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A thin-film rechargeable battery for integration in stand-alone microsystems

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Abstract

Thin-film solid-state rechargeable batteries on silicon are ideal power sources for microsystems applications, where a high level of integration is required. This paper presents a lithium solid-state thin-film battery for integration in stand-alone microsystems. The thin-films were deposited by direct current (DC) and radio-frequency (RF) reactive sputtering techniques. The materials of the battery includes SnO₂, Li₃PO₄N and LiCoO₂ as anode, electrolyte and cathode, respectively. The SnO₂ gives the battery a maximum storage capacity of 781 mAhg⁻¹, the LiCoO₂ can maintain a capacity of 140 mAhg⁻¹. The two materials used as anode and cathode with the Li₃PO₄N as electrolyte can obtain an output voltage in the range 3–4.2 V.

Keywords: Thin-films, solid-state battery, microbattery.

1. Introduction

There is great interest in developing rechargeable lithium batteries with higher energy capacity and longer cycle life for applications in portable electronic devices, electric vehicles and in biomedical applications. Silicon is an attractive anode material for lithium batteries because it has a low discharge potential and the highest known theoretical charge capacity (4200 mAhg⁻¹). Although this is more than ten times higher than existing graphite anodes and much larger than various nitride and oxide materials, silicon anodes have limited applications because silicon's volume changes by 400% upon insertion and extraction of lithium, which results in pulverisation and capacity fading [1].

This paper presents a battery that overcomes the pulverisation problem associated with silicon anodes and simultaneously maintains the compatibility with the silicon. The silicon is the substrate material to allow the integration of battery with microelectronics, while at same time it provides good thermal contact with heat source or sink. Moreover, their insulating properties prevents the discharge due to undesirable currents across the substrate.

The goal of this battery is to be integrated in thermoelectric energy scavenging microsystems. Also, this thin-film battery is integrated in the same microsystem with a thermoelectric microconverter, as well an ultra low-power electronics to charge the battery and to perform DC-DC conversion. Figure 1 shows an artwork of the thermoelectric

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microconverter with a solid-state battery placed on the top. When the heat flows across the junction, an electrical power current is generated by the Seebeck effect [2-4].

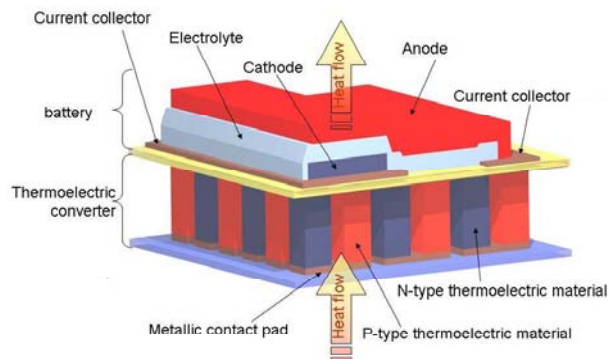


Fig. 1: Integration of the battery in a thermoelectric microsystem.

2. Battery design

A direct current (DC) and radio-frequency (RF) reactive sputtering technique were used in the thin-films depositions. Figure 2 shows a cross-section of the proposed thin-film rechargeable battery, where tin dioxide (SnO_2), lithium phosphorus oxynitride ($\text{Li}_3\text{PO}_4\text{N}$) also known as LiPON and lithium cobaltate (LiCoO_2) are the materials in the anode, electrolyte and cathode, respectively. A protective coating of silicon nitride (Si_3N_4) prevents the reaction of lithium when the battery is exposed to the air [5].

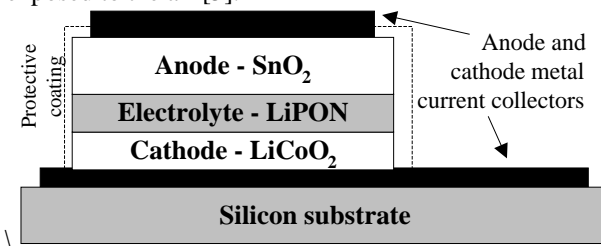


Fig. 2: Cross-section of the thin-film rechargeable battery.

The current collector under the cathode connects to the outside of the battery. Simultaneously it protects the silicon substrate to be pulverised due to the expansions and compressions that take place into the cathode. The repetitive insertion and extraction of Li^+ ions are the main reason of these severe molecular-level mechanic actions. The lithium cobaltate is the cathode material due to its excellent electrochemical cycling stability.

In the case of electrolyte deposition, the LiPON is obtained using lithium phosphate (Li_3PO_4) as sputtering target in an argon (Ar)/nitrogen (N_2) plasma. The LiPON has an exceptional electrochemical stability and very good conductivity of Li^+ ions. This is of great interest, specially when the LiCoO_2 is the cathode material, which is cycled in safety and simultaneously the specific capacity is maintained at 140 mAhg^{-1} for output voltages of 3-4.2 V. LiPON films has an acceptable ionic conductivity of $2 \times 10^{-6} \text{ Scm}^{-1}$ and present an electronic resistivity greater than $10^{14} \Omega\text{cm}$, helping to minimise the short circuit self-discharge across the electrolyte and increase the battery's life. Tin dioxide (SnO_2) has a high-lithium storage capacity and low potential of lithium ion intercalation and an anode made of this material can give a maximum charge-storage capacity of 781 mAhg^{-1} .

3. Experimental results

All films were reactively sputtered in argon (Ar)/oxygen (O_2) plasmas and the sputtering chamber was evacuated to 10^{-6} mbar by a turbomolecular vacuum pump before every deposition. Table 1 shows argon and oxygen flows, the pressure in the chamber and the measurement of the deposited thin-films, in several sputtering series.

