THIN-FILM SOLID-STATE RECHARGEABLE LITHIUM BATTERY

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***Abstract* — This paper describes the optimization and the materials technology required for fabricating thin-film solid-state rechargeable lithium batteries. The following materials were selected, deposited and optimized: a glassy lithium-phosphorus oxynitride electrolyte (LiPON) between a lithium (Li) anode and crystalline lithium-cobalt dioxide cathode ($LiCoO_2$), deposited by RF-sputtering. Ti/Pt layers, deposited by evaporation (using the e-beam technique) were used in contacts and a silicon nitride thin film (Si_3N_4), deposited by Hot-wire CVD protects the battery. This technology allows batteries with a potential of 4.5 V, typical capacities of 50 µA.cm^{-2} and charge discharge rates up to 4C.**

***Keywords :* Solid-state, thin-film battery, materials technology, lithium, energy-harvesting, microsystems**

I – Introduction

It's undeniable the fact that batteries are systems with the highest number of applications known up to know. Since the invention of the first pile by Volta on 1800, batteries are used in applications that range from vehicles to the most modern cell phones, toys/gadgets and biomedical devices. Despite the developments made by the microelectronic industry, the battery technology didn't accompany these breakthroughs [1]. The increased demand of stand-alone microsystems in critical energy applications, such as radio-frequency identification tags, integrated circuit smart cards [2], data acquiring systems on extreme industrial harsh environments, oil drilled sinks and wireless sensor networks, led to the investigation and development of solid-state rechargeable batteries [3]. In energy harvesting systems, thin-film batteries of solid-state materials are suitable power sources to fill the time gaps, when the external power source is not available, thus assuring that microsystems are still powered and active. This is of special concern when the target applications are in the biomedical field or for long cycle operations without requiring human activity [4, 5].

Two forms of film batteries have been developed so far: the polymer based lithium batteries and the film lithium batteries. The polymer batteries (that are already common in the market) have high capacity and stability but low charge/discharge rates, mainly due to temperature limits. Solid-state film batteries show faster charge rates and very high cycle life, compared with classical liquid electrolyte batteries, withstanding several thousands of cycles with no pronounced fading. The integration of batteries with solid-state circuits requires the use of solid-state anode, cathode and electrolyte. These batteries are intrinsically safe since all materials are solid and no leaking or explosion could occur. Moreover, this technology allows the fabrication of batteries that are not damaged during the soldering process of microchips. Film battery chemistry is being developed at ORNL (Oak Ridge National Laboratories) [4] with a solid electrolyte between the anode and cathode. These batteries have a potential of 4.5 V, typical capacities below 100 µAcm^{-2} and charge times of 2C to 5C. As illustrated in Figure 1, the film batteries present the highest volumetric energy density (800 Whl^{-1}) and gravimetric energy density (350 Whg^{-1}) and charge-discharge rates up to 5C (only exceeded by super-capacitors) [6, 7]. However, due to the process of deposition of thin-films, the thickness is limited to few micrometers, resulting in a small capacity. The market of film batteries is in the trial stage and it's predictable to reach 10 billion units by 2012.

This paper presents the fabrication process and characterization details of all materials used in a thin-film lithium rechargeable battery for integration with stand-alone microsystems.

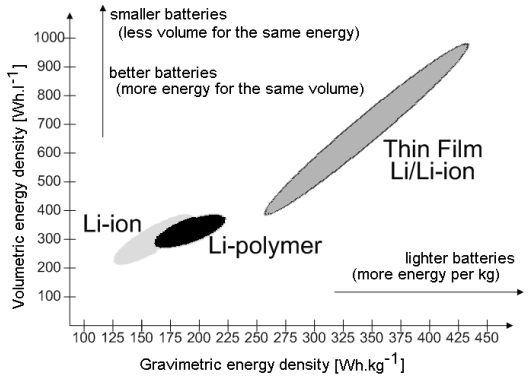

Fig 1: *Size and capacity with different battery technologies.*

II – Materials Selection

The integration of batteries with solid-state circuits requires the use of solid-state anode, cathode and electrolyte. The Figure 2 shows an artwork of a film battery fabricated by successive layers deposition on top of a silicon compatible substrate (among the glass, the [100] undoped double-side polished silicon wafer was used for thin-films depositions). The first layer are the battery contacts, and platinum was chosen for allowing a good distribution of electrons trough the cathode surface without reacting with it. The cathode is a lithium cobalt dioxide ($LiCoO_2$) thin-film; the electrolyte is a glassy lithium-phosphorus oxynitride electrolyte (LiPON) thin-film and anode is a lithium (Li) thin-film. The

protection layer is a silicon nitride (Si_3N_4) thin-film [8]. This protective layer avoids the reaction of lithium with air.

