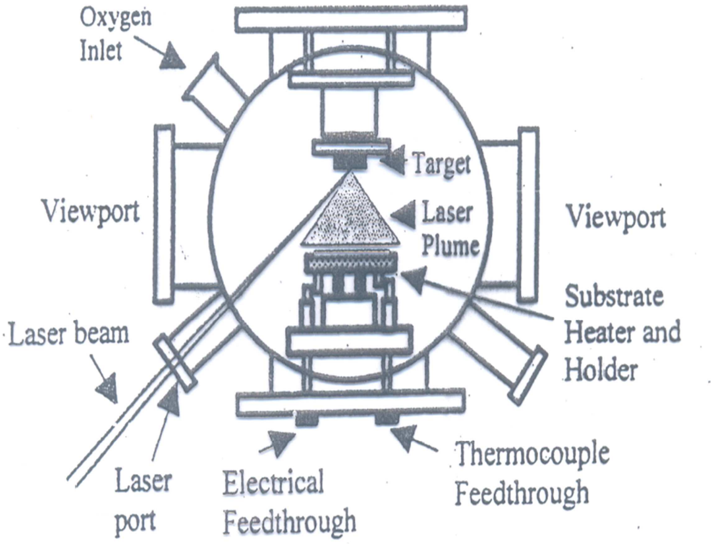

Figure 2 Schematic diagram of the pulsed laser deposition chamber

In thin film deposition, the substrate temperature plays the important role of determining the morphology of films. We have also studied other materials like CdTe, ZnSe and CdSe nanopolymers are of great industrial interest for developing photoluminescence based biomedical labeling reagents [20-23]. 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 [24-40]. In this study, we have deposited $LiNiO_2$ thin films on silicon substrates and investigated the microstructural and electrochemical properties of these thin films.

EXPERIMENTAL SECTION

$LiNiO_2$ thin films were grown by pulsed laser deposition technique on silicon substrates maintained. PLD target was prepared by sintering a mixture of high purity $LiNiO_2$ and Li_2O powders (Cerac products) with excess of lithium i.e. Li/Ni > 1.0 by adding Li_2O to compensate the loss of lithium during the deposition. The mixture was crushed, pressed and sintered at 800 ^oC 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 Jcm^{-2}. The target substrate distance was 4 cm [41-69]. 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 $LiNiO_2$ 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 $Li/LiNiO_2$ cells with lithium metal foil as anode and a $LiNiO_2$ film as cathode of 1.5 cm^2 active area using 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 $LiClO_4$ dissolved in propylene carbonate. Cyclic voltammetry measurements have been carried out at sweep rate α = 1 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 2.6 and 4.0 V. Quasi open-circuit voltage profiles were recorded using current pulses of 5 μAcm^{-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 $LiNiO_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of $LiNiO_2$ films are 250 nm. The influence of oxygen partial pressure (pO_2) and deposition temperature (T_s) on the microstructural properties were systematically studied. The chemical compositional studies made on $LiNiO_2$ films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

Composition

Composition of the $LiNiO_2$ thin films deposited on silicon wafers was determined from the Rutherford backscattering spectroscopic analysis. The Li/Ni ratio has been studied as a function of the substrate temperature. The films prepared in the substrate temperature range 300-700 ^{0}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 $LiNiO_2$ film grown in oxygen partial pressure pO_2 = 100 mTorr on silicon wafers maintained at 700 ^{o}C is shown in Figure 3. The SEM micrograph of film grown at 700 ^{o}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 ^{o}C is 165 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 [70, 71]. TEM measurements were performed to confirm the crystalline nature of the samples and to study the morphology of the particles. The TEM images of $LiNiO_2$ thin films are depicted in Figure 4. The particles are more or less uniformed in size and of irregular shape.

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.

