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# Seebeck coefficient in multiphase thin films

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## ABSTRACT

Mg-Ag-Sb thin films were deposited by magnetron sputtering using a commercial  $\text{Mg}_{1/3}\text{Ag}_{1/3}\text{Sb}_{1/3}$  target. All the films contain principally the two phases  $\text{Ag}_3\text{Sb}$  and  $\alpha\text{-MgAgSb}$  in same proportions but exhibit different microstructures. The films have the same Seebeck coefficient despite the difference of interface density and structure. Theoretical calculations show that the film effective Seebeck coefficient  $S_{film}$  is depending only on the volume of each phase present in the film and their Seebeck coefficients. The multiple interfaces between the different phases have no effect on  $S_{film}$ .

*Keywords:* Thermoelectricity, Seebeck coefficient, Interface, Thin film, MgAgSb

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Several solutions allowing the production of efficient thermoelectric materials were recently proposed [1]. Among them, charge carrier energy filtering is considered as one of the most promising strategy [1,2]. The principal method consists in the creation of specific interfaces in the material acting as energy filtering barriers, promoting a significant increase of the Seebeck coefficient ( $S$ ) and of the thermoelectric power factor. Experimental variations of  $S$  in materials containing inclusions are regularly attributed to energy filtering. However, when several phases are present in a thermoelectric polycrystalline material, the effective Seebeck coefficient  $S_{eff}$  is depending on  $S_{\varphi_i}$  of each present phase  $\varphi_i$ . Assuming a constant temperature ( $T$ ) gradient in the film, and excluding any interface effects,  $S_{eff}$  of a material containing  $n$  different phases can be expressed such as:

$$S_{eff} = \sum_i^n f_{\varphi_i} \times S_{\varphi_i} \quad (1)$$

with  $f_{\varphi}$  the volume fraction of the phase  $\varphi_i$  (Fig. 1). In the present work, we investigate the interface influence on the  $S$  of a polycrystalline material containing several phases.  $\alpha$ -MgAgSb is a ternary semi-conductor [3], which usually contains inclusions of the metallic binary phase Ag<sub>3</sub>Sb [3]. The  $S$  of  $\alpha$ -MgAgSb was reported to significantly vary depending on the fabrication process [4–6].  $\alpha$ -MgAgSb has been to date only studied in its bulk state, but  $\alpha$ -MgAgSb thin films produced by sputtering are expected to be useful for the integration of energy harvesting devices in the CMOS technology [7].

Mg-Ag-Sb thin films were deposited in a magnetron sputtering system exhibiting a base pressure of  $10^{-8}$  Torr, using a 99.9999% pure Ar gas flow to sputter in the DC mode a 99.99% pure Mg<sub>1/3</sub>Ag<sub>1/3</sub>Sb<sub>1/3</sub> target purchased from CODEX international. The films were deposited on glass substrates for  $S$  measurements, or on the native oxide of Si(001) substrates

for electron microscopy observations. Four 300 nm-thick Mg-Ag-Sb films were deposited. Two films were deposited at room temperature (RT), the first one (#1) was kept as-deposited, while the second one (#2) was ex situ annealed under vacuum ( $10^{-7}$  mbar) at 523 K for 30 min. The two other films were deposited at 523 K (#3) and 573 K (#4), respectively. The structure of the films was investigated using X-ray diffraction (XRD) in the Bragg-Brentano ( $\theta$ - $2\theta$ ) geometry using a Cu  $K_\alpha$  source ( $\lambda_{K\alpha} = 0.154$  nm), as well as using scanning electron microscopy (SEM) in cross-section. The  $S$  of the films was measured using a home-made setup.  $T$  and the electrical potential were measured with the same probes at two different locations on the specimens separated by 1 cm.  $S$  was measured between  $T = 220$  and 330 K, corresponding to the temperature range of the targeted CMOS applications. The experimental  $S$  were compared to theory, running the BoltzTraP code [8] with material bulk parameters determined from ab-initio calculations. Ab-initio calculations were carried out using the first-principles pseudopotential method based on the DFT and the plane-wave self-consistent field method (PWSCF) which is implemented in the QUANTUM ESPRESSO package [9]. The Generalized Gradient Approximation (GGA-PBE) [10] was used for exchange-correlation functional. The ultrasoft pseudopotential (USP) method was used to treat the valence electron configuration.

