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## Compositional studies on laser ablated LiCoO<sub>2</sub> thin films

M.C.Rao

Department of Physics, Andhra Loyola College, Vijayawada - 520 008, (INDIA)

E-mail : raome72@gmail.com

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### ABSTRACT

Thin films of LiCoO<sub>2</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. The composition of the experimental films was analyzed using X-ray photoelectron spectroscopy (XPS). The binding energy peaks of Co(2p<sub>3/2</sub>) and Co(2p<sub>1/2</sub>) are observed at 779.3eV and 794.4eV which can be attributed to the Co<sup>3+</sup> bonding state of LiCoO<sub>2</sub>. The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the LiCoO<sub>2</sub> 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 FTIR displayed the characteristic IR dominant bands at 250 and 554cm<sup>-1</sup> for LiCoO<sub>2</sub>. © 2010 Trade Science Inc. - INDIA

### KEYWORDS

LiCoO<sub>2</sub> thin films;  
PLD;  
Compositional;  
FTIR.

### INTRODUCTION

Lithiated transition metal oxides such as LiMO<sub>2</sub> (Where M = Co, Ni, Mn etc.) have received considerable attention in recent years as high voltage positive electrode materials for use in secondary lithium batteries<sup>[1]</sup>. Among these, the high cycling stability and high cell potential against lithium makes LiCoO<sub>2</sub> an attractive cathode material in the fabrication of all solid state rechargeable microbatteries<sup>[2,3]</sup>. Its theoretical specific capacity and energy densities are 274mAh/g and 1070Wh/kg respectively.

The layered LiCoO<sub>2</sub> consists of a close packed network of oxygen ions with Li and Co ions on alternative (111) planes of the cubic rocksalt sub-lattice. The edges of CoO<sub>6</sub> octahedral were shared to form CoO<sub>2</sub> sheets and lithium ions can move in two-dimensional directions between CoO<sub>2</sub> sheets. Thus the layered LiCoO<sub>2</sub> has an anisotropic structure and thereby electrochemi-

cal lithium insertion / extraction behaviour must depend strongly on the orientation of the microcrystallites. The growth of LiCoO<sub>2</sub> thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as RF sputtering<sup>[2,4]</sup>, pulsed laser deposition<sup>[4-8]</sup>, electrostatic spray deposition<sup>[9]</sup> and chemical vapour deposition<sup>[10]</sup> were employed for the growth of LiCoO<sub>2</sub> thin films. A brief literature survey reveals that it is difficult to grow stoichiometric and stable c -axis oriented LiCoO<sub>2</sub> thin films by several physical vapour deposition methods due to many growth kinetic processes which occur in vacuum or at low oxygen partial pressures.

Pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films<sup>[11]</sup>. 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

