Vacuum 82 (2008) 1499–1502

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Optimization of Bi_2Te_3 and Sb_2Te_3 thin films deposited by co-evaporation on polyimide for thermoelectric applications

L.M. Goncalves [a,*], P. Alpuim [b], Gao Min [c], D.M. Rowe [c], C. Couto [a], J.H. Correia [a]

[a] University of Minho, Department of Industrial Electronics, Portugal
[b] University of Minho, Department of Physics, Portugal
[c] University of Cardiff, School of Engineering, United Kingdom

Keywords:
Thin film Peltier
Thermoelectric
Microcooler
Thermopile

A B S T R A C T

The optimization of the deposition process of n-type Bismuth Telluride and p-type Antimony Telluride thin films for thermoelectric applications is reported. The films were deposited on a 25 μm-thick flexible polyimide (kapton) substrate by co-evaporation of Bi and Te, for the n-type element, and Sb and Te, for the p-type element. The evaporation rate of each material was monitorized by an oscillating crystal sensor and the power supplied to each evaporation boat was controlled with a PID algorithm in order to achieve a precise user-defined constant evaporation rate.

The influence of substrate temperature (in the range 240–300 °C) and evaporation rates of Bi, Te and Sb on the electronic properties of the films was studied and optimized to obtain the highest Seebeck coefficient. The best n-type Bi_2Te_3 films were deposited at 300 °C with a polycrystalline structure, a composition close to stoichiometry, electrical resistivity ~20 μΩ m and Seebeck coefficient −195 μV/°C. The best p-type Sb_2Te_3 films were deposited at 240 °C, are slightly Te-rich, have electrical resistivity ~20 μΩ m and Seebeck coefficient +153 μV/°C. These high Seebeck coefficients and low electrical resistivities make these materials suitable for fabrication of Peltier coolers and thermopile devices.

1. Introduction

Efficient solid state thermoelectric microdevices are desirable for several applications, including local cooling and thermoelectric microgeneration. Thermoelectric cooling and generation based on Peltier and Seebeck effects, respectively, have the advantages of not using any moving mechanical parts, being environmental friendly, allowing integration with microelectronic circuits and being easy to control. Tellurium alloys (n-type Bi_2Te_3 and p-type Sb_2Te_3) are well-established low-temperature thermoelectric materials widely used in the thermoelectric industry due to their high Seebeck coefficient, low electrical resistivity and low thermal conductivity [1].

Because of the reduced dimensions of the microdevices, the conventional processes used to produce bulk thermoelectric materials are not applicable to the present case. Instead, thin film planar technology was considered adequate for this task, due to the large choice of substrates that it allows, to the possibility of patterning the devices to micro or submicrodimensions by the use of masks or photolithography and to the ease of integration with standard Si technology.

Tentative deposition of Bi_2Te_3 films by direct evaporation of the bulk materials proved to be impossible due to the large differences in vapour pressure of Bismuth and Tellurium, resulting in a compositional gradient along the film thickness [2]. Other deposition processes have been reported for the deposition of Bi_2Te_3 thin films. Thermal co-evaporation [3], co-sputtering [4], electrochemical deposition [5], metal-organic chemical vapour deposition [6] or flash evaporation [7] are some examples. George and Pradeep [8] and Charles et al. [9] reported the deposition of stoichiometric n-type Bi_2Te_3 thin films at flow ratios of Te/Bi > 2 with substrate temperatures between 250 °C and 310 °C. However, films co-evaporated by both groups were n-type only due to an excess Tellurium present in the films. Zou [3] fabricated stoichiometric n-type Bi_2Te_3 and p-type Sb_2Te_3 films, and reported some influence of substrate temperature and evaporation rates of the compounds during the film growth process. This work was based on a small number of samples, and no consistent relation could be established between growing conditions and material performance. da Silva and Kaviany [2] reported the fabrication of a microcooler based on co-evaporated films, but due to limitations on fabrication process, optimal growing conditions could not be achieved. To the best knowledge of the authors, no consistent data is available and no report on repeatability of properties of co-evaporated materials performance has been reported to date.