Figure 2 presents the X-ray diffractograms measured on the four specimens. Fig. 2a shows that only the binary phase  $\text{Ag}_3\text{Sb}$  is detected in the film after deposition at RT. Seven diffraction peaks are detected corresponding to the  $\text{Ag}_3\text{Sb}$  atomic planes (110), (002), (111), (022), (130), (023), and (132) at  $2\theta = 34.32^\circ$ ,  $37.24^\circ$ ,  $39.23^\circ$ ,  $51.56^\circ$ ,  $61.77^\circ$ ,  $68.44^\circ$ , and  $74.29^\circ$ , respectively. Fig. 2b shows that annealing the same film at 523 K for 30 min allows the phase  $\alpha\text{-MgAgSb}$  as well as the phase Sb to form in the film in addition to the phase  $\text{Ag}_3\text{Sb}$ . In addition to the same  $\text{Ag}_3\text{Sb}$  diffraction peaks, five diffraction peaks corresponding

to  $\alpha$ -MgAgSb(110),  $\alpha$ -MgAgSb(202),  $\alpha$ -MgAgSb(114),  $\alpha$ -MgAgSb(330), and  $\alpha$ -MgAgSb(006) are respectively observed in the diffractogram at  $2\theta = 13.01^\circ$ ,  $24.16^\circ$ ,  $31.88^\circ$ ,  $41.25^\circ$ , and  $42.06^\circ$ , as well as two peaks corresponding to Sb(102) and Sb(213) at  $2\theta = 28.69^\circ$  and  $48.35^\circ$ . Fig. 2c and Fig. 2d show that the same diffraction peaks are observed in the samples heated at 523 K or 573 K during deposition. Only the peak Ag<sub>3</sub>Sb(130) is only observed in the specimen ex situ annealed. The (qualitative) volume fraction  $f$  of each phase present in the different films was determined using the integration of each detected peak of each phase. Due to the uncertainties related to the Bragg-Brentano geometry, the values of  $f$  should not be considered quantitatively. Nevertheless, the fractions corresponding to the three phases present in the films are the same in the three different films #2, #3, and #4:  $f_\alpha \sim 33\%$ ,  $f_{Ag_3Sb} \sim 60\%$ , and  $f_{Sb} \sim 7\%$ . Fig. 3 presents cross-sectional SEM images obtained on the films #1 (Fig. 3a), #2 (Fig. 3b), #3 (Fig. 3c), and #4 (Fig. 3d). The SEM images show in the four films the coexistence of multiple grains of different phases exhibiting different contrasts. However, the microstructures of the samples #2, #3, and #4 are different. According to the XRD analyses, the matrix should correspond to the phase Ag<sub>3</sub>Sb, while the inclusions should be  $\alpha$ -MgAgSb grains. The inclusions in the film #2 exhibit a higher density ( $\rho \sim 1.5 \times 10^{11} \text{ cm}^{-2}$ ) and smaller sizes ( $10 \leq l \leq 50 \text{ nm}$ ) than in the film #3 ( $\rho \sim 8.2 \times 10^9 \text{ cm}^{-2}$ ,  $23 \leq l \leq 70 \text{ nm}$ ) and #4 ( $\rho \sim 3.5 \times 10^9 \text{ cm}^{-2}$ ,  $65 \leq l \leq 90 \text{ nm}$ ). Furthermore, the film #3 is rougher and facets are less easily observed on the inclusions compared to film #4. Fig. 4 presents  $S$  measured on the four different films versus  $T$ .  $S$  measured on the films #2 (open up triangles), #3 (solid circles), and #4 (solid squares), are similar in the considered  $T$  range. However,  $S$  measured on the as-deposited film #1 (solid down triangles) is significantly lower than the three other films. Indeed,  $S$  measured in the film #1 should correspond to the phase Ag<sub>3</sub>Sb, while  $S$  measured on the three other films should correspond to an effective coefficient resulting from the presence of the different phases. Fig. 4 shows also the theoretical  $S$  of the

