

Effect of target composition on the growth of stoichiometric LiCoO_2 , $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films

M. C. RAO

Department of Physics, Andhra Loyola College, Vijayawada – 520008, India

Thin films of LiCoO_2 , $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ 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. The composition of the experimental films was analyzed using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). The binding energy peaks of $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ are observed at 779.3 eV and 794.4 eV which can be attributed to the Co^{3+} bonding state of LiCoO_2 . The energy separation (ΔE) of the spin orbit splitting of Cobalt 2p levels is 15.1 eV. The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the LiCoO_2 films deposited in an oxygen partial pressure of 100 mTorr and at different substrate temperatures indicated that the films are nearly stoichiometric. The $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films prepared in the substrate temperature range 500-700 °C were found to be nearly stoichiometric.

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1. Introduction

Due in large part to high-energy storage capacity, LiCoO_2 is the prototypical positive electrode material for lithium ion batteries. The increasing interest of LiCoO_2 thin films comes both from the technological application in all-solid-state microbatteries and the fundamental studies of lithium intercalation process into the oxide matrix [1, 2]. LiCoO_2 crystallizes in the layered rock-salt $\alpha\text{-NaFeO}_2$ type structure with hexagonal lattice parameters $a = 2.815 \text{ \AA}$ and $c = 14.049 \text{ \AA}$ [1]. The rock salt LiCoO_2 lattice consists of a close packed network of oxygen ions with lithium and cobalt ions on alternating (111) planes of the cubic rock salt sublattice. The Co and Li cations occupy the octahedral 3a and 3b sites, respectively, while oxygen anions are located on the 6c sites. The CoO_6 octahedra are shared edges to form CoO_2 sheets and Li ions can move in two dimensional (2-D) directions between the CoO_2 slabs.

LiCoO_2 is considered to have high specific density, high voltage, long cycle life and good reversibility for lithium intercalation – deintercalation process. It is easy to prepare but its high cost and toxicity remain problems to be solved. Preparation of titanium doped LiCoO_2 films may have advantages from a point of view of fundamental studies (because it is a binder free material with a well-defined interfacial area) and of the emerging field of microbatteries as well. Intensive investigations have been carried out on doped $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ oxides (M = Mn, Cr, Al, Ti, B, Mg, etc.), which show interesting structural and electrochemical properties. Doping with non-transition metals such as titanium and nickel has gained increasing interest for the following reasons: (1) the low cost and low

toxicity, (2) the fact that titanium and nickel substitutions for transition metal oxides leads to higher lithium intercalation voltages, (3) the titanium and nickel doping stabilizes the layered structure and extends the cyclability and enhances the capability of the electrochemical cells. The growth of LiCoO_2 thin films with preferred orientation is known to be crucial. Various aspects of LiCoO_2 thin films prepared by RF sputtering [3, 4], pulsed laser deposition [4-8], electrostatic spray [9], and chemical vapour deposition [10], have been reported.

PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [11]. 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. Preliminary investigations on pulsed laser deposited LiCoO_2 thin films were carried out by Julien et al., [5]. Iriyama et al., [6] prepared thin films of LiCoO_2 by PLD and studied the electrochemical performance. However the investigations on the Raman spectroscopic features of the films that are essentially depend upon the deposition parameters give a scope for effective utilization of these thin films in the fabrication of microbatteries. In this paper, we present compositional studies of LiCoO_2 , $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited on silicon substrates using the PLD technique from a sintered target.

2. Experimental

LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ thin films were grown by pulsed laser deposition technique on silicon substrates. LiCoO₂ target was prepared by sintering a mixture of high purity LiCoO₂ and Li₂O powders (Cerac products) with excess of Li i.e. Li/Co > 1.0 by adding Li₂O. The mixture was crushed and pressed at 5 tons.cm⁻² to make tablets of 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800 °C. 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 target substrate distance was 4 cm. 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 LiCoO₂ thin films was analyzed using X-ray photoelectron spectroscopy. The composition of the LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ thin films were analyzed using Rutherford backscattering spectroscopy. X-ray photoelectron spectroscopy is also known as electron spectroscopy for chemical analysis (ESCA) is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy of the emitted electrons. Mg K_α X-rays (1253.6 eV) or Al K_α X-rays (1486.6 eV) are ordinarily used. These photons have limited penetrating power in solid. They interact with atoms in this surface region causing electron emission as per the photoelectric effect. The emitted electrons have kinetic energies given by the relation,

$$KE = hv - BE - q \phi_{sp} \quad (1)$$

Where hv is the energy of the photon, BE is the binding energy of the atomic orbital from which the electron originates, and $q \phi_{sp}$ the work function of the spectrometer. The kinetic energy of the escaping photoelectrons limits the depth from which it can emerge, giving XPS as high surface sensitivity with sampling depth of a few nanometers. Photoelectrons are collected and analyzed by the instrument to produce a spectrum of emission intensity versus electron binding energy. Since each element has a unique set of binding energies, XPS can be used to identify the elements on the surface. Also, peak areas at nominal binding energies can be used to quantify concentration of the elements. Small shifts in these binding energies (chemical shifts) provide powerful

information about sample chemical states and short range chemistry.