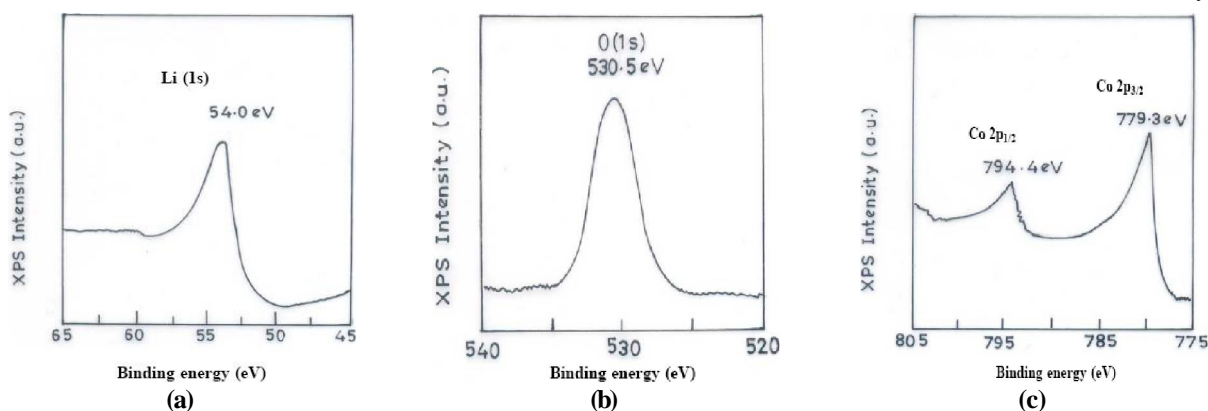


Figure 1 : The XPS binding energy core levels of (a) Li (1s) (b) O (1s) (c) Co ( $2p_{3/2}$ ) and Co ( $2p_{1/2}$ )

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  $\text{LiCoO}_2$  thin films were carried out by Julien et al.<sup>[5]</sup>, Iriyama et al.<sup>[6]</sup> and studied the electrochemical performance. They observed that the reactivity in single-phase region at potentials more positive than 4.0V was lower than that of randomly oriented films. Poly-crystalline layered  $R\bar{3}m$  phase thin films of  $\text{LiCoO}_2$  were grown by PLD using Nd:YAG laser by Julien et al.<sup>[12]</sup>. This  $\text{LiCoO}_2$  cathode active films were found to deliver a specific capacity of  $195\text{mC}/\text{cm}^2\mu\text{m}$  in the voltage range 2.0-4.2V. In the present study the influence of deposition parameters on the Compositional and FTIR studies of pulsed laser deposited  $\text{LiCoO}_2$  thin films were reported.

## EXPERIMENTAL

$\text{LiCoO}_2$  films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 200-700°C.  $\text{LiCoO}_2$  target was prepared by sintering a mixture of high purity  $\text{LiCoO}_2$  and  $\text{Li}_2\text{O}$  powders (Cerac products) with excess of Li i.e.  $\text{Li}/\text{Co} > 1.0$  by adding  $\text{Li}_2\text{O}$ . The mixture was crushed and pressed at  $5\text{ tonns}/\text{cm}^2$  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 experi-

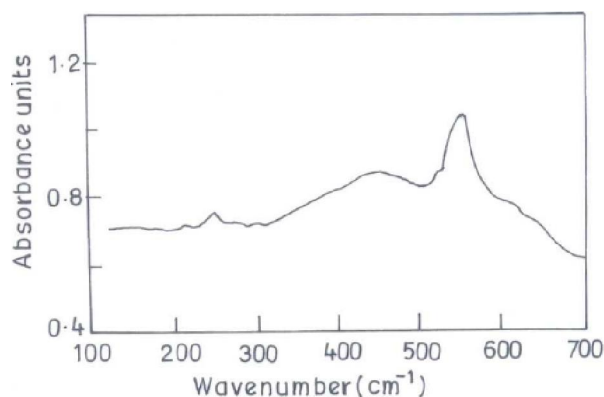
ments is the 248nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was  $1\times 3\text{ mm}$  and the energy 300mJ. The target substrate distance was 4 cm. The deposition temperature was maintained with thermocouple 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 experimental films was analyzed using X-ray photoelectron 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  $K_\alpha$  X-rays (1253.6eV) or Al  $K_\alpha$  X-rays (1486.6eV) 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,

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

where  $h\nu$  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 quan-

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**Figure 2 :** FTIR spectra of  $\text{LiCoO}_2$  deposited at  $700^\circ\text{C}$  in  $p\text{O}_2 = 100$  mTorr.

tify concentration of the elements. Small shifts in these binding energies (Chemical shifts) provide powerful information about sample chemical states and short range chemistry.

FTIR absorption spectra were recorded at room temperature using a Bruker IFS 113v interferometer. In the study region ( $100\text{-}1200\text{cm}^{-1}$ ), the spectrometer was equipped with a  $3.5\mu\text{m}$ -thick beam splitter, a globar source, and a DTGS/PE far -infrared detector. Samples were ground to fine powders painted onto polyethylene slabs. Data were collected in transmission mode at a spectral resolution of  $2\text{cm}^{-1}$  after several scans.

