Integrated thin-film rechargeable battery in a thermoelectric scavenging microsystem

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Abstract — **Thin-film solid-state rechargeable batteries are ideal power sources for microsystems applications, where a high level of integration is required. The technology and the steps involving the fabrication of such a battery are discussed in this paper. A DC reactive sputtering technique was used in the thin-films depositions. The battery uses SnO_2, Li_3PO_4 and $LiCoO_2$ materials in the anode, electrolyte and cathode, respectively. The application of the battery is for use in thermoelectric energy scavenging microsystems, which converts the small thermal power available in human-body. This Lithium solid-state thin-film battery is integrated in the same device as well as the ultra low-power electronics to charge battery and perform DC-DC conversion.**

Index Terms— **Battery, thermoelectric microsystems, energy scavenging, renewable power source.**

I. INTRODUCTION

The three most important energy sources of interest for use in remote micro/nano systems are thermal gradient, vibration and photovoltaic. Direct thermal-to-electric energy conversion without moving mechanical parts is attractive for a wide range of applications because it provides compact and distributed power, quiet operation, and is usually environmentally friendly. Thus, worldwide efforts are undertaken to expand the technology of thermoelectric devices into the field of micro-systems technologies. An emerging technology for ultra-low power communication platforms triggered renewed interest in power sources for wireless-sensor, in special wireless-wearable-sensors, with power consumption nodes of few mW. Today, almost all of these platforms are designed to run on batteries which not only have a very limited lifetime, but are also in many areas a cost-prohibitive solution. An attractive alternative is powering the sensors with energy harvested from the environment. Thus, a solution for energy microgeneration through energy harvesting by taking advantage of temperature differences must be found. A viable energy source for low-powered devices such as micro sensor systems is possible, since a temperature difference exists, between the two surfaces of a thermoelectric microgenerator (in a wearable device, the difference between the body and environment can be tens of degree, depending on the environment temperature). This temperature difference can be converted into electrical energy using the Seebeck principle. Since many of wireless sensors are powered in a peak basis (e.g., the transmission of data needs much more current than standby or receiving mode) and the temperature gradient could not always be present, the energy will be stored in a rechargeable thin-film battery of Li-ion type (integrated in the system). Ultra-low power electronics performs DC-DC rectification with a variable conversion factor and recharge the battery on optimal conditions. Since, a small volume is required, integration into an IC is desirable.

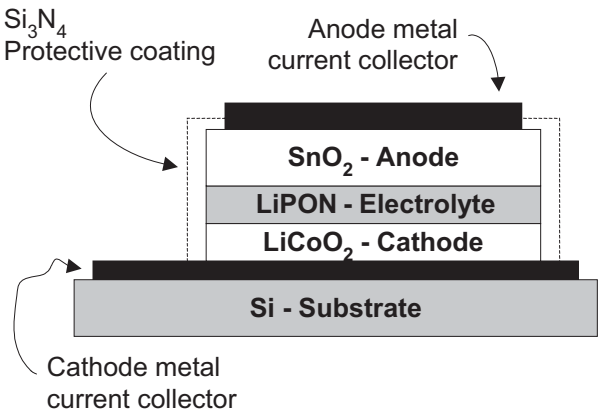


Fig. 1: Cross-section of the thin-film rechargeable battery.

The goal in development of the thin-film rechargeable battery, described in this paper, is to be used together with a single-chip regulated thermoelectric power source, which must operate from low temperature gradients (a minimum temperature difference of 3 ºC between ambient and target thermo-source must provide an IC-compatible voltage). The fabrication of the thermoelectric devices is based in Bismuth and Antimony tellurides since these materials have the highest performance figure-of-merit (*ZT*) at room temperature [1]. The co-deposition method will be used to deposit these thermoelectric thin-films. A very stable evaporation rate of each element (Bi/Te and Sb/Te for the bismuth telluride and antimony telluride, respectively) allows the deposition of polycrystalline n-type and p-type materials, when the substrate is heated in the range 200-300 ºC. The design of a thermoelectric microdevice, with vertical microcolumns, connected in series by metal contact areas, requires the

application of microsystem technologies [2].