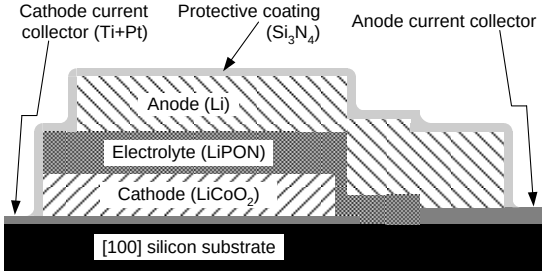

Fig 2: *Artwork of a thin-film battery.*

The operation of lithium batteries is based on reversible insertion and removal of lithium ions to and from their positive and negative electrodes [9]. Metals that are compounds of lithium (Li) and presents a layered structure, especially the ones containing 3D transition metals such as nickel (Ni), manganese (Mn), vanadium (V) and cobalt (Co). The lithium oxides containing these materials are excellent candidates as active compounds for use as high capacity cathode materials due to their high energy density, a long life cycle, a very good safety, constant discharging properties and a wide range of operation temperatures [10], without compromising the structural stability [11]. Compared with other materials such as the $LiMn_2O_4$ and $LiNiO_2$, the $LiCoO_2$ is easy to fabricate and has a relatively high charge storage capacity (140 $mAhg^{-1}$).

Thin-film solid electrolytes are required to have high ionic conductivity, a negligible electronic conductivity and be stable in contact with the anode and cathode electrodes [7] that will allow for a high current capacity and low self-discharge current, respectively. As suggested by Hamon et al [12], the LiPON films with an amorphous structure are the most suitable candidates for obtaining films with high ionic conductivity when compared with crystalline structures. LiPON films present an exceptional electrochemical stability, an electronic resistivity greater than 10^{12} Ωm and ionic conductivity in of 10^{-6} Scm^{-1} range. Films of LiPON can obtained by RF sputtering of a lithium phosphate (Li_3PO_4) target in an argon (Ar)/nitrogen (N_2) plasma. Behind electronic properties, LiPON have low stress (typically, less than 100 MPa) and a good stability in air atmosphere [13].

The transition metal oxides were used as anode materials in previous works [14, 15], as it is the case of the tin dioxide (SnO_2). However, this compound presents a serious problem related with an irreversible reaction during the first battery charge, resulting in small clusters of tin metal (Sn) with lithium oxide (Li_2O). An anode material with higher degree of reversibility results in a battery with higher specific capacity. For this reason, the lithium (Li) metal was selected for the anode material, but also because it exhibits the highest capacity and discharge rate despite the fast oxidation in contact with the air. A way to overcome the last drawback is covering the battery with a protective layer of silicon nitride (Si_3N_4)**.** Multilayers of SiNx thin films are used to achieve higher protection against moisture and avoid reaction with air. Each layer has a low-frequency Ar-plasma treatment for surface compaction.

II - Fabrication Details

On top a silicon wafer where a thin layer of dioxide was grown by thermal oxidation, the current collector (contact) of platinum (100 nm) was deposited by e−beam. A titanium (Ti) layer with a thickness of 30 nm was previously deposited to improve the adhesion of the platinum to the substrate.

The 1 μm thick $LiCoO_2$ cathode was deposited by RF magnetron sputtering technique using a RF power source 13.56 MHz at 150 W, a pressure of 0.2 Pa in a 30 sccm flow of argon (Ar) and 10 sccm flow of oxygen (O_2). A deposition rate from 3.5 $Å s^{-1}$ to 4.5 $Å s^{-1}$ was obtained. This process is still the most effective way to provide the required crystalline structure of $LiCoO_2$ films. The best annealing temperature was found experimentally using a different temperatures (from 500 ºC to 800 ºC), during 30 minute, in vacuum.

