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Structural and electrochemical studies on thin film $LiNi_{0.8}Co_{0.2}O_2$ by PLD for micro battery

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ABSTRACT

Thin film of $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) has been prepared by Pulsed Laser Deposition (PLD) technique at various post annealing temperatures. XRD results of LNCO thin film deposited on both Pt and Si substrates reveal relatively good crystalline nature at 500 °C which is in good agreement with the electrochemical results. ICP-AES composition analysis indicates 10 to 5% Li loss in the post annealed (400–700 °C) LNCO/Pt thin films; however the as prepared LNCO/Pt films show 17% excess of Li which are comparable with the LNCO target results. SEM analysis indicates phase separation at 600 °C and porous nature at 700–800 °C for LNCO/Pt films. Cyclic voltammetry (CV) scans of $LiNi_{0.8}Co_{0.2}O_2$ film post annealed at 500 °C show a pair of main cathodic and anodic peaks at 3.64 and 3.4 V, respectively with a narrow peak separation reveals good stability upon cycling. Whereas the LNCO films annealed at 600 °C and 700 °C indicate an additional anodic peak at lower potential besides a pair of major peaks which may be due to the phase separated morphology as evidenced from SEM analysis. Based on the structural and electrochemical results, a lithium-ion micro cell has been constructed with LNCO/$Li_{3.4}V_{0.6}Si_{0.4}O_4$(LVSO)/SnO configuration with the thickness of 1.535 μm and its electrochemical properties have been studied.

1. Introduction

Thin film lithium or lithium ion micro batteries have received a lot of attention due to their potential application as backup power in micro electromechanical systems (MEMS), smart card, micro sensors, and biochips [1–3]. Recently many researches have focused on lithiated transition metal oxides of layered structure [4–6] such as $LiCoO_2$, $LiNiO_2$ and $LiNi_{1-x}Co_xO_2$, spinel structure ($LiMn_2O_4$) [7] and phospho olivine structured $LiFePO_4$, $LiCoPO_4$ [8,9] as cathode materials for thin film batteries. Among the various cathode materials, the lithiated oxides $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) are of great interest for use as positive electrodes in rechargeable lithium- ion batteries because of their high specific capacity, high voltage and long cycle-life. These compounds crystallize with the layered α-$NaFeO_2$ structure ($R\bar{3}\,m$ symmetry) in which Li^+ and Ni^{III}, Co^{III} cations fill alternately the octahedral sites in the oxygen cubic close packing [10]. The theoretical gravimetric capacity of a fully dense $LiNi_{0.8}Co_{0.2}O_2$ is 274 mAh g^{-1} when all Li ions are extracted from the host lattice [11]. Recently thin films of $LiNi_{1-x}Co_xO_2$ have been fabricated by RF sputtering [12], laser ablation [11,13], electron beam evaporation [14] and sol- gel method [15] but some of the films have suffered from a low discharge capacity. Recently Wang et al. [13] used PLD technique to grow $LiNi_{0.8}Co_{0.2}O_2$ films on Ni substrate which yields discharge capacity of 60 μAh/cm^2μm with good capacity retention. Kim et al. [12] reported discharge capacity of 61 μAh/cm^2μm for 90% dense $LiNi_{0.5}Co_{0.5}O_2$ film grown on Pt/Ti/SiO_2/Si (100) using lithium rich target by RF magnetron sputtering. Ramana et al. [11] have reported 83 μAh/cm^2μm for $LiNi_{0.8}Co_{0.2}O_2$ films grown on Ni substrates at $T_s = 450$ °C by PLD from lithium rich target. Most of these thin films were fabricated by using lithium rich targets in order to avoid lithium loss during deposition. Even though many researches have been carried out on LNCO thin films, researches about the micro cells based on $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) thin films and its electrochemical properties are scarce. Many researches indicate Pulsed Laser Deposition (PLD) is one of the best techniques to obtain stoichiometric thin films [16–18]. Even though, in PLD technique, there are many parameters such as oxygen pressure, laser power, distance between target and substrate, deposition duration and post or in-situ annealing temperatures which mainly define the structure and stoichiometry retaining of thin films from the host target material.

In the present investigation, an attempt has been done to prepare crystalline $LiNi_{0.8}Co_{0.2}O_2$ thin films on the Pt and Si substrates by PLD at different post annealing temperatures. The composition of LNCO has been confirmed by ICP-AES analysis. The structural and electrochemical properties of the post annealed LNCO thin films grown with fixed deposition parameters have been studied by XRD, SEM and electrochemical cyclic voltammetry (CV) and compared to investigate the

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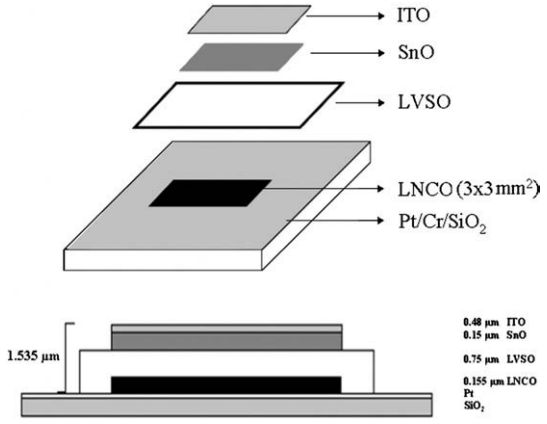

Scheme 1. Schematic representation of the thin film micro cell.

profound nature of LNCO to construct micro batteries. Based on the structural and electrochemical results, a lithium-ion micro battery has been constructed with LNCO/$Li_{3.4}V_{0.6}Si_{0.4}O_4$(LVSO)/SnO on Pt coated SiO_2 substrate and its electrochemical properties have been studied.