Figure 1 shows a cross-section of the thin-film rechargeable battery presented in this paper. As it can be seen, the deposition is made onto an insulating substrate, by way of successive film depositions of the metal current collectors, cathode, electrolyte and anode. The depositions of these layers were made by sputtering. A protective coating of Silicon nitride (Si_3N_4) is required to prevent the reaction of lithium when the battery is exposed to the air [3]. A silicon substrate will be used for integration with microelectronics, while at same time providing good thermal contact with heat source and sink. On the thermoelectric generator will be placed the thin-film integrated battery and all the electronic circuitry to receive the energy and to recharge the battery.

II. Battery Design

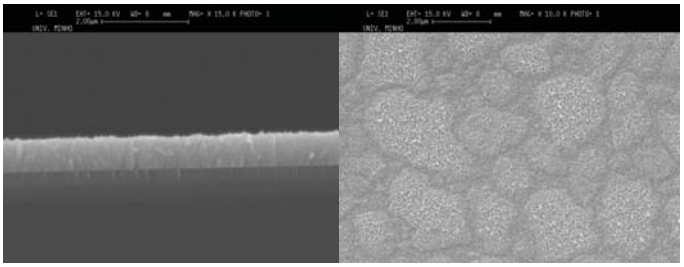
It exists a variety of materials available for the deposition of the cathode, electrolyte and anode. The deposition of the film used as cathode, relied on the lithium cobaltate ($LiCoO_2$), which is the same material used in commercial Lithium batteries [4]. This compound has an excellent electrochemical cycling stability, which is a result of the structural stability of the material, in which the layered cation ordering is extremely well preserved even after a repeated process of insertion and extraction of Li^+ ions [5].

The target material chosen for the electrolyte deposition is the lithium phosphate. The chemical formula of this material is Li_3PO_4 and after the sputtering deposition with a N_2/Ar plasma a LiPON is obtained. This electrolyte material has found wide use because of its exceptional electrochemical stability and good Li^+ ion conductivity [3]. This is specially useful with the use of the $LiCoO_2$ materials in the cathode, which can be safely cycled at the same time it maintains a specific capacity of 140 mAh/g between 3.0 and 4.2 V [6].

Tin dioxide (SnO_2) is an n-type semiconductor oxide with a wide band gap (E_g=3.6 eV at 300 K) and was chosen for the anode material due to their high-lithium storage capacity and low potential of lithium ion intercalation. A SnO_2 anode can give a maximum theoretical 781 mAh/g charge-storage capacity [7].

III. Experimental Details

Several sputtering sessions were performed, however the film thickness was meant to be constant between sessions. A *FerroTec* 2" planar magnetron sputtering cathode and a *PFG 1500 DC* (1500 W DC generator) for plasma applications were used in thin-films depositions. A *MKS* type *246C* single channel power supply/readout was used to power and measure the flow rate of gases (Argon and Oxygen), through an analog *MKS* mass flow controller of type *1179A* and from an analog *MKS* mass flow meter of type *179A*. All films were reactively sputtered in Ar/O_2 plasmas. A *Sycon Instruments STM-100/MF* thickness/rate monitor was used to control the deposition of the films. The sputtering chamber was evacuated to 10^{-6} mbar by a turbomolecular vaccum pump before every deposition. In all sputtering sessions, the Argon and Oxygen flows in the plasma were kept at 50 sccm and 10 sccm, respectively. Figure 2 shows SEM images of a $LiCoO_2$ thin-film deposited in glass, with a pressure of 10^{-2} mbar.



a) b)

Fig. 2: a) Cross-sectional and b) surface SEM images of a $LiCoO_2$ thin-film deposited in glass.

LiPON electrolyte has an acceptable lithium ionic conductivity (2×10^{-6} S/cm). In addiction, the electronic resistivity of the LiPON films is greater that $10^{14}\Omega$.cm, which greatly minimizes the short circuit self-discharge of the battery, increasing the useful life of the battery. For the SnO_2 films, the average resistivity are in the range 10-17 mΩ.cm for films with thickness less than 100 nm. However, for values of the thickness greater than 100 nm, the values decay to the range 5-9 mΩcm.

