

Investigations on sputter deposited LiCoO₂ thin films from powder target

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Received: 02 December 2012, Revised: 11 January 2013 and Accepted: 12 January 2013

ABSTRACT

LiCoO₂ thin films used as cathode layers in thin-film solid-state batteries have been deposited from LiCoO₂ powder target using radio frequency (rf) magnetron sputtering in a cost effective approach in terms of material consumption and processing time. X-ray diffraction (XRD) studies of the films after post deposition annealing treatment revealed (104) orientation, which is the characteristic of rf sputtered LiCoO₂ films. Raman spectroscopy was used to identify the different modes of vibration of atoms in the film. The surface morphology and cross-section of the samples were characterized using field emission scanning electron microscopy (SEM). The chemical analysis of LiCoO₂ thin films was examined by X-ray photoelectron spectroscopy (XPS) showed atomic ratio of Li/Co as 0.9 which is close to the ideal value 1. Electrochemical characterization such as charge – discharge and cyclic voltammetry were conducted for LiCoO₂ films deposited on platinized silicon substrates in the potential range 3.0 to 4.2 V vs Li/Li⁺. The maximum discharge capacity of 64 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ and 52 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ were achieved when discharged at a current of 5 μA and 50 μA for the first discharge cycle respectively. Moreover the electrochemical investigations of LiCoO₂ thin films on flexible copper substrates also investigated and achieved an initial discharge capacity of 83 mAh/g. The possible reasons for degradation in the electrochemical properties have been discussed. The present work indicates suitability of sputtering from powder targets for thin film battery fabrication. Copyright © 2013 VBRI press.

Keywords: Powder target; rf sputtering; thin film cathodes; LiCoO₂ thin films.



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polymer surfaces and their conditioning.

Introduction

Batteries with very small sizes are of immense interest, as the sizes of portable microelectronic devices and sensors decrease continuously. Thin film batteries can be used as power sources for various low power electronic devices [1] such as portable electronic devices and micro electro mechanical systems (MEMS) which require very low power and current levels and hence can be powered by thin film batteries. The major advantage of the thin film battery is that it can be fabricated by using the same techniques available in the microelectronic industries and can be directly incorporated with the devices because thin film battery can be deposited in any two dimensional shape or size according to the device requirement. Materials like TiS_2 [2], TiO_yS_z [3], V_2O_5 [4] were used as cathode layers and the success was limited in terms of the specific capacity and cycling. In 1980 Mizushima et al. [5] proposed LiCoO_2 as the cathode material due to its high operating voltage and cycle life [6]. LiCoO_2 thin films have been deposited by several techniques such as pulsed laser deposition [7], sol-gel [8] and rf sputtering [9,10]. In earlier reports, rf sputtering has been carried out using solid target as the sputtering source. However, in order to make a sputtering target in the form of a pellet, a binder material has to be added to the ceramic powder and then pressed and sintered. More over solid ceramic targets are fragile and are not good conductors of heat and hence easily crack at high sputtering powers. To obtain good quality thin films, sputtering from a virgin target requires conditioning of the target which involves pre sputtering for at least 2 to 3 hours at high rf power which in turn dictates surface chemical composition, morphology and electrochemical performance of LiCoO_2 thin films. In particular, it was shown that LiCoO_2 target becomes lithium deficient due to sputtering over prolonged period [11]. To avoid these issues associated with solid target sputtering an effort has been made to deposit LiCoO_2 thin films from powder itself. Powder target can be made more conveniently in a cost effective approach. In the case where mixed compositions and doping are required, this process is much easy to control, without any need to make targets of each of the composition. Also, only one third the mass of powder is required to prepare powder target compared to that of pellet. This process is economical in terms of material consumption. High deposition rates, ease of making mixed target, processing time are the prominent advantages of powder sputtering [12-15]. The objectives of this study are deposition of LiCoO_2 thin films, a prominent material for

energy storage [16] using powder target, examine the physiochemical properties of the films and to utilize the deposited films for fabrication of thin film battery.

Experimental

Materials

LiCoO_2 powder (LICO Technology Corporation, Battery grade, 99% pure, Taiwan) was used for the preparation of powder target without any binders. Platinum coated silicon (Silicon Valley Microelectronics Inc, USA) and flexible copper foil (Alfa Aesar, 99% pure) were used as the substrates. Lithium metal ribbon (Sigma Aldrich, 99.9% pure, Battery grade) was used as reference and counter electrode. 1M LiAsF_6 salt (Sigma Aldrich, 98% pure USA) dissolved in 1:1 (volume ratio) of ethylene carbonate (Sigma Aldrich, 98% pure, USA) and dimethyl carbonate (Sigma Aldrich, 99% pure, USA) (EC:DMC) was the electrolyte and polypropylene membrane (Celgard 2300, USA) as separator to avoid physical contact between electrodes.