2. Experimental analysis

$LiNi_{0.8}Co_{0.2}O_2$ thin films have been grown on both Pt and Si (111) substrates by PLD with Nd:YAG 4ω 266 nm laser beam of power 40 to 50 mJ/pulse with 10 Hz repetition rate from $LiNi_{0.8}Co_{0.2}O_2$ stoichiometric target. Prior to deposition, the chamber is made vacuum below 4.5×10^{-5} Pa pressure. The chamber is filled with oxygen of desired pressure (P_{O_2}) 2.14×10^{-1} Pa and then pre laser ablated for about five minutes to remove the contaminants from the target surface and sustain a steady state plume. The target has been prepared by Modified Polymerizable Pechini Method from solution of $LiNO_3$, Co $(NO_3)_2 6H_2O$ and $Ni(NO_3)_2 6H_2O$ powders esterified with citric acid: ethylene glycol (1:4) at 150 °C. After pyrolysis at 350 °C, the powder precursor is calcinated at 900 °C for 2 h in air. $LiNi_{0.8}Co_{0.2}O_2$ formation has been confirmed with ICP and XRD measurements and the powder sample is isotactically pressed at 28 MPa/cm^2 to a target with 23.4 mm diameter. The final target is formed by sintering at 800 °C for 8 h with (3.6 g cm^{-3}) 75% of theoretical density. All the films are deposited for 40 min duration with same laser power at ambient temperature. The as deposited thin films show amorphous structure which are post annealed at temperatures ranging from 400 to 800 °C with oxygen atmosphere for 30 min and the structural properties have been studied. The thickness of the LNCO grown on SiO_2 has been measured by surface profilometer (Kosaka Lab, SE-3000). Thickness measurements of all the LNCO thin films grown on SiO_2 substrates for 40 min duration indicate thickness ranging from 110–120 nm with large experimental error of ±50 nm. XRD measurements have been carried out at 0.5°/min with Rigaku XRD-6000 equipped with a Cu-Kα source to observe the crystal structure of all thin films. The composition of LNCO target and LNCO/Pt thin films have been confirmed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) measurements by using Perkin Elmer Optima 3300 spectroscope. FE-SEM measurements have been carried out for all the films by using LEO-982 at different magnitudes.

The LNCO films grown on Pt substrate (8×8 mm^2) have been used for electrochemical measurements. The mass of thin film is measured by weighing the film before and after deposition. The deposition rate has been found to vary from 2 nm/min to 3.8 nm/min for laser power 40 to 50 mJ/pulse, respectively. For electrochemical measurements, a three electrode beaker cell has been constructed with LNCO/Pt thin film placed in 1 M $LiClO_4$ in propylene carbonate (PC) (Kishida Chem) solution and Li metal for the counter and reference electrodes. This beaker cell is scanned between 3.0 V to 4.2 V versus Li/Li$^+$ with sweep rate of 10 to 30 mV/min by using a Hokuto Denko HSV 100. Thin film micro cell has been fabricated with ITO/SnO/LVSO/LNCO/Pt/Cr/SiO_2

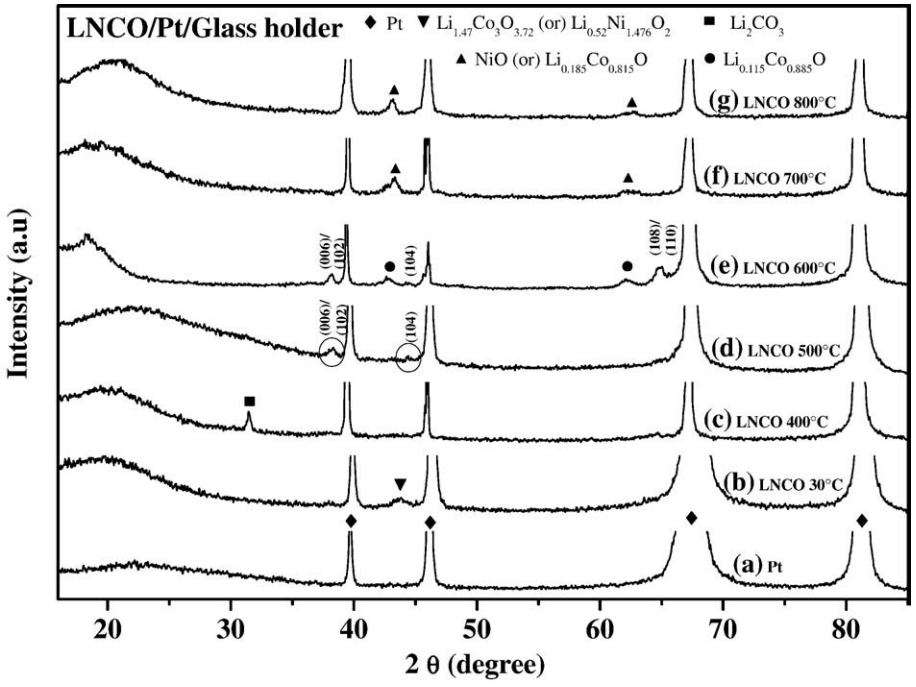

Fig. 1. (a-g). XRD patterns of $LiNi_{0.8}Co_{0.2}O_2$ thin films grown on Pt substrates by PLD at various post annealing temperatures.