Figure 3 shows SEM images of a deposited LiCoO₂ thin-film with a pressure of 10⁻² mbar of oxygen and argon gases. The SEM images in Figure 4 are for a SnO₂ thin-film deposited under the optimal settings. The crystalline structure of the tin dioxide films were characterised by X-ray diffraction (XRD) technique. The resistivity of the films were also measured. These measurements were made before and after annealing the films at 300 °C.

Table 1: Process conditions during the sputtering sessions of selected samples.

SnO ₂ sample	Ar [sccm]	O ₂ [sccm]	Pressure inside the chamber [mbar]	Film thickness [nm]
1	30	10	10 ⁻²	490
2	30	20	10 ⁻²	500
3	20	20	10 ⁻²	630
4	30	5	10 ⁻²	500

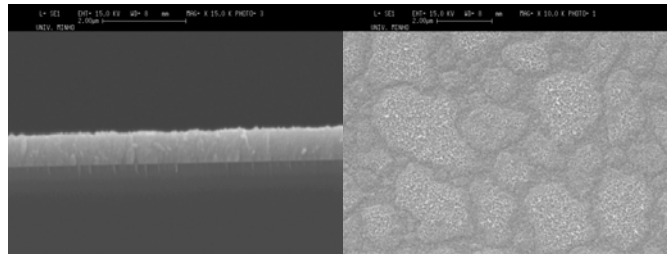


Fig. 3: Cross-section and surface SEM images of a LiCoO₂ thin-film.

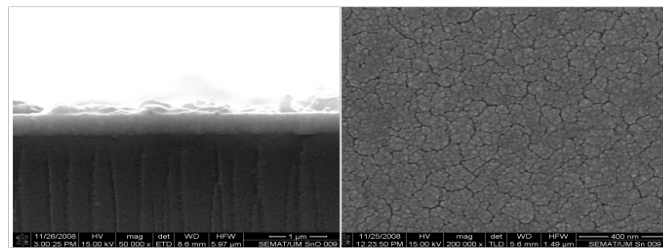


Fig. 4: Cross-section and surface SEM images of a SnO₂ thin-film deposited under the optimal process conditions.

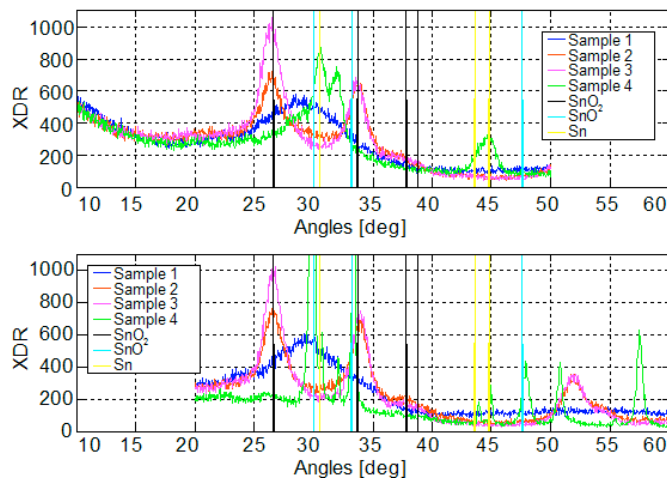


Fig. 5: XRD spectra of the deposited SnO₂ films before (top) and after (bottom) annealing at 300°C.

Figure 5 shows the XRD spectra of the films, before (top plot) and after the annealing (bottom plot). In both plots, only the third sample presents crystalline structure of single phase SnO₂. The remain samples have Sn and SnO materials. After the annealing (except for sample 1) all the films have sharper peaks in the XRD, representing a

larger grain size in the structure. Figure 6 shows the measured resistivity of the films. Except the Sn rich film (sample 4), all films have high resistivity before annealing (represented as $10^{+3} \mu\Omega\text{mm}$). The annealing decreased four-orders of magnitude the resistivity.

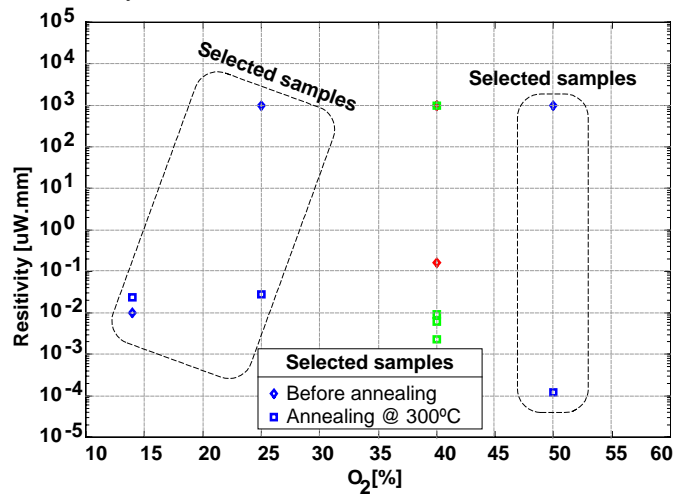


Fig. 6: SnO₂ films resistivity before and after the annealing.

4. Conclusions

This paper presents a thin-film rechargeable lithium battery for integration in stand-alone microsystems with all the electronic apparatus and with a thermoelectric microgenerator that converts thermal gradients into electrical energy (using the Seebeck effect). Moreover, integrated thin-film batteries are ideal power sources for microsystems applications, where high levels of integration is required. Thin-films batteries have very high-life cycles and are intrinsically safe which complies with the strict requirements of the biomedical microsystems, where the toxicity of the batteries must be low.

Acknowledgements

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