Methods

LiCoO_2 powder (approx. 20 gms) was filled in a copper disc of 3 inch diameter having a trench of depth 3 mm and pressed manually with a solid piece of stainless steel to make it compact. The as prepared target is fixed on the magnetron cathode (Angstrom science) in the sputter-up geometry. The sputtering chamber is evacuated to a base vacuum of 1.0×10^{-6} mbar using diffusion pump backed by a rotary pump in a custom built high vacuum sputtering system. The pressure inside the chamber was maintained at $3-5 \times 10^{-3}$ mbar using argon (5N) as sputtering gas and oxygen (5N) as reactive gas in the ratio 9:1 using different mass flow controllers (Aalborg, USA). The sputtering cathode was powered by rf power supply (13.56 MHz, Advanced Energy) coupled with a matching network. Pre-sputtering was carried out for 2 hours initially to enhance compactness in the target at low power density to avoid spilling out of powder and thereafter 20 minutes pre sputtering before every deposition to remove surface adsorbed impurities. A rotatable substrate holder was positioned above the target. The rf power density used for depositions was 4.4 W/cm^2 , substrate to target distance of 5 cm and substrate temperature of 200°C . Post deposition annealing at 700°C for one hour was carried out in oxygen ambience to induce high temperature (HT) crystalline phase of LiCoO_2 films in rhombohedra geometry with space group (R3-m) [17]. The thickness of the film was measured by stylus profilometer (Veeco Dektak 150). The thickness of the LiCoO_2 films was 450 nm at a deposition rate of 15 nm/min. The crystalline phase of the thin film was examined by X-ray diffractometer (Bruker D8 Advance) using copper $\text{K}\alpha$ radiation at a scan rate of $2^\circ/\text{min}$. The surface morphology and cross section of the films were examined by field emission scanning electron microscope (SIRION-FESEM). X-ray photo electron spectroscopy, XPS (SPECS, Phoibos 100 MCD Analyzer) characterization was carried out after sputter etching the film surface to a few nano meters thick with $30 \mu\text{A}$ ion current and at a pass energy of 40 eV using Al $\text{K}\alpha$ anode (1486.6 eV) in ultrahigh vacuum (5×10^{-10} mbar). Raman

scattering measurements were performed with an Ar-ion laser operating at 514.5nm (HORIBA Jobin Yvon). The electrochemical characterization was carried out assembling 3-electrode glass cells in an argon filled glove box (MBraun model unilab, USA) with oxygen impurity level less than 1ppm. Half cells were tested at room temperature using CH Instruments electrochemical workstation (CH Instruments Model 660C) in the potential between 3.0 to 4.2V vs Li/Li⁺. Cyclic voltammetry (CV) was carried out at a scan rate of 0.05 mV/s. The discharge capacity of the films was calculated by multiplying the discharge current (μ A) and time (h).

Results and discussion

Structural & microscopy studies

The XRD pattern of LiCoO₂ film deposited on platinum coated silicon is shown in the **Fig. 1**, along with that of virgin powder. The reflection at 45.5° corresponds to the existence of (104) orientation and two less intense reflections at 61° and 66.2° correspond to (110) and (018) (JCPDS file no.44-0145). The peak positions are shifted by 0.1- 0.3°, might have been caused due to thermal stress induced because of difference in thermal expansion coefficient of film and substrate during annealing process. It was reported that the crystallographic evolution of thin films was influenced by two major factors such as surface energy and volume strain energy [18].

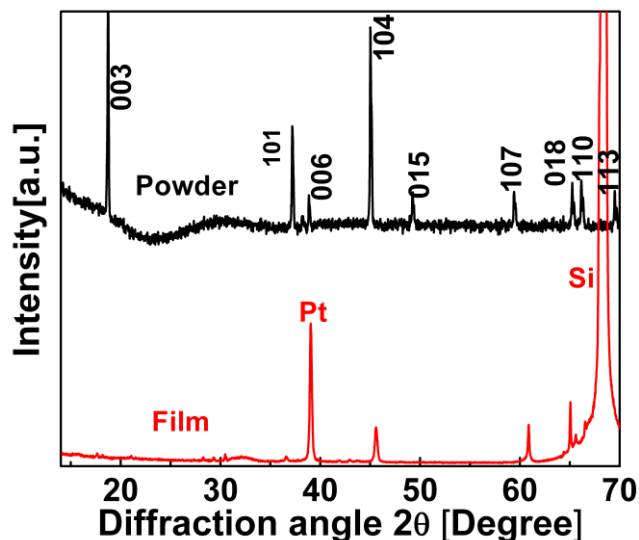


Fig. 1. XRD pattern of LiCoO₂ thin film and powder.

