MICROFABRICATION AND CARACTERIZATION OF THIN-FILMS SOLID-STATE RECHARGEABLE LITHIUM BATTERY

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***Abstract* — This paper presents the microfabrication and materials characterization of thin-film solid-state rechargeable lithium batteries. Film solid-state batteries are ideal power sources for stand-alone microsystems where a high-level of integration is required. Solid-state thin-film batteries are intrinsically safe, have a larger life cycle, a faster charge/discharge cycling and a bigger capacity by cm^3 then the conventional ones. The fabrication materials used are $LiCoO_2$, LIPON and metal lithium in cathode, electrolyte and anode respectively. The $LiCoO_2$ and LIPON films were deposited by RF magnetron sputtering technique and the metal lithium by thermal-evaporation technique.**

***Keywords :* Solid-state films battery, integrated batteries, energy-harvesting microsystems**

I - Introduction

There is a great interest in size reduction of batteries due it integration with portable microsystems [1-2] for biomedical Microsystems [3-4] such as wireless neural electrodes [5]. Solid-state batteries are intrinsically safe and have advantages in life time, capacity, power and cost [6-7].

In this paper a battery fabricated by thin-film techniques in a Si (silicon) substrate is presented. The materials used are $LiCoO_2$ (lithium-cobalt oxide), LIPON (lithium-phosphorus oxynitride) and metal Li (lithium), for the cathode, electrolyte and anode respectively. Platinum current collectors of cathode and anode ensure good electrical contact without reacting with the electrodes. A silicon-nitride (Si_3N_4) encapsulation ensures oxidation protection. An artwork of the battery is presented in Figure 1. The $LiCoO_2$ is the material commonly used as cathode in batteries [8, 9] because of the good electrochemical cycling stability and the capacity of insertion and extraction of Li^+ ions without losing the structural stability [10].

The solid electrolyte ensures the intrinsically safe operation. LIPON is a good alternative due to its high-electrical resistivity and high-ionic conductivity. A good electrochemical stability in contact with lithium also makes the LIPON an excellent material for electrolyte in solid-state batteries [11, 12, 13].

The anode of battery is metallic Li because it exhibits the highest capacity and discharge rate [14], despite the fast oxidation in contact with air.

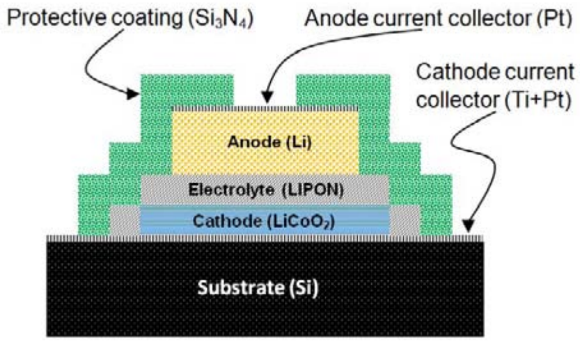

Figure 1: *Artwork of the battery, with $LiCoO_2$ cathode, LIPON electrolyte and Li anode, between Pt current collectors, covered by a protective Si_3N_4 film.*

II - Fabrication Details

The active material of the battery was deposited using PVD (Physical Vapor Deposition) techniques in a [100] silicon substrate. The platinum cathode current collector with 70 nm thick was deposited by E-Beam technique. In order to improve adhesion between silicon and platinum, a 30 nm thick titanium layer was deposited between them by the same technique.

The cathode of the battery was deposited by RF magnetron sputtering technique (a RF power source 13.56 MHz at 150 W, a pressure of 0.2 Pa in a 30 sccm flow of Ar and 10 sccm flow of O_2). A $LiCoO_2$ target was used for depositing a layer 1 µm thick. A crystalline structure of $LiCoO_2$ is desirable for a good cathode. Three different temperatures were tested (873 K, 973 K and 1023 K) and crystalline structure compared in: 30 min annealing at vacuum atmosphere.

Electrolyte (LIPON) was deposited by RF magnetron sputtering technique (a layer 1 µm thick). A Li_3PO_4 target was used in a 20 sccm reactive nitrogen flow. The power source (13.56 MHz) was biased at 200 W and three different pressures were tested (Table 1).

Table 1: *Parameters used in LIPON deposition*

LIPON film	Target	N_2 (SCCM)	RF power (W)	Pressure (Pa)
#1	Li_3PO_4	20	200	1
#2	Li_3PO_4	20	200	0.7
#3	Li_3PO_4	20	200	0.3

The anode of the battery (metallic Li) was deposited by thermal evaporation. The platinum anode current collector, with 100 nm thick was deposited by e-beam. The protection layer, Si_3N_4 film, was deposited by low-temperature CVD [15].

III – Experimental Results

A. $LiCoO_2$ films

After annealing, $LiCoO_2$ films exhibit a polycrystalline structure with strong orientation in the [104] planes and fewer at [003] and [101] planes [16]. This structure improves the ion diffusion. Figure 2 shows the X-ray diffraction pattern (XRD).