The electrolyte (LiPON) was deposited by RF magnetron sputtering technique with 1 μm thickness. A Li_3PO_4 target was used in a 20 sccm reactive Ar/N_2 plasma. The depositions were done with controlled: the pressure inside the deposition chamber (from 0.03 Pa to 1 Pa) and controlled power in the RF source (13.56 MHz) of the sputtering system (150W to 200W), with a deposition rate from 0.4 $Å s^{-1}$ to 2.5 $Å s^{-1}$.

The lithium anode was deposited by thermal evaporation, in a large molybdenium boat (3 cm^3). A base pressure of 10^{-6} mbar and a deposition rate of 30 $Å s^{-1}$ were measured.

A thin layer of Si_3N_4 is deposited just after lithium (without open the chamber). This layer (100 nm) is deposited by RF magnetron sputtering technique at 300 W, a pressure of 0.2 Pa in a 20 sccm flow of N_2. This layer offers the necessary air protection to transfer the battery to the Hot-wire chemical vapor deposition (HWCVD) chamber, where the silicon nitride capping multilayer is deposited. These were obtained by using a sequence of HWCVD deposition of the SiNx followed by a low-frequency (100 kHz) Ar-plasma treatment for surface compaction. The final thickness of the structure was 120 nm, composed of 4×30 nm. The HWCVD deposition of SiN_x was performed at 25 mTorr from silane and ammonia gaseous mixtures using two hydrogen dilutions, namely 88% and 90%. The Ta current filament was 16 A, corresponding to a filament temperature of 2000 ºC. The Ar treatment was performed at 230 mTorr using a pulsed source for a short time. The sequence of SiNx deposition and Ar treatment was performed without breaking the vacuum, by moving the sample between two twin chambers connected by a gate valve. For each hydrogen dilution, two samples were deposited under a different NH_3 to SiH_4 flow rate ratio, R, namely R = 2 and R = 3, so fabrication receipt could be tuned.

IV –Results and Discussion

A. $LiCoO_2$ cathode

The Figure 3 shows the X−ray diffraction (XRD) spectrum of the $LiCoO_2$ films for three annealing temperatures (600 ºC, 650 ºC and 700 ºC). The joint analysis between the difractograms of the Figure 3 and the peak positions of planes [003], [101], [104], [018] and

[110] confirms the predominance of crystalline $LiCoO_2$ in the composition of the selected samples (diffraction patterns 016-0427 [16] were used in crystallographic analysis).

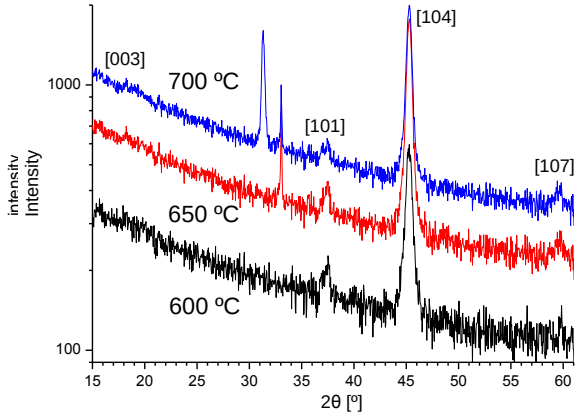

Fig 3: *XRD spectrogram of three $LiCoO_2$ films annealed at different temperatures (600 ºC, 650 ºC and 700 ºC).*

In the Figure 3 it is also possible to observe the evolution of $LiCoO_2$ peaks in XRD pattern with the increase in the annealing temperature. The annealing temperature increase resulted in a polycrystalline structure with strong orientation in the [104], [018] and [110] planes and fewer at [003] and [101] planes as it was presented before [17]. This structure improves the ion diffusing, thus increasing ionic conductivity and ion insertion and extraction. However, a phase transition occurs at 650 ºC, as depicted in Figure 4. The in-plane resistivity was measured using the Van der Pauw technique, for $LiCoO_2$ samples annealed at different temperatures (see the Figure 4).