Table I shows for the sputtering sessions, the Argon and Oxygen flows [sccm], in the plasma, the pressure in the chamber and the measurement of the deposited thin-films. The crystalline structure of the SnO_2 films were characterised by X-ray diffraction (XRD) technique. Diffractograms were recorded from 10º to 60º with a step of 0.04º. Then, the resistivity of the films were measured. It must be noted, that these measurements were made before and after the films were exposed to an annealing at 300ºC. Figure 3 shows the XRD spectra of the SnO_2 films, before (plot in the top) and after the annealing (plot in the bottom). Both plots show that only the third sample has a composition, which is mainly made of SnO_2. The remain samples presents are much more rich in Sn and SnO materials. After the annealing and excepting the sample 1, all the films have sharper peaks in the XRD signature, which means that become more easy to evaluate its composition. Figure 4 shows the measured resistivity of the films, and excepting the case of the sample 4, which has a resistivity of 10^{+4} $\mu\Omega$.mm, theirs resistivity were out of range (but represented with the value 10^{+9} $\mu\Omega$.mm). The anneling decreased four-orders of magnitude the resistivity of the third film.

The optimization of the cathode and anode electrode must be performed, as well as, the deposition and optimization of the solid electrolyte in a low-temperature process. Another future task includes efforts in the increase of the capacity and energy density utilization of $LiCoO_2$ cathodes, in order to improve the cycling stability above 4.2 V.

TABLE I: CONDITIONS MAINTAINED DURING THE SPUTTERING SESSIONS.

SnO_2 sample #	Ar [sccm]	O_2 [sccm]	Pressure in the chamber [mbar]	Film thickness [nm]
1	30	10	2×10^{-5}	490
2	30	20	2×10^{-5}	500
3	20	20	2×10^{-5}	630
4	30	5	10^{-2}	500

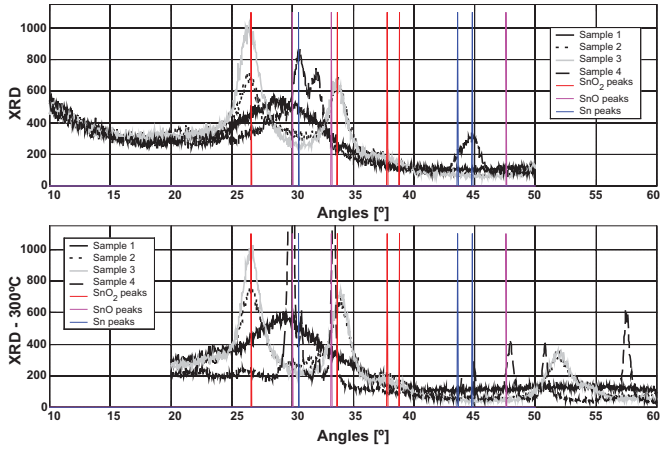


Fig. 3: XRD spectra of the deposited SnO_2 films (top) before and (bottom) the anneling be performed at 300ºC.

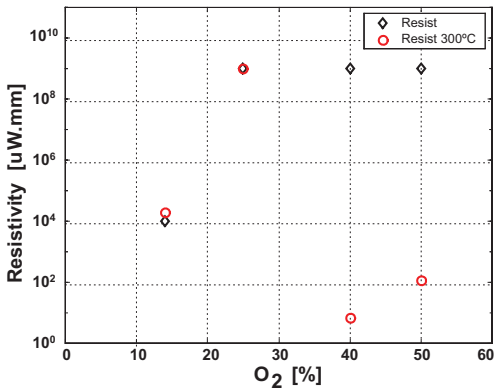


Fig. 4: SnO_2 film resistivity (blue diamonds) before and (red circles) after the annealing

IV. THERMOELECTRIC SCAVENGING MICROSYSTEM

The goal of the battery is the integration in thermoelectric scavenging energy systems, for use in biomedical applications. In relation to thermoelectric scavengers, previous works [8][9] has demonstrated the maximum amount of thermal energy that can be removed from human-body in a wearable thermal-generator without compromising the comfort, and maximizing the thermoelectric conversion.

