Sputtered SnO_2 for application in thin-film solid state microbatteries

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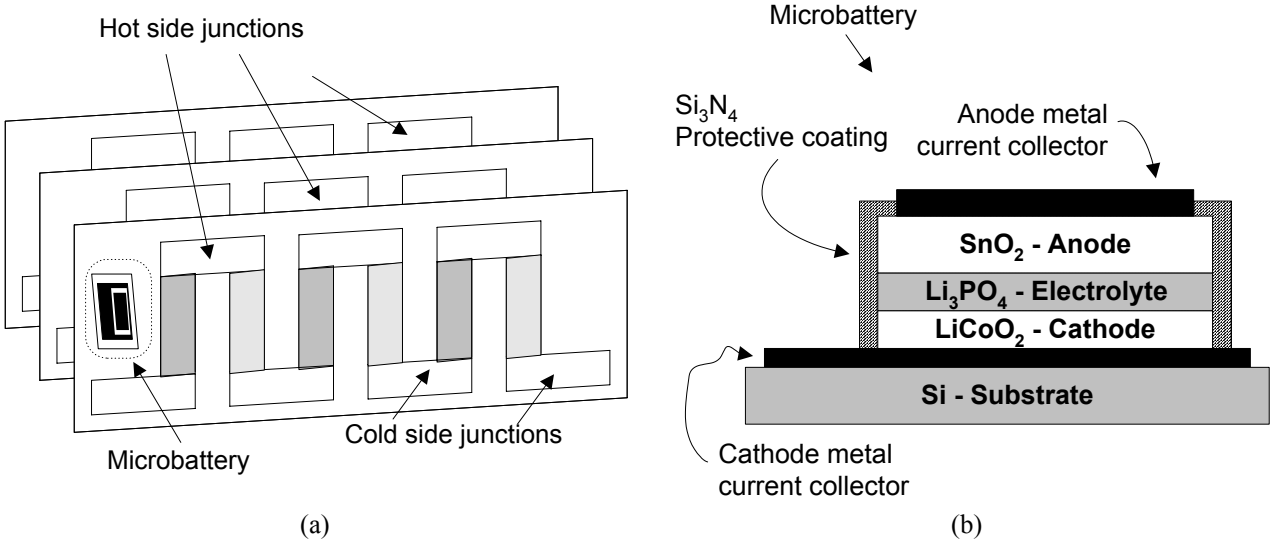
Abstract. Thin-film solid-state rechargeable batteries are ideal power sources for microsystems applications, where a high level of integration is required. This paper describes the deposition and characterization of tin dioxide (SnO_2) thin-films, which will be the anode of the microbattery.

Introduction

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. The energy harvested wireless sensors must be powered in a peak basis because a temperature gradient could not always be present, thus the energy must be stored in a capacitor (storage capacitor) for later use by the electronic system to be powered, or in a rechargeable microbattery of Li-ion type (integrated in the system). Currently, 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]. Figure 1(a) shows an artwork of a thermoelectric microdevice, whose vertical microcolumns are connected in series by metal contact areas, which is responsible to recharge the attached battery. The zoomed part showed in the Figure 1(b), is a cross-section of a thin-film rechargeable battery. As it can be seen, the deposition is to be 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 will be made by sputtering technique.



(a) (b)

Fig. 1: An artwork of (a) a thermoelectric microdevice and of a (b) cross-section of the microbattery.

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 [2]. 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 microbattery and all the electronic circuitry to receive the energy and to recharge the microbattery. The focus of this paper, is to describe the deposition and characterization of tin dioxide (SnO_2) thin-films, which is the material of the anode of microbattery.

Tin dioxide depositions

Tin dioxide (SnO_2) is an n-type semiconductor oxide and was chosen as anode material due to their high-lithium storage capacity and low potential of lithium ion intercalation [3]. Figure 2 shows the laboratory setup. Several sputtering sessions were performed, however the film thickness was meant to be constant between sessions.

Fig. 2: Laboratory setup.

A 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 to 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.

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.

Experimental results

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.

