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Studies on the target conditioning for deposition of $LiCoO_2$ films

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ABSTRACT

Deposition of good quality thin films of Lithium Cobalt Oxide ($LiCoO_2$), by sputtering is preceded by target conditioning, which dictates the surface composition, morphology and electrochemical performance of the deposited film. Sputtering from a virgin target surface, results in films with excess of the more reactive elements. The concentration of these reactive elements in the films decreases until the system reaches a steady state after sufficient sputtering from the target. This paper discusses the deposition kinetics in terms of target conditioning of $LiCoO_2$. The composition, morphology and texturing of deposited film during various hours of sputtering were analyzed using X-ray photoelectron spectroscopy (XPS) and Field Emission Scanning electron microscopy (FESEM). The compositional stability is not observed in the films formed during the initial hours of sputtering from the fresh target, which becomes stable after several hours of sputtering. The Li and Co concentration in the films deposited subsequently is found to be varying and possible causes are discussed. After the compositional stability is reached, electrochemical analysis of $LiCoO_2$ thin films was performed, which shows a discharge capacity of 129 $\mu Ah/cm^2$.

1. Introduction

Lithium cobalt oxide ($LiCoO_2$) thin film electrodes have been found favorable for a reliable power source due to the superior properties in terms of cycle stability and energy density. RF-magnetron sputtering from a $LiCoO_2$ target results in preferential (110) out-of-plane crystallographic orientated thin films [1]. For high temperature stable phase of $LiCoO_2$ thin films, the films have to be deposited either with substrate biasing or heating during film deposition [2,3], or post-deposition annealing in oxygen ambient at about 700 °C [4,5]. HT-$LiCoO_2$ exhibits an ideal layered α-$NaFeO_2$ structure with alternating layers of Li and Co cations occupying in the octahedral interstices between the hexagonal stocked close-packed oxygen anions layers. The deposition parameters like Rf power, substrate-to-target distance, Ar:O_2 ratio influence the structural, morphological and electrochemical performance of the deposited $LiCoO_2$ thin films.

A new aspect of conditioning of a fresh multi-elemental target is identified as an important growth parameter for depositing stoichiometric thin films. For a compound target, since the sputter yield of all constituent elements is different, conditioning of target takes several hours of sputtering to reach compositional stability. Earlier reports on the growth of High Tc thin films of $YBa_2Cu_3O_7$ indicate that a preconditioning of the target is essential before realizing stoichiometric films [6]. Also, the surface of a new target is non-stoichiometric, if reactive elements like lithium are present. The top layers would be lithium rich, forming impurities with oxides and hydroxides making a barrier layer over the surface. Impurities like Na, F and Cl are surface contaminations, which must be removed before a functional film deposition. The surface analysis of deposited thin films directly reflects the target surface elemental composition. The present study deals with the conditioning of the $LiCoO_2$ target during Rf sputtering. The films have been deposited at fixed intervals of time and the characteristics of the films analyzed. Major interest has been in studying the chemical composition variation in the deposited films as the target is being conditioned. XPS analysis of films performed on these films reveals the elemental composition and phase formation for being electrochemically active. Along with this, the morphological features of the deposited films have been studied and discussed.

2. Experimental

Lithium cobalt oxide ($LiCoO_2$) thin films were prepared using a custom designed high vacuum chamber, equipped with Rf-magnetron cathode in sputter-up geometry. A base vacuum of 5×10^{-7} mbar was obtained with a turbo molecular pump backed by a rotary pump. $LiCoO_2$ target was made by cold pressing and

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sintering powder of pure $LiCoO_2$ (Sigma Aldrich, 99%) at 800 °C for 20 h. The target size is 75 mm in diameter and 5.5 mm thick. Thin films have been deposited onto Si substrates held at a distance of 6 cm away from the target. An Rf power density of 4.4 W/cm^2 is kept constant for all depositions. The sputtering pressure was maintained to be $1–3 \times 10^{-2}$ mbar with an Ar:O_2 ratio of 9:1. The deposited film was found to be in low temperature (LT) phase of $LiCoO_2$ with only 6% of Li existing in octahedral sites of Co layer resulting in cubic symmetry (space group Fd3m). A post-deposition annealing in O_2 ambient for 1 h at 700 °C was performed to induce high temperature (HT) phase of $LiCoO_2$ thin film with rhombohedral (space group R3-m) structure [7,8]. Annealing was performed in the deposition chamber itself without exposure to atmosphere to avoid contaminations.

The films deposited after every 15 min of sputtering from a new target have been analyzed to reveal the aspect of target conditioning. The surface chemistry of the deposited $LiCoO_2$ thin films was examined with X-ray photoelectron spectroscopy (XPS). From XPS core-level spectra of Cobalt, Oxygen, and Lithium near the thin film surface are obtained. XPS analyzes the chemical environments of Co, O and Li in order to provide insight to compositional variations and shift present in the surface of $LiCoO_2$ thin film.