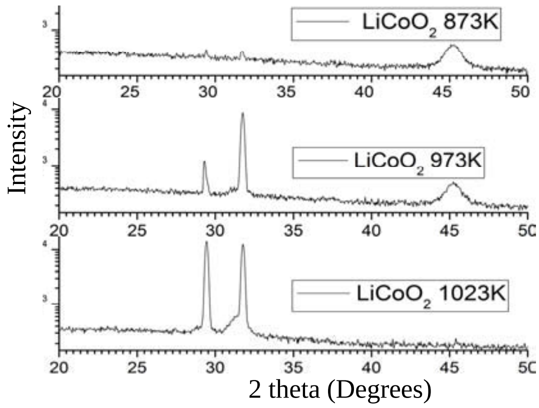

Figure 2: *XRD diffraction of $LiCoO_2$ films after annealing at temperatures of 873, 973 and 1023 K.*

A SEM image of $LiCoO_2$ film was also performed and can be seen in Figure 3. The in-plane resistivity of 2.5 Ωcm was measured using the Van der Pauw technique (Figure 4). The $LiCoO_2$ cathode has a capacity of 140 $mAhg^{-1}$ (about 1 Li per 2 CoO_2).

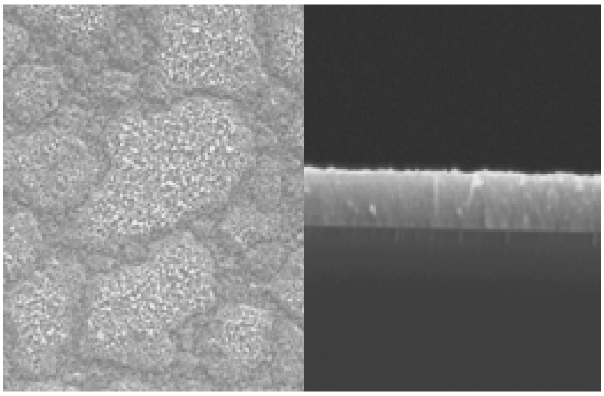

Figure 3: *Cross-section and surface SEM images of $LiCoO_2$ film.*

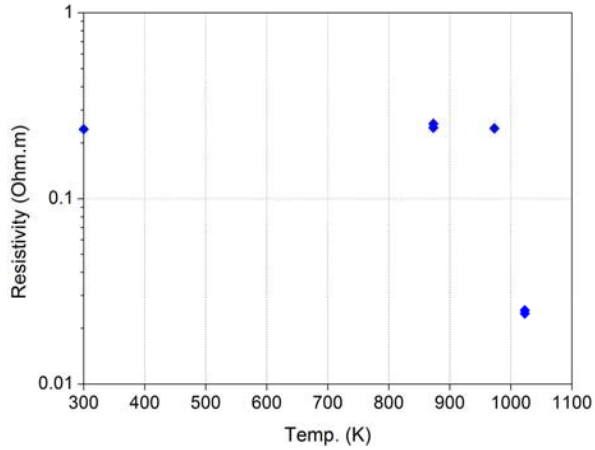

Figure 4: *Resistivity of $LiCoO_2$ films, as function of annealing temperature (left point represents the deposition without annealing).The resistivity decreases with temperature annealing above 1000 K.*

B. LIPON films

The deposition pressure in LIPON depositions was correlated with ionic conductivity. The ionic conductivity of LIPON was measured with Nyquist diagrams of impedance, performed at different temperatures (Figure 5).

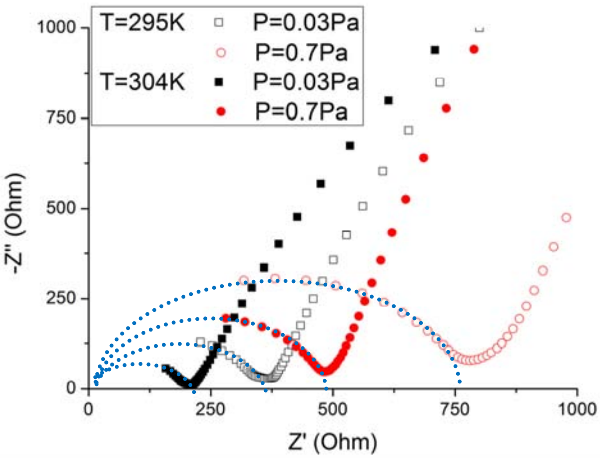

Figure 5: *Nyquist (impedance) diagram of LIPON films, deposited at N_2 pressures of 0.03 (#3) and 0.7 Pa (#2), measures at temperatures of 295 K and 304 K. Dashed lines show fitting for ionic conductivity calculation.*

When the dashed lines in Nyquist diagram of impedance cross the x- axis, the resistivity of the film at different conditions of pressure and temperature can be measured. The best result of ionic conductivity of LIPON was achieved with a pressure of 0.03 Pa (#3) and a temperature of 304 K. The best ionic conductivity was achieved between 10^{-7} and 10^{-6} Scm^{-1} (Figure 6).