two major phases present in the samples (i.e.  $\text{Ag}_3\text{Sb}$  and  $\alpha\text{-MgAgSb}$ ) calculated using the BoltzTraP code and ab-initio calculations. The theoretical coefficient of  $\text{Ag}_3\text{Sb}$  (solid line) is in good agreement with the experimental coefficient measured on the film #1 (solid down triangles), containing only  $\text{Ag}_3\text{Sb}$ . Furthermore, the theoretical coefficient of  $\alpha\text{-MgAgSb}$  is in good agreement with the experimental value reported by Kirkham et al. [4] (solid diamonds). XRD measurements suggest that the phase  $\alpha\text{-MgAgSb}$  occupies in average only 30% of the volume of the films #2, #3, and #4. Neglecting the presence of Sb in the samples,  $S_{eff}$  of a hypothetic film containing the two phases  $\text{Ag}_3\text{Sb}$  and  $\alpha\text{-MgAgSb}$  was calculated using the theoretical values of  $S_{\text{Ag}_3\text{Sb}}$  and  $S_\alpha$  and eq. 1, with  $f_\alpha = 0.3$  and  $f_{\text{Ag}_3\text{Sb}} = 0.7$ .  $S_{eff}$  (dash line in Fig. 4) is in good agreement with the  $S$  measured on the three films #2, #3, and #4. Neither nano-size effect [11-12] nor interfacial effect [1-2] are observed on  $S$ . Indeed, the microstructures of the films may be too far from the structure of superlattice-type materials, the size of  $\alpha\text{-MgAgSb}$  inclusions being too large ( $> 5 \text{ nm}$  [11-12]) and exhibiting a significant size distribution. Furthermore, the nature of the  $\text{Ag}_3\text{Sb}/\alpha\text{-MgAgSb}$  interface may not promote the suitable energy barrier (ohmic instead of Schottky contact).

In conclusion, Mg-Ag-Sb thin films were elaborated by magnetron sputtering in different conditions allowing the production of different films containing principally the phase  $\text{Ag}_3\text{Sb}$  and the phase  $\alpha\text{-MgAgSb}$  in same proportions. These films exhibit the same  $S_{eff}$  despite a significant difference of interface density and structure.  $S_{eff}$  can be determined considering the Seebeck coefficients of the two different phases and their volume in the films, without considering any influence of the interfaces.

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## CAPTIONS

**FIG. 1.** Schematic showing the serial electrical circuit corresponding to the case of a thermoelectric material made of two different phases  $\varphi 1$  and  $\varphi 2$  in a temperature gradient,  $S_{\varphi 1}$  (resp.  $S_{\varphi 2}$ ) and  $\sigma_{\varphi 1}$  (resp.  $\sigma_{\varphi 2}$ ) being the Seebeck coefficient and the electrical conductivity of the phase  $\varphi 1$  (resp.  $\varphi 2$ ). Any  $\varphi 1/\varphi 2$  interface effect is neglected.

**FIG. 2.** Ex situ X-ray diffractograms acquired in the  $\theta$ - $2\theta$  geometry on the four different films: #1 (a), #2 (b), #3 (c), and #4 (d).

**FIG. 3.** Cross-sectional SEM images acquired on the four different films: a) RT as-deposited film (film #1), b) RT deposited film annealed under vacuum at 523 K for 30 min (film #2), c) film deposited at 523 K (film #3), and d) film deposited at 573 K (film #4).