3. Results and discussion

Pulsed laser deposited LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ thin films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ thin films are 250 nm. The influence of oxygen partial pressure (p_{O_2}) and deposition temperature (T_s) on the compositional studies were systematically studied. The chemical compositional studies made on LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ thin films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

3.1 LiCoO₂ thin films

A typical X-ray photoelectron spectra of LiCoO₂ thin films deposited at 700 °C and in an oxygen partial pressure of 100 mTorr is shown in Fig. 1. The binding energy peak position of lithium, cobalt and oxygen are evidenced in the XPS spectra. There is no sign of broadening or splitting of the peaks. The binding energy peaks of Co(2p_{3/2}) and Co(2p_{1/2}) are observed at 779.3 eV and 794.4 eV which can be attributed to the Co³⁺ bonding state of LiCoO₂ and are in good agreement with the previous results [12]. The energy separation (ΔE) of the spin orbit splitting of Cobalt 2p levels is 15.1 eV. The binding energy of lithium is at 54.0 eV indicating that the lithium atoms are in an octahedral environment of oxygen atoms. The oxygen O(1s) core level was observed at 530.5 eV. The Li/Co ratio estimated from ICP-AES data for these films is found to be 1:1. The intensity of core level binding energy peak of Co(2p) decreased for the films deposited at lower substrate temperatures. However the peak positions are observed to be similar except the broadening of the binding energy peaks. These results indicated that there is no severe variation in the composition of the films deposited in the temperature range 300 – 700 °C.

The composition of films was found to be a strong function on oxygen partial pressure. A shift in Co(2p_{3/2}) towards higher energy value was observed with a reduction in the energy separation (ΔE) of spin orbit splitting of Co(2p) levels was observed for the films formed at lower oxygen partial pressures (< 100 mTorr). The oxygen to cobalt ratio for the films deposited at lower oxygen partial pressures decreased and found to be 1.76 for the films formed at an oxygen partial pressure of 50 mTorr. The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the LiCoO₂ films deposited in an oxygen partial pressure of 100 mTorr and in the substrate temperature range 300-700 °C indicated that the films are nearly stoichiometric.