A thermal resistance of 100-300 $KW^{-1}cm^{-2}$ is expected in the wrist, where thermal flow can be converted with a thermo-bracelet. Also, temperatures between 27 ºC and 36 ºC can be found on different parts of body. Figure 5 shows a typical temperature map of a hand [10]. The ambient air temperature and thermal-converter to air thermal resistance also limits the maximum power available. Thermal resistance bellow 50 $KW^{-1}cm^{-2}$ can be achieved with a pin-heatsink.

Maximum voltage output is obtained when the thermal-resistance of the thermoelectric legs is equal to the human-body and heatsink thermal resistance. A thermal-resistance above 200 $KW^{-1}cm^2$ is desirable in the thermoelectric converter. Since each thermoelectric junction of Bi_2Te_3-Sb_2Te_3 can deliver an output voltage of 300 µV/K, more than 4000 junctions are necessary to obtain an output voltage (without load) of 10 V, under a temperature difference of 10 ºC, when body and heatsink thermal resistances are considered. Figure 6 shows the open-circuit voltage and power that can be obtained in a 1 cm^2 Bi_2Te_3-Sb_2Te_3 thermoelectric generator, as function of length of the column.

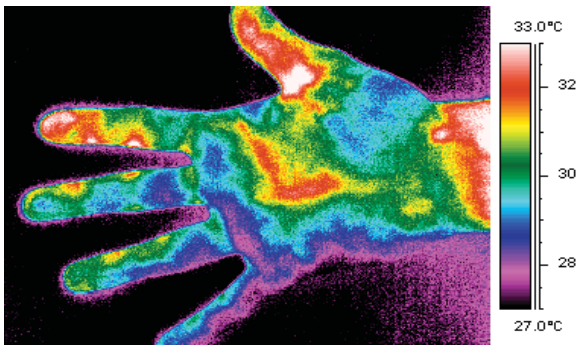


Fig. 5: Hand temperature obtained by thermal imaging [10].

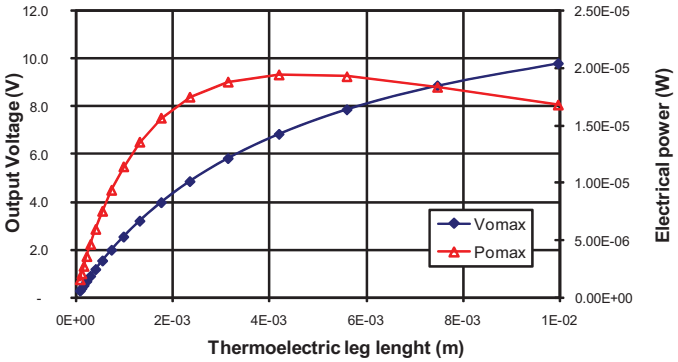


Fig. 6: The output voltage and power of a 1 cm^2 Bi_2Te_3-Sb_2Te_3 thermoelectric generator, measured in open-circuit and plotted as function of column length.

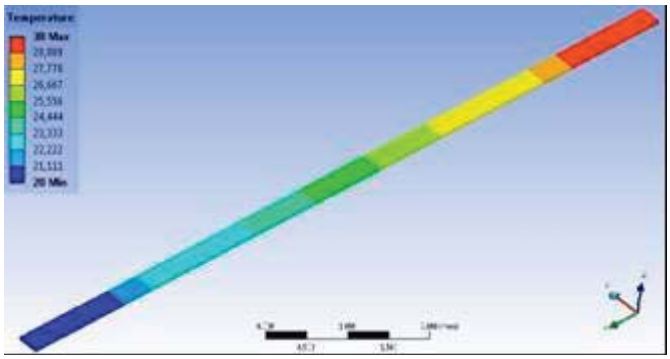


Fig. 7: For a pair in contact with body, the temperature map obtained by FEM.