XPS analysis was performed with SPECS GmbH spectrometer (Phoibos 100MCD Energy Analyzer) using MgKα radiation (1253.6 eV). The residual pressure inside the analysis chamber was in 10^{-10} mbar range. The spectrometer was calibrated by using photoemission lines of Ag (Ag $3d_{3/2} = 367$ eV with reference to Fermi level). Peaks were recorded with constant pass energy of 50 eV. XPS signals were analyzed using CASA XPS software. The crystal structure of the films was characterized by X-ray diffraction (XRD) using Bruker D8 Advance (Cu-Kα radiation). The morphology

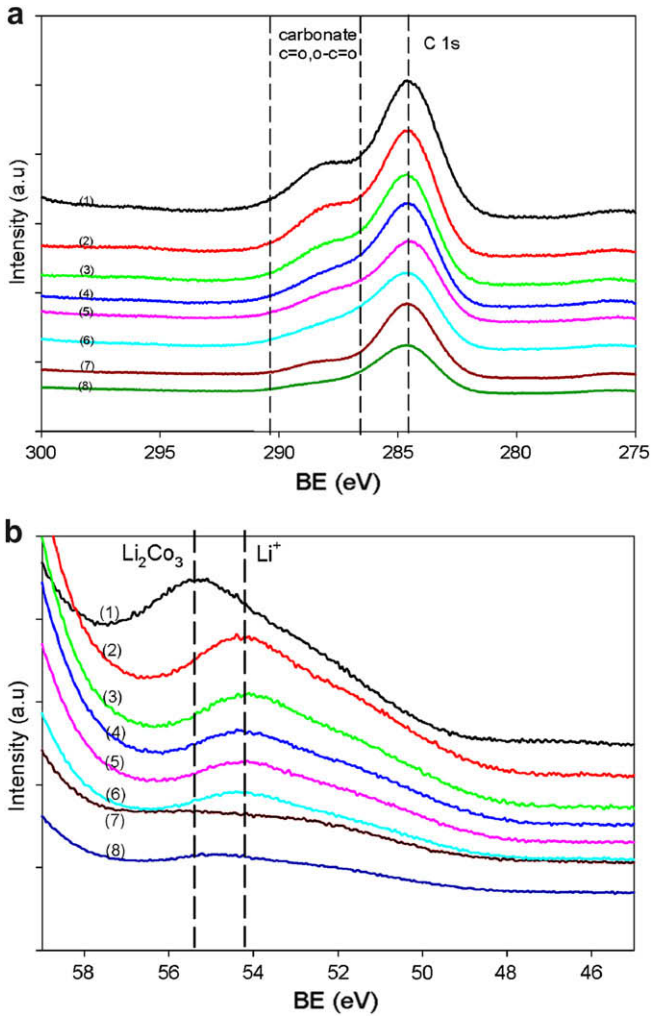

Fig. 1. (a–b) C 1s and Li 1s XPS spectra of $LiCoO_2$ thin films of (1) 0–15 min, (2) 15–30 min, (3) 30–45 min, (4) 45–60 min, (5) 60–75 min, (6) 75–90 min, (7) 90–105 min, (8) 105–120 min.

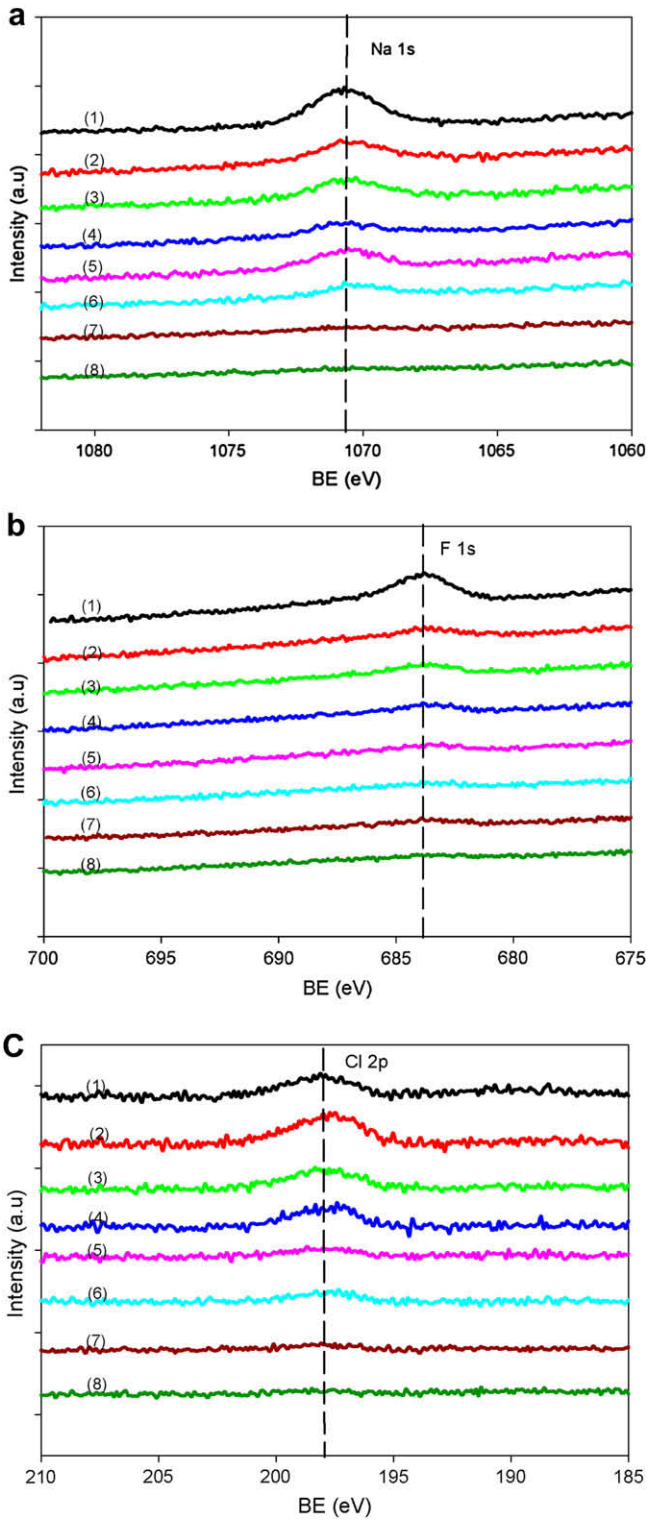

Fig. 2. (a–c) Reduction in Na, Cl and F impurity removal during target conditioning from samples 1–8.