In this case, substrate heating might have changed the energy of the condensing atoms and are oriented in (104) direction to minimize the volume strain energy. The reflection from (003) orientation which is the characteristic peak of the LiCoO₂ films obtained using PLD [19] has not been observed. For rf sputtered films Li-ion transport through (104) and (101) oriented grains is more rapid and yields higher discharge capacities compared to the grains oriented in (003) direction. Also, the preferred (104) orientation observed in case of films deposited by sputtering of LiCoO₂ target, has been observed in films sputtered from powder target also. It gives clear evidence

that LiCoO₂ thin films sputtered from powder target also possess preferred orientation same as that of films sputtered from solid target [20, 21]. **Fig. 2** shows the Raman spectra of LiCoO₂ film and the powder with intense peaks observed at 485 cm⁻¹ (E_g) and 594 (A_{1g}) cm⁻¹ represents bending and stretching modes between cobalt and oxygen atoms in LiCoO₂, is in good agreement with the earlier report [22]. A peak at 520 cm⁻¹ is also seen in the spectra and it corresponds to silicon substrate.

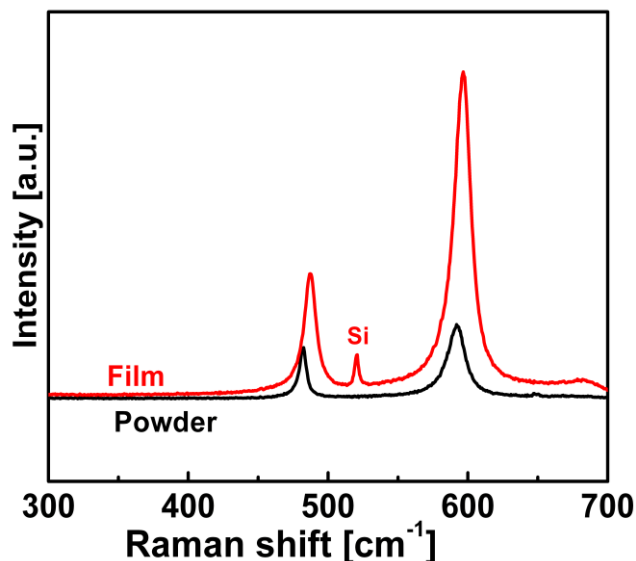


Fig. 2. Raman spectra of LiCoO₂ thin film and powder.

The SEM image of the LiCoO₂ film morphology and cross section (inset) showed in **Fig. 3**. The morphology of the sample shows uniform distribution of well defined grains which are formed after high temperature annealing and cross section image shows dense columnar growth of deposited film. The grain size is in the range 50-100 nm. Larger grain size in the deposited film could have good contact with electrolyte which affects the electrochemical performance.

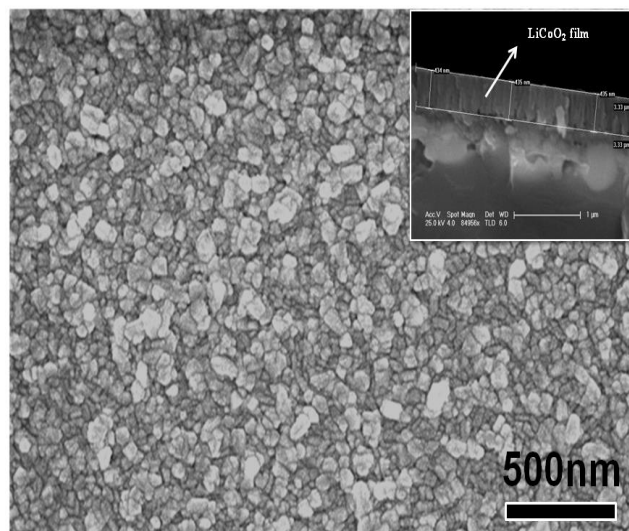


Fig. 3. Surface morphology (inset cross-section) of the LiCoO₂ film.