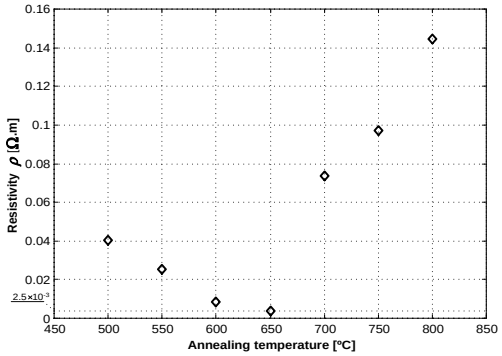

Fig 4: *Resistivity of $LiCoO_2$ samples, as function of annealing temperature.*

A decrease of resistivity was found with an increase of annealing temperature. The minimum resistivity value of 2.5×10^{-3} Ωm was measured (at room temperature) in sample annealed at 650 ºC. However, for annealing temperature above 650 ºC, the resistivity rapidly increases with annealing temperature. This behavior was also reported before [17].

B. LiPON electrolyte

The ionic conductivity of LIPON was measured on the best samples with the procedure described [12]. A sinusoidal voltage with amplitude of 25 mV (peak to peak) was used to measure the impedance of the sample at several values of frequency (from 0.5 Hz to 65 kHz). The inset in Figure 5 shows the LiPON thin-film with top and bottom contacts of platinum (Pt) for measuring the ionic conductivity. Both real (Z') and imaginary (Z'') parts of the impedance were respectively projected in x−axis and y−axis, in order to obtain a two dimensional Nyquist plot.

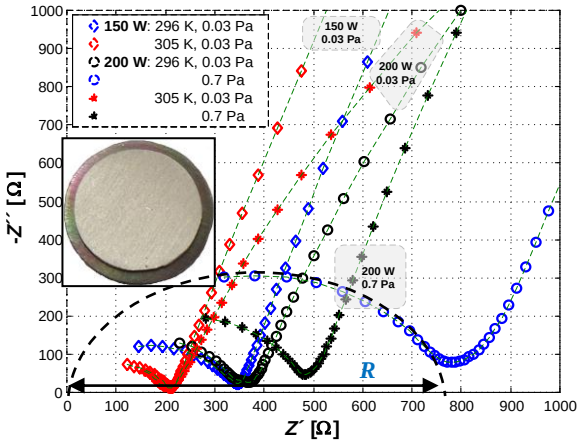

Fig 5: *Typical Nyquist plots of LIPON samples.*

Nyquist plots (measured at temperatures of 296 K and 305 K) are presented in Figure 5, for samples deposited at N_2 pressures of 0.03 Pa and 0.7 Pa, with RF sputtering power of 150 W and 200 W. The diameter of each semi−circle indicates the resistance of the electrolyte (R), whose values were obtained with the help of Autolab software.

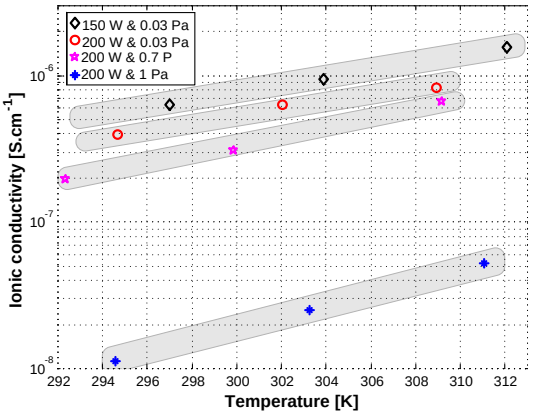

Figure 6: *Ionic conductivity of LIPON thin-films.*

Considering the area (A) and the thickness (d) of the electrolyte, the ionic conductivity, σ [Scm^{-1}], of LiPON is given by σ =d/(A*R) where and R [Ω] is the resistance from Nyquist diagram. The best ionic conductivity archived was between 10^{-7} $S.cm^{-1}$ and 10^{-6} $S.cm^{-1}$. The Figure 6 shows the ionic conductivity of LiPON films deposited at N_2 pressures from 0.03 Pa to 1 Pa and with RF power of magnetron sputtering from 150 W to 200 W, measured in temperature range of 292 K to 312 K. The highest ionic conductivity of LIPON (10^{-6} Scm^{-1} at 304 K) was measured in the sample deposited at N_2 pressure of 0.03 Pa and a RF power of 150W. It was observed the decreases of ionic conductivity with increase of power or pressure.