Figure 7 shows the temperature map of a single junction (two thermoelectric elements) with the hot side in contact with the human-body (30 ºC, 150 $KW^{-1}cm^{-2}$) and the cold side kept at air (20 ºC) with a 50K/W/cm^2 heatsink, obtained with FEM simulation tool. The temperature difference of 5 ºC is obtained between the junctions (27 ºC at hot-side and 22 ºC at cold-side). The task of battery recharging is performed by ultra-low power electronics, which makes DC-DC rectification with a variable conversion factor. Using components off-the-shelf, it was mounted a first circuit prototype to make DC-DC step-up conversion. Figure 8 shows such a circuit, which is composed by a charge-pump (CP) [11] followed by a DC-DC step-up converter [12]. The voltage at the output of the energy scavenger is monitored and when this voltage crosses above 300 mW, the output of CP will enable the step-up which will rise the voltage at the output of scavenger to the desired value.

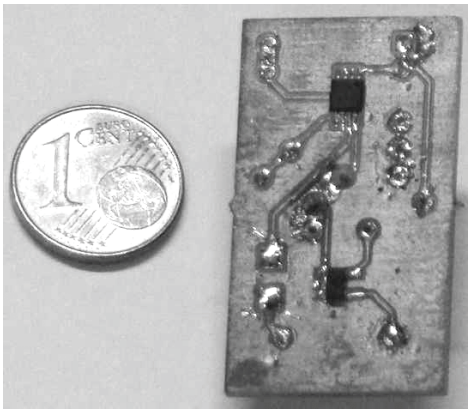


Fig. 8: Photography of the CP, followed by a DC-DC step-up.

Figure 9 shows an artist impression of a thermoelectric microdevice, with vertical microcolumns, connected in series by metal contact areas. On this thermoelectric generator will be placed the thin-film integrated battery and all the electronic circuitry to receive the energy and to recharge the battery. The fabrication of such a tridimensional (3D) structure, a device as suggested in this figure is proposed.

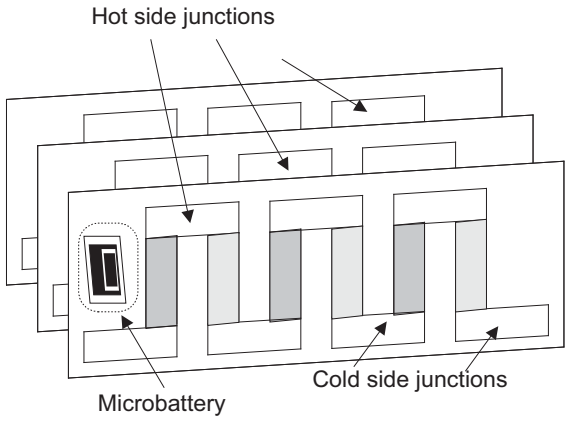


Fig. 9: An artwork of the proposed device. Foils with thermoelectric junction are stacked to obtain a large number of junctions. The last foil includes de Lithium battery and the charge-control circuit.

On a kapton polyimide substrate, 30 μm of thickness, thermoelectric elements with 10 μm of film thickness are patterned, to obtain 4 mm × 100 μm columns, connected in series with metal contacts. To obtain the suggested number of junctions, several substrates are stacked. The last substrate is reserved for fabrication of the thin-film battery, where microelectronics die is also glued.

V. Conclusions

This paper presented the development of a thin-film rechargeable battery. The fabrication of the battery is to be made by way of successive film depositions of the metal current collectors, cathode, electrolyte and anode. The materials used in the deposition of these films were the lithium cobaltate $LiCoO_2$, lithium phosphorus oxynitride (LiPON) and tin dioxide SnO_2, respectively. It were also described the procedures and the instrumentation, regarding the DC sputter deposition of the films.

The quality of deposited films were measured, in order to evaluate the effects in terms of the homogeneity, composition and electrical properties, caused by the changes in the flow of the oxygen, but more experimental tests must be done. Thin-film solid-state batteries show a very high life cycle and are intrinsically safe. This is of special concern in the design of thermoelectric energy scavenging microsystem, specially when the thought applications are in the biomedical field or for long cycle operations without requiring human activity.

Acknowledgments

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