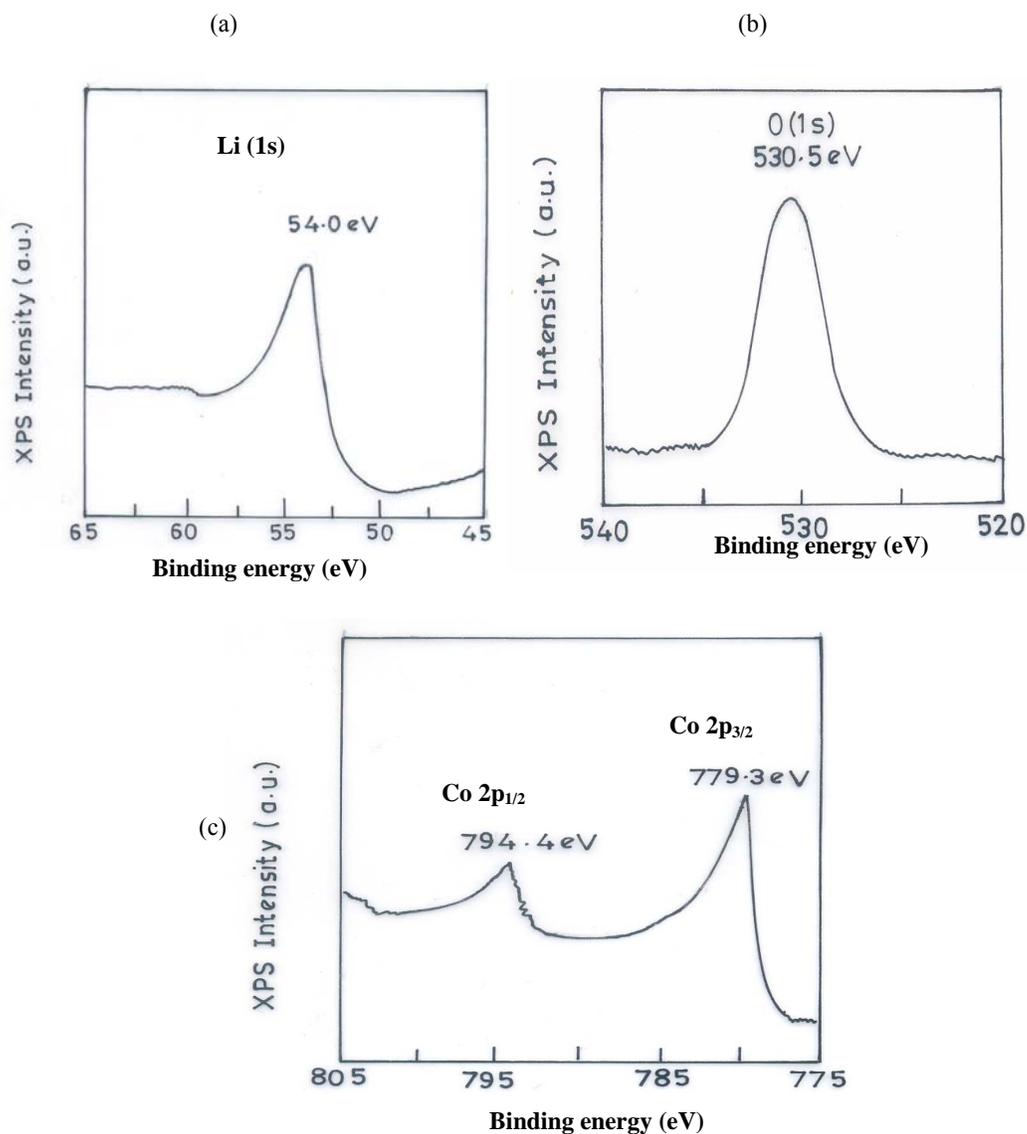


Fig. 1. The XPS binding energy core levels of (a) Li (1s) (b) O (1s) (c) Co (2p_{3/2}) and Co (2p_{1/2}).

3.2 $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin films

$\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin films were prepared by sintering a mixture of high purity LiCoO_2 and Ti powders with excess of Li i.e., $\text{Li/Co} + \text{Ti} = 1.1$ by adding Li_2O . Composition of the $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited on silicon wafers was determined from the Rutherford backscattering spectroscopic analysis. The Li/Co ratio has been studied as a function of the substrate temperature (T_s) as shown in Fig. 2. The films prepared in the substrate temperature range 500-700 °C were found to be nearly stoichiometric.

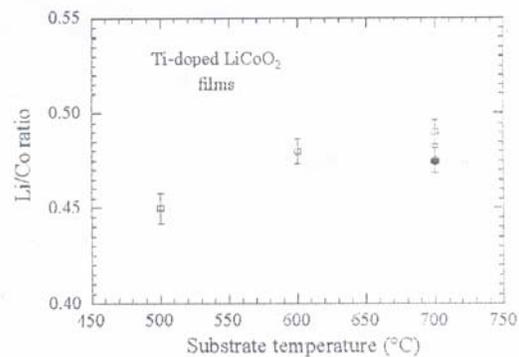


Fig. 2. RBS data of the Li/Co ratio for $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited at different substrate temperatures in the range 500-700 °C.

3.3 LiNi_xCo_{1-x}O₂ thin films

LiNi_xCo_{1-x}O₂ thin films were prepared by sintering a mixture of high purity LiCoO₂ and Ni powders with excess of Li i.e., Li/Co + Ni = 1.2 by adding Li₂O. Composition of the LiNi_xCo_{1-x}O₂ thin films deposited on silicon wafers was determined from the Rutherford backscattering spectroscopic analysis. The Li/Co ratio has been studied as a function of the substrate temperature (Ts) as shown in Fig. 3. The films prepared in the substrate temperature range 500-700 °C were found to be nearly stoichiometric.

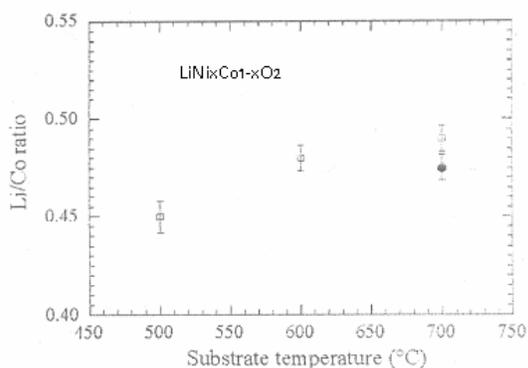


Fig. 3. RBS data of the Li/Co ratio for LiNi_xCo_{1-x}O₂ thin films deposited at different substrate temperatures in the range 500-700 °C.

4. Conclusions

Thin films of LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ were prepared by pulsed laser deposition. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. The binding energy peaks of Co(2p_{3/2}) and Co(2p_{1/2}) are observed at 779.3 eV and 794.4 eV which can be attributed to the Co³⁺ bonding state of LiCoO₂. The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the LiCoO₂ films deposited in an oxygen partial pressure of 100 mTorr and in the substrate temperature range 300-700 °C indicated that the films are nearly stoichiometric. The LiTi_xCo_{1-x}O₂

and LiNi_xCo_{1-x}O₂ films prepared in the substrate temperature range 500-700 °C were found to be nearly stoichiometric. These results suggest that the open and porous structured LiCoO₂, LiTi_xCo_{1-x}O₂ and LiNi_xCo_{1-x}O₂ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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*Corresponding author: raomc72@gmail.com