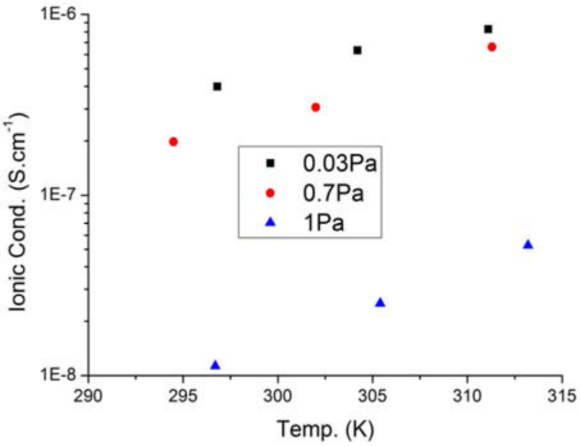

Figure 6: *Ionic conductivity of LIPON deposited at N_2 pressures of 0.03 (#3), 0.7 (#2) and 1 Pa (#1) measured in temperature range of 295-315 K.*

C. Li Films

The Li resistance was measured during the deposition using a four point setup and values between 2.5 Ω and 3.5 Ω were measures for 3 µm thick layers (Figure 7).

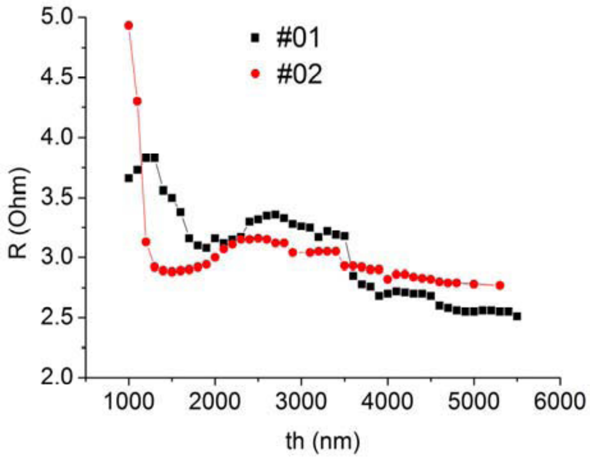

Figure 7: *Resistance of Li in function of thickness during the deposition.*

After the deposition, the resistivity of Li was measured at room atmosphere without any protective layer in order to evaluate the oxidation of Li (Figure 8). Results show that a protective layer is essential to keep the battery functional.

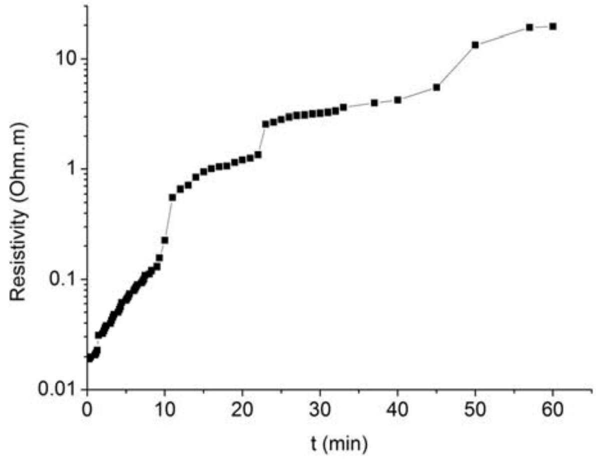

Figure 8: *Resistivity of Li as function of time at room atmosphere.*

IV - Conclusions

This paper presented the microfabrication and characterization of materials for thin-films solid-state rechargeable lithium battery. RF magnetron sputtering, e-beam and low-temperature CVD was used in the deposition of the layers. The battery is composed of a $LiCoO_2$ cathode, a LIPON electrolyte and a Li anode. The contacts are made of Pt to avoid unwanted reactions. A Si_3N_4 protective layer protects the battery layers.

$LiCoO_2$ films show different phases, as function of annealing temperature. Best results were obtained with annealing on vacuum, at temperature above 1000 K. A resistivity of 2.5 Ωcm was measured. The best LIPON films have an ionic conductivity of $2E^{-6}$ Scm^{-1}, deposited at 20 sccm flow of N_2 and 0.03 Pa of pressure. The Li anode deposited by thermal evaporation has a low resistivity (0.02 Ωcm), however, a rapid oxidation occurs in contact with atmosphere. These materials have good properties as standard large-sized batteries, and are suitable for the fabrication of lithium thin-film batteries.

Thin-films solid-state rechargeable battery show a high-cycle life, a high charge/discharge rate and are intrinsically safe. This is a special concern in biomedical applications such as wireless neural microsystems.

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