**FIG. 4.** Comparison between experimental (solid symbols) and calculated (lines) Seebeck coefficients ( $S$ ) for  $220 \leq T \leq 330$  K: The solid down triangles, the solid circles, and the solid squares correspond to the RT as-deposited film (film #1), the film deposited at 523 K (film #3), and the film deposited at 573 K (film #4). The open up triangles corresponds to the RT deposited film annealed under vacuum at 523 K for 30 min (film #2) and the solid diamonds corresponds to the phase  $\alpha$ -MgAgSb from [4]. The lines correspond to the  $S$  theoretical values of bulk  $\text{Ag}_3\text{Sb}$  (solid line), bulk  $\alpha$ -MgAgSb (dash dot line), and a film containing in its volume 70% of  $\text{Ag}_3\text{Sb}$  and 30% of  $\alpha$ -MgAgSb, neglecting  $\text{Ag}_3\text{Sb}/\alpha$ -MgAgSb interface effects (dash line).



**Figure 1**

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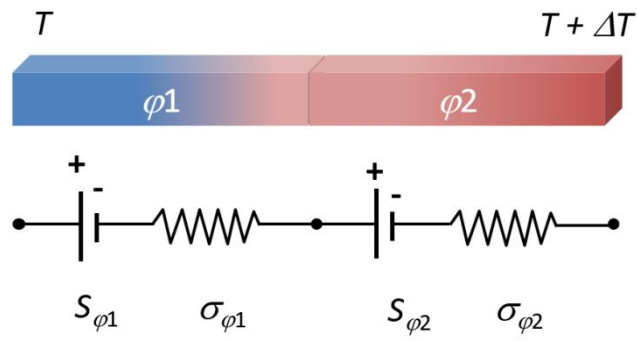
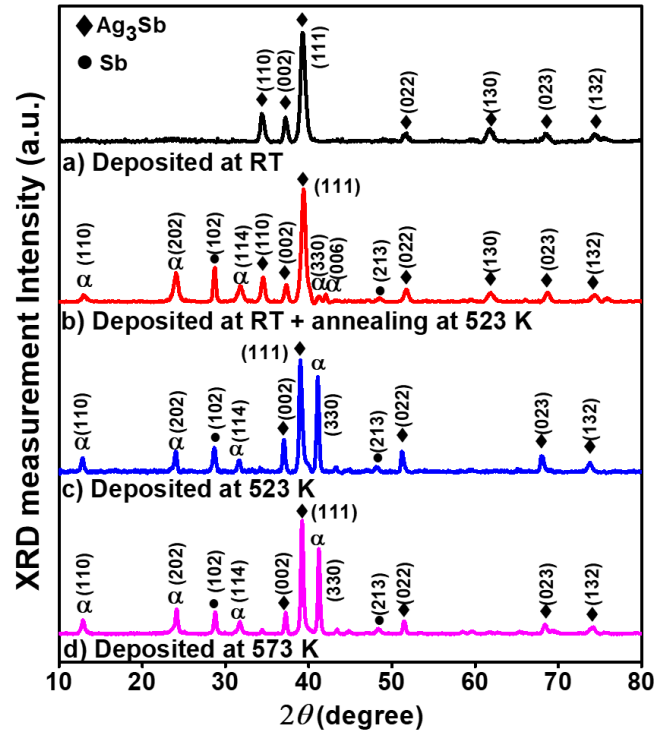


Figure 2

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**Figure 3**

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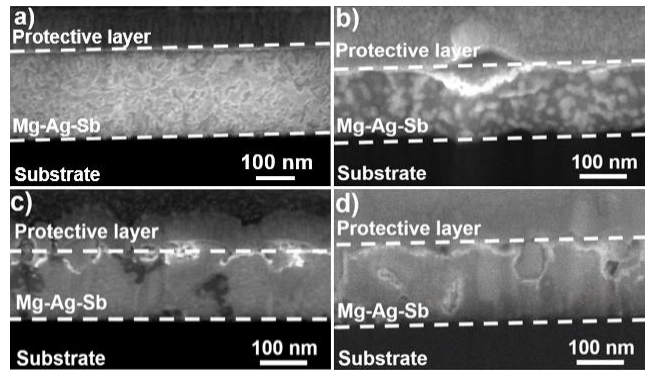


Figure 4

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