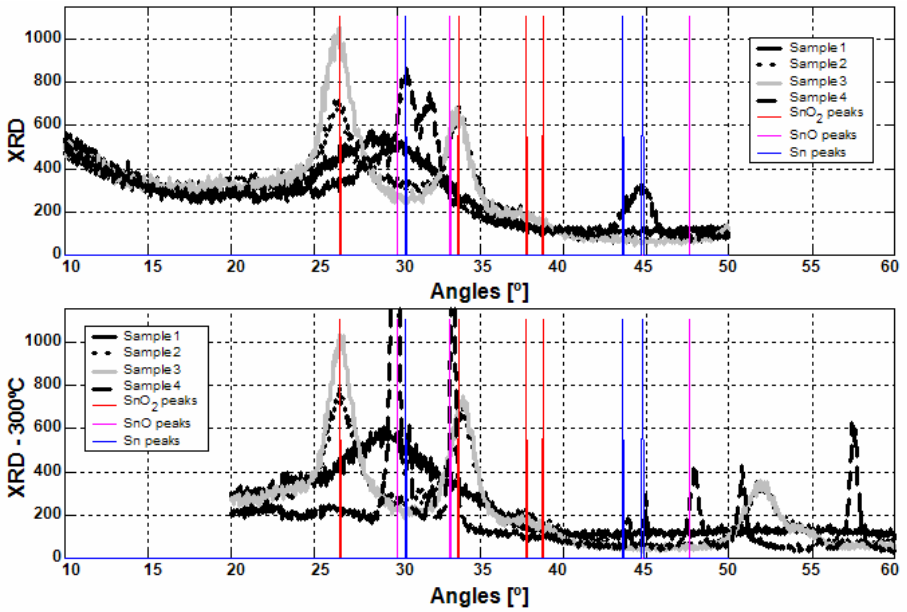


Fig. 3: XRD spectra of the deposited tin dioxide films (top) before and (bottom) the annealing be performed at 300ºC.

Table 1: 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

Figure 3 shows the XRD (X-ray diffraction) spectra of the films, before (top plot) and after the annealing (bottom plot). For both plots, only the third sample presents crystalline structure of single phase SnO2. The remain samples have Sn and SnO materials. After the annealing and excepting the sample 1, all the films have sharper peaks in the XRD, representing a larger grain size in the structure. Figure 4 shows the measured resistivity of the films, and excepting the case of the sample 4, which has a resistivity of 10^{+4} μΩ.mm, theirs resistivity were out of range (but represented with the value 10^{+9} μΩ.mm). The annealing decreased four-orders of magnitude, the resistivity of the third film.

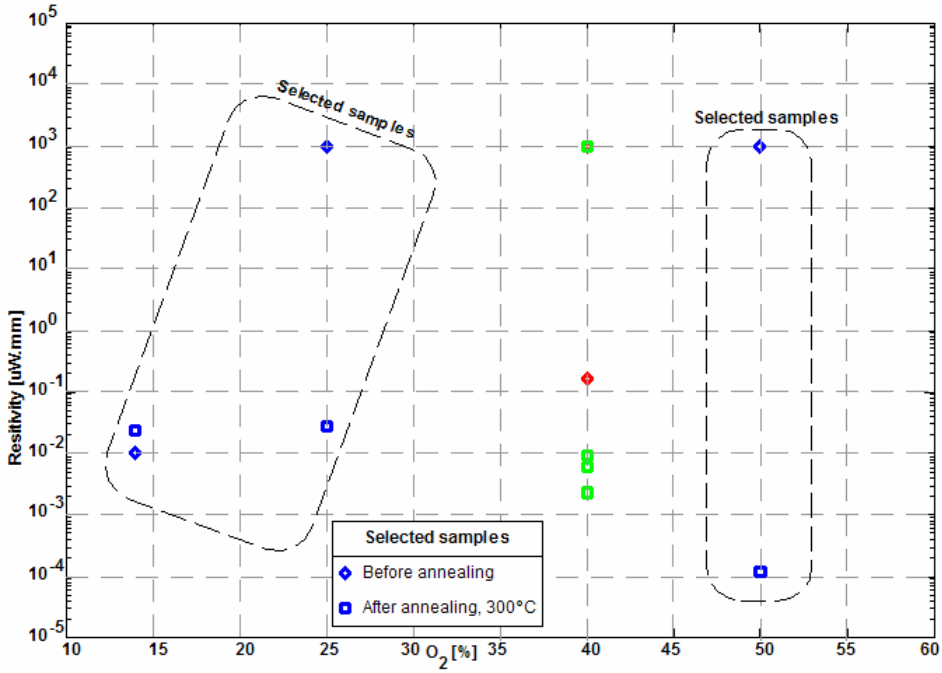


Fig. 4: SnO_2 film resistivity (diamonds) before and (squares) after the annealing. Blue color is for the selected samples