Chemical analysis

Surface analysis was carried out by taking in to consideration Shirley type background and relative sensitivity factor of each constituent element using integrated area of core level spectra. All peaks were calibrated with advantageous carbon at 284.6 eV. The survey spectra for powder and LiCoO₂ film are shown in the **Fig. 4 (a)**. The Core level emission spectra of cobalt, oxygen (after fitting) and lithium for film are shown in the **Fig. 4 (b), (c) and (d)** respectively. Due to spin-orbit splitting Co2p is splits in to two components 2p_{3/2} and 2p_{1/2} at 779.9 eV and 795.1 eV respectively which are in the intensity ratio of about 2:1. The origin of satellite peaks has also reported [23] and they arise because of electron shakeup process. Moses et al. [24] also reported that the Co 2p spectrum is characteristic of Co³⁺ and the sharp peak shape of the 2p_{3/2} and 2p_{1/2} emission is a characteristic feature of spin-paired t_{2g} and empty e_g levels and as a consequence the satellite peaks will be weak. In our case also we observed less intense satellite peaks giving clear evidence that the chemical environment (oxidation state) of the cobalt cation as Co³⁺ in LiCoO₂ structure. A single broad peak is observed for oxygen at 531.2 eV and for lithium at 54.2 eV. **Fig. 4 (c)** after fitting the spectra shows two peaks at 529.3 eV correspond to oxygen from crystalline structure of LiCoO₂ and 531.4 eV corresponds to surface adsorbed oxygen were observed. The ratio of Li/Co is 0.9. The results are in consistence with the literature reported earlier [25-27].

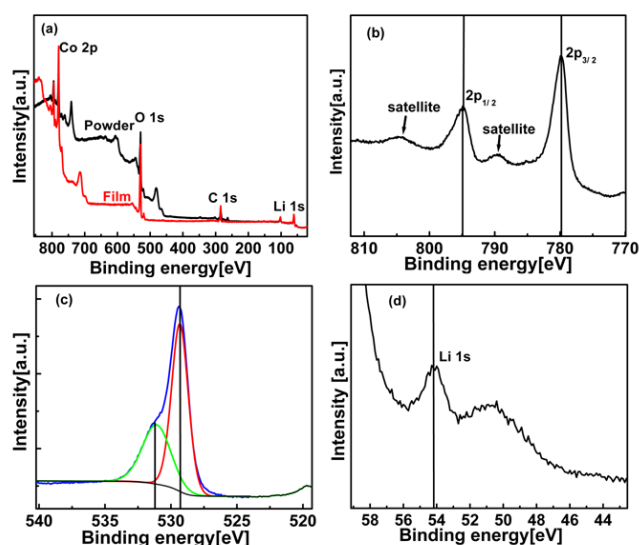


Fig. 4. XPS studies (a) Survey (b) Cobalt 2p (c) Oxygen 1s (fitted) (d) Lithium 1s emissions.

Electrochemical study

Charge and discharge studies have been carried out for LiCoO₂ films on platinized silicon substrates as shown in **Fig. 5 (a) and 5 (b)**, delivered a first discharge capacities of 64 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ (columbic efficiency 76 %) and 52 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ (columbic efficiency 47 %) at a current of 5 μA and 50 μA respectively. The values are close to the ideal value 70 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$. In the discharge profiles during charging and discharging a plateau observed at 3.9

V and 4.0 V respectively attributed to the characteristic feature of layered HT-LiCoO₂. Liao et al. [28] studied the deposition of LiCoO₂ thin films prepared by radio frequency magnetron sputtering on Pt coated silicon and reported a discharge capacity of 61.16 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ for the first discharge. Zhu et al. [29] and Jeevan kumar et al. [30] studied the deposition of the LiCoO₂ films by rf sputtering and achieved a first cycle discharge capacity 60.5 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ and 65 $\mu\text{Ah}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ respectively. It was reported that the poor cycle life of the LiCoO₂ electrodes may result due to Li-ions trapping, stress accumulation, phase changes in the film which increases electric and ionic resistance at the electrodes interface after continues contact with the electrolyte [31, 32] and also changes in the lattice parameters of the Li_xCoO₂ (0<x<1) layered structure could induce strains with in Li_xCoO₂ grains which may leads to the formation of micro cracks [33] and cobalt dissolution [34, 35] from Li_xCoO₂ surface as a consequence cracked parts may completely loose the contact with the film body. More over the charge - discharge were carried out for LiCoO₂ thin films deposited on flexible copper substrates and achieved a gravimetric capacity of 83 mAh/g (columbic efficiency of 71 % for first cycle) as shown in **Fig. 5 (c)**. The charge and discharge profile is shown for the three cycles labelled as 1, 2 and 3. Yazami et al. [36] achieved 138 mAh/g capacity for first discharge and discussed the potential reasons for capacity decay. Chiu [37] and Ziebert et al. [38] studied thin films of lithium cobalt oxide deposited by magnetron sputter deposition and achieved a maximum capacity of 110 mAh/g and 130 mAh/g respectively. Song et al. [39] reported the growth of Co₃O₄ impurity phase in LiCoO₂ thin film after charge discharge studies degrade the cycle life. The redox behavior of the working electrode was investigated using cyclic voltammetry technique. CV plot as shown in **Fig. 5 (d)**.