## RESULTS AND DISCUSSION

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

A typical X-ray photoelectron spectra of  $\text{LiCoO}_2$  thin films deposited at  $700^\circ\text{C}$  and in an oxygen partial pressure of  $100\text{mTorr}$  is shown in figure 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  $\text{Co}(2p_{3/2})$  and  $\text{Co}(2p_{1/2})$  are observed at  $779.3\text{eV}$  and  $794.4\text{eV}$  which can be attributed to the  $\text{Co}^{3+}$  bond-

ing state of  $\text{LiCoO}_2$  and are in good agreement with the previous results<sup>[13]</sup>. The energy separation ( $\Delta E$ ) of the spin orbit splitting of Cobalt  $2p$  levels is  $15.1\text{eV}$ . The binding energy of lithium is at  $54.0\text{eV}$  indicating that the lithium atoms are in an octahedral environment of oxygen atoms. The oxygen  $\text{O}(1s)$  core level was observed at  $530.5\text{eV}$ . The  $\text{Li/Co}$  ratio estimated from ICP-AES data for these films is found to be  $1:1$ . The intensity of core level binding energy peak of  $\text{Co}(2p)$  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  $300\text{-}700^\circ\text{C}$ .

The composition of films was found to be a strong function of oxygen partial pressure. A shift in  $\text{Co}(2p_{3/2})$  towards higher energy value was observed with a reduction in the energy separation ( $\Delta E$ ) of spin orbit splitting of  $\text{Co}(2p)$  levels was observed for the films formed at lower oxygen partial pressures ( $< 100\text{mTorr}$ ). 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  $50\text{mTorr}$ . The core level binding energy peak positions observed from XPS data and the estimated  $\text{Li/Co}$  ratio of the  $\text{LiCoO}_2$  films deposited in an oxygen partial pressure of  $100\text{mTorr}$  and in the substrate temperature range  $300\text{-}700^\circ\text{C}$  indicated that the films are nearly stoichiometric.

Experimental FTIR spectra of  $\text{LiCoO}_2$  thin films have been recorded at various stages of pulsed laser deposition.  $\text{LiCoO}_2$  possesses the  $R3m$  space group,  $D_{3d}^5$  spectroscopic symmetry. According to the results of the theoretical factor-group analysis, four modes are active in the infrared spectrum ( $2A_{2u}$  &  $2E_u$ ) of the  $\text{LiCoO}_2$  crystal<sup>[14]</sup>. The FTIR spectrum of  $\text{LiCoO}_2$  thin films deposited on silicon substrate maintained at temperature  $700^\circ\text{C}$  in an oxygen partial pressure  $p\text{O}_2 = 100\text{mTorr}$  displayed the characteristic IR dominant bands at  $250$  and  $554\text{cm}^{-1}$  for  $\text{LiCoO}_2$ . The former is attributed to the asymmetric stretching mode of the octahedral  $\text{LiO}_6$  units, while the latter is due to the asymmetric stretching vibration of  $\text{CoO}_6$  groups. FTIR features in good agreement with elemental analysis.

## CONCLUSIONS

Thin films of  $\text{LiCoO}_2$  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  $\text{Co}(2p_{3/2})$  and  $\text{Co}(2p_{1/2})$  are observed at 779.3eV and 794.4eV which can be attributed to the  $\text{Co}^{3+}$  bonding state of  $\text{LiCoO}_2$ . The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the  $\text{LiCoO}_2$  films deposited in an oxygen partial pressure of 100mTorr and in the substrate temperature range 300-700°C indicated that the films are nearly stoichiometric. The FTIR displayed the characteristic IR dominant bands at 250 and 554 $\text{cm}^{-1}$  for  $\text{LiCoO}_2$ . These results suggest that the open and porous structured  $\text{LiCoO}_2$  PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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