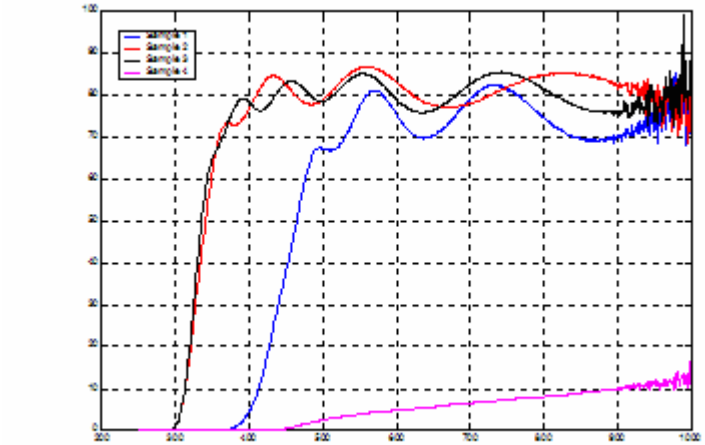


Fig. 5: Optical transmittance [%] of the deposited SnO_2 films, after the annealing process.

Figure 5 shows the optical transmittances [%], which were measured for all annealed samples, in order to verify the optical properties of films. Samples 2 and 3 have tin dioxide in its composition, and both present the same behavior for all the wavelenghts. The SEM images presented in Figure 6, are for a tin dioxide thin-film deposited under the optimal settings.

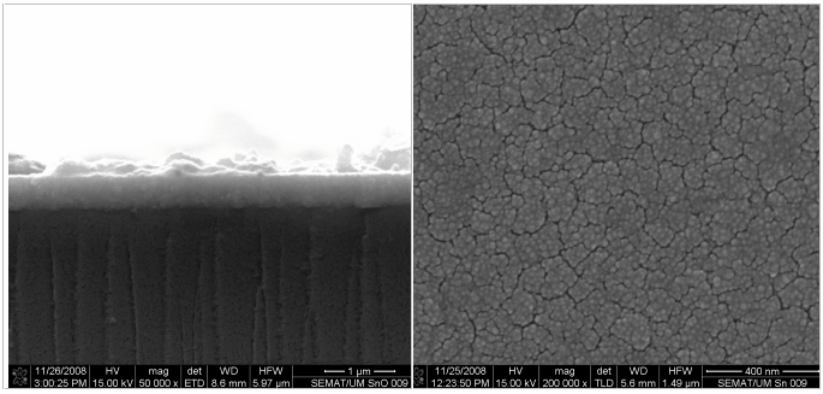


Fig. 6: Cross-sectional and surface SEM images of a tin dioxide thin-film deposited under the optimal settings.

Summary

This paper presented the deposition technology of thin-films made of tin dioxide (SnO_2). The purpose of such films, is to use it as anode materials in lithium thin-film rechargeable batteries 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 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 target applications are in the biomedical field or for long cycle operations without requiring human activity.

Acknowledgements

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References

[1] L. M. Gonçalves, *et al*, "Thermoelectric properties of Bi_2Te_3/Sb_2Te_3 thin films", *Materials Science Forum*, Vols. 514-516, pp. 156-160, May 2006.

[2] N. J. Dudney, B. J. Neudecker, "Solid state thin-films lithium battery systems", *Solid State & Materials Science*, Vol. 4, pp. 479-482, 1999.

[3] Z. Wang *et al*, "Coating of multi-walled carbon nanotube with SnO_2 films of controlled thickness and its application for Li-ion battery", Journal of Power Sources, 2008.