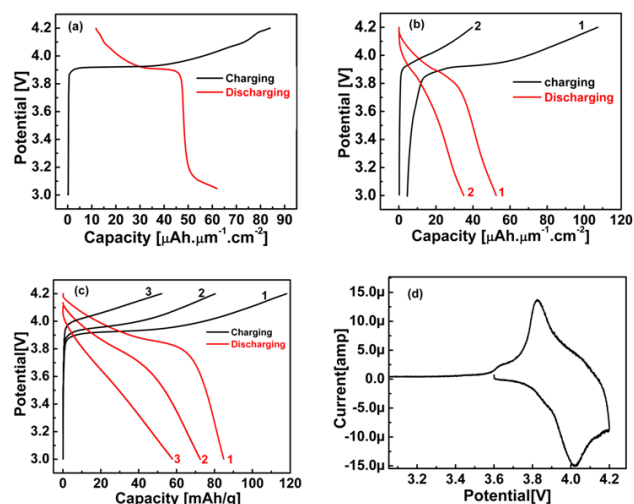


Fig. 5. Electrochemical studies (a) 5 μA (b) 50 μA (c) flexible substrate (d) CV.

With broad oxidation peak at 4.01V and reduction peak at 3.82 V. The redox couple corresponds to Ist order phase transitions between LiCoO₂ and Li_xCoO₂ (0<x<0.5) which are induced by reversible Li-ion migration during charging

and discharging. After electrochemical characterisation of the thin film electrodes on platinized silicon were rinsed in ethanol, dried for surface morphology investigation, it posses void type morphology (size 80-140 nm) and film is about to peel off from the substrate as shown in the Fig. 6.

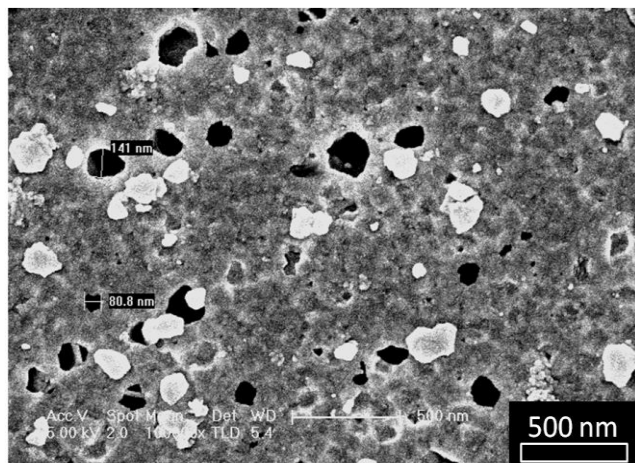


Fig. 6. Surface morphology after electrochemical testing.

We suspect that after cycling the film body might have lost contact with the conductive substrate. The observed physiochemical properties of the films nearly correlate with that of the LiCoO_2 films deposited from solid target. For the observed properties of powder sputtered films, we speculate that powder target becomes physically compact after prolonged sputtering because of localized sintering at high power densities. Also, sputtering from loosely held powder results in higher sputter rate and also facilitates better composition control.

Conclusion

The deposition of LiCoO_2 films from powder target using rf sputtering has been demonstrated. XRD, Raman and XPS results of LiCoO_2 thin films are in consistent with the reported literature. The charge and discharge tests suggested a good initial capacity of $64 \mu\text{Ah} \cdot \mu\text{m}^{-1} \cdot \text{cm}^{-2}$ and $52 \mu\text{Ah} \cdot \mu\text{m}^{-1} \cdot \text{cm}^{-2}$ when discharged at a current of $5 \mu\text{A}$ and $50 \mu\text{A}$ respectively. We predict that surface parasitic reactions such as cobalt dissolution, growth of impurity phases during cycling may be the potential causes for poor cycle life. The comparison between LiCoO_2 thin films deposited from powder sputtering and pellet sputtering using gives clear evidence of nearly similar physical, electrochemical properties. Powder sputtering technique is highly economical in terms of less material consumption, mixed oxide preparation, doping by metallic impurities and processing time. Further studies on the enhancement in the performance of the discussed properties of the films are underway.

Acknowledgements

This work is supported by the Ministry of Communication and Information Technology, Govt. of India under a grant for the Centre of Excellence in Nano electronics, Phase II.

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