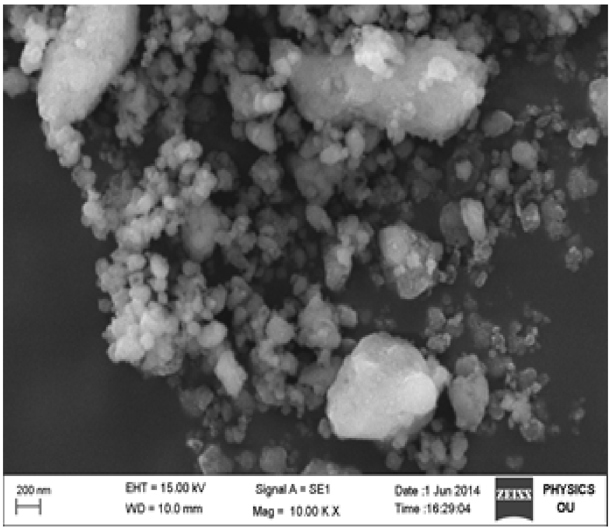

Figure 3: SEM image of LiNiO2 thin film deposited at 700 oC in pO2 = 100 m Torr

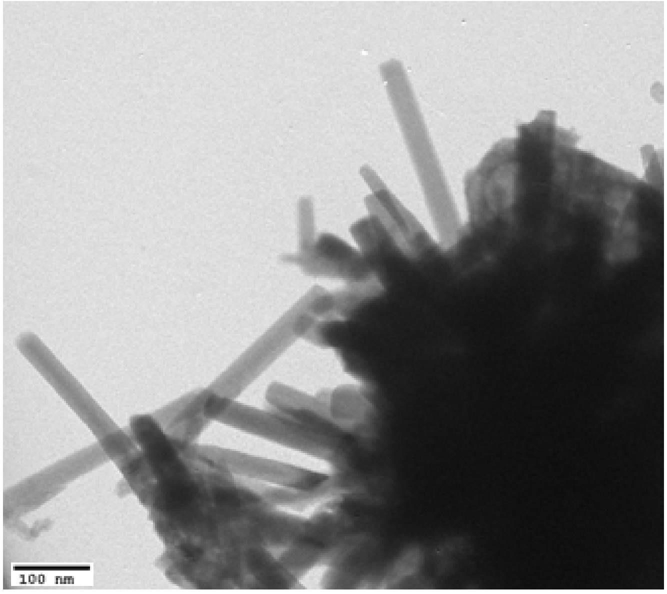

Figure 4: TEM image of LiNiO2 thin film deposited at 700 oC in pO2 = 100 m Torr

Electrochemical properties

Figure 5 shows the cyclic voltammogram for a Li//$LiNiO_2$ cell with a film grown at temperature 700 ^oC 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 3.78 and 3.68 V for the $LiNiO_2$ film. These CV features are associated with the redox process of Ni^{2+} to Ni^{3+} and vice-versa, when lithium is extracted from, and inserted into the Li_xNiO_2 phase. The redox couple with a mid peak potential of about 3.73 V is considered to be a single phase insertion/deinsertion reaction of lithium ions in $LiNiO_2$.

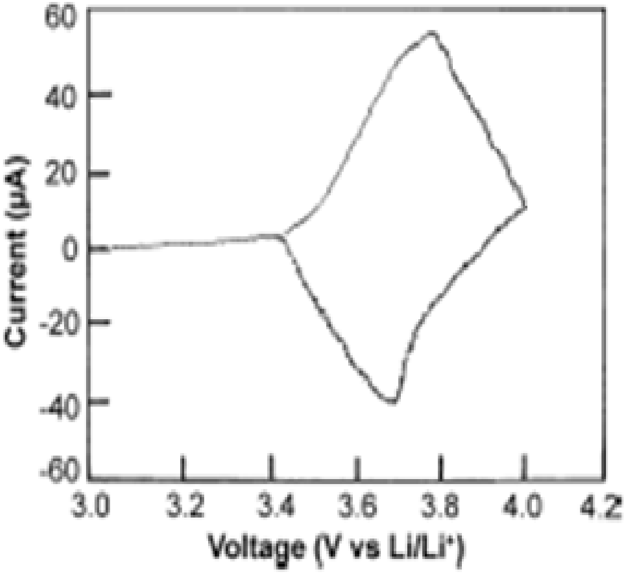

Figure 5: Cyclic Voltammogram of Li//$LiNiO_2$ cell deposited at 700 ^oC in pO_2 = 100 m Torr

Figure 6 shows the typical charge – discharge curves of Li//$LiNiO_2$ cells using pulsed laser deposited film grown at temperature 700 ^oC in an oxygen partial pressure of 100 mTorr. The electrochemical measurements were carried out on Li//$LiNiO_2$ cells with a lithium metal foil as anode and a polycrystalline film as cathode of 1.5 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 $LiClO_4$ 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 2.6 and 4.0 V, as such, the voltage profile should provide a close approximation to the open-circuit voltage (OCV) [72]. The initial open circuit voltage of the film is 2.6 V and it is cycled between 4.0 and 2.6 V. The $LiNiO_2$ film grown at 700 ^oC has interesting electrochemical properties for the microbattery application. In the high voltage region, such a cell delivered a specific capacity of 200 mC/μm cm^2.

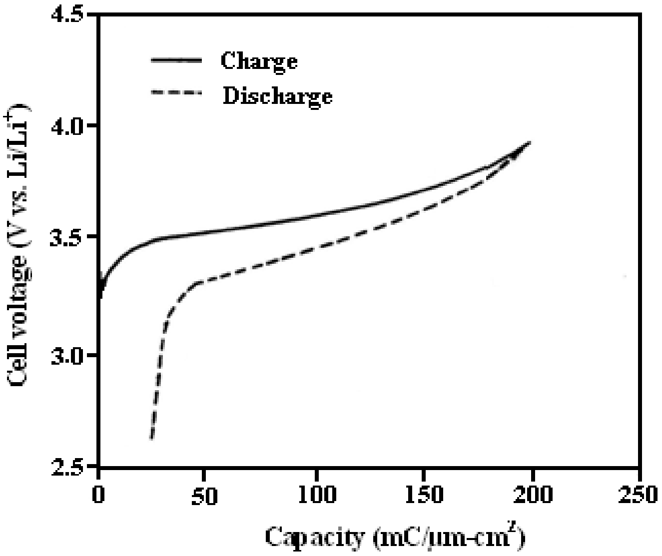

Figure 6: Charge - discharge profile of Li//$LiNiO_2$ cell

CONCLUSION

$LiNiO_2$ 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 α =1 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 200 mC/cm^2μm was measured for the film grown at 700 ^oC. This performance is due to the good crystallinity of the $LiNiO_2$ films grown by PLD technique. These results suggest that the open and porous structured $LiNiO_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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