C. Li anode

The Li resistivity was measured during the deposition using a four point setup and values around 10 μΩm were measured for 3 μm thick film. After the deposition, the resistivity of Li was measured at room temperature and atmospheric pressure without any protective layer in order

to evaluate the oxidation of Li. These results show that a protective layer is essential to keep the battery functional.

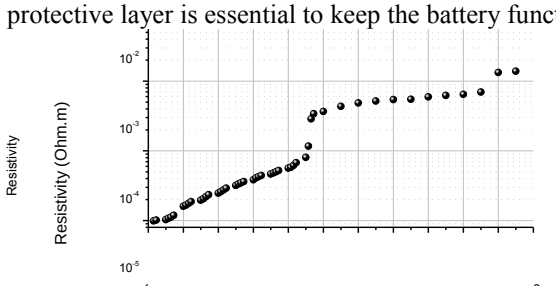

Fig 7: *Evolution of lithium resistivity in contact with air.*

D. Silicon nitride capping layer

Multilayers of SiNx thin-films, having refractive index of 2 (at 650 nm), were obtained. The final thickness of the structure was 120 nm, composed of 4×30 nm. All the samples are highly transparent in the visible/NIR range reaching more than 85% of transmission at 650 nm. The spectral refractive index was obtained from the transmission spectra in the visible and near infrared range (from 250 to 2500 nm) [18]. The multilayers will be electrically characterized by measuring the disruption field and the transport mechanism in the dielectric, under low and high applied electric field, in metal-insulator-metal (MIM) patterned structures defined lithographically. The quality of the multilayer as a device encapsulation barrier will be tested by measuring the water vapor transmission rate using the calcium test. The best samples will then be grown on top of the battery and the lifetime of the battery will be compared with that of batteries without encapsulation.

E. Battery

A battery, including all described materials, was fabricated using shadow masks to pattern different regions. Figure 8 shows a SEM image of the battery.

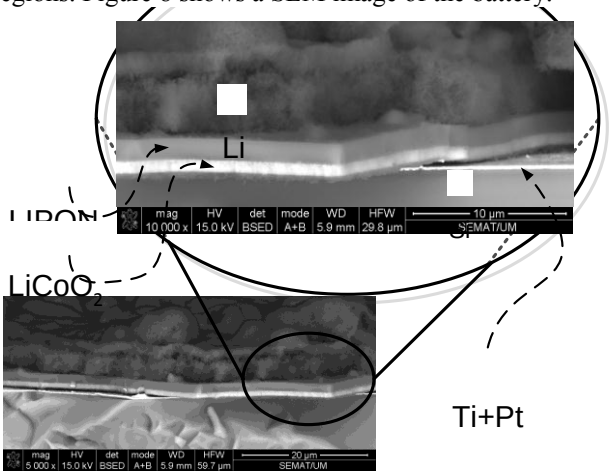

Fig 8: *Cross-sectional SEM image of the thin-film battery.*

IV - Conclusions

This paper presented the materials technology of rechargeable solid-state film lithium batteries for integration in stand-alone harvesting microsystems.

The RF magnetron sputtering, the e-beam evaporation and Hot-wire CVD were the techniques used for depositing the successive layers of the battery. The elements of the film battery are a $LiCoO_2$ cathode, a LiPON amorphous electrolyte and a Li anode. The contacts are made of platinum and battery is protected with a Si_3N_4 layer. The best $LiCoO_2$ films, annealed at 650ºC showed a resistivity of 0.25 Ωm. The best LiPON films have an ionic conductivity of 10^{-6} Scm^{-1} (at 304 K), obtained from a deposition at 20 sccm of N_2 with a pressure of 0.03 Pa and with an applied power of 150 W. The Li anode was deposited by thermal evaporation and presents a low resistivity (10 μΩm). However, a rapid oxidation of Li occurs in contact with atmosphere, so a protective layer must be deposited at the same run. These materials have as good properties as standard large sized batteries and are suitable for the fabrication of solid-state lithium film batteries.

Acknowledgements

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