* Corresponding author. Fax: +351 253 510189.
E-mail address: lgoncalves@dei.uminho.pt (L.M. Goncalves).

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doi:10.1016/j.vacuum.2008.03.076

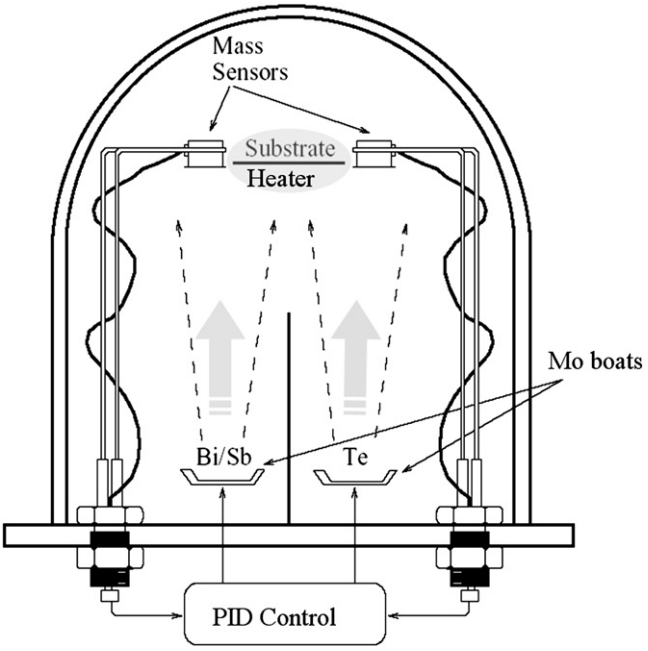

Fig. 1. Co-evaporation system.

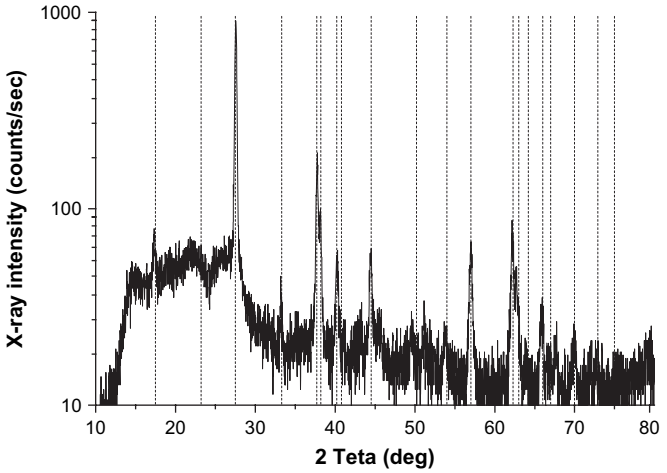

Fig. 2. XRD analysis of an n-type Bi_2Te_3 thin film. The peaks agree with the powder diffraction spectrum for Bi_2Te_3 (dashed lines).

In the present work the influence of growing parameters is studied in detail and more than 100 samples were fabricated to allow a consistent correlation of the growing conditions and the thermoelectric properties of the films.

Glass, silicon and polyimide (kapton) were used as substrates, with good film-to-substrate adhesion. However, for thermoelectric applications, 25 μm-thick kapton film was chosen as substrate because of the low thermal conductivity ($0.12\,W\,m^{-1}\,K^{-1}$) and appropriate value of thermal expansion coefficient ($12\times10^{-6}\,K^{-1}$) which closely matches the thermal expansion coefficient of the telluride films, thus reducing residual stress and increasing adhesion. Flexible substrates add uncommon mechanical properties to the composite film-substrate and enable their integration with many novel types of devices [10].

2. Experimental

Bi_2Te_3 films were fabricated using the co-evaporation resistive method in a high-vacuum chamber with base pressure $< 5\times10^{-6}$ Torr, using two Molybdenum boats, filled with Bismuth pellets and Tellurium lumps, respectively, both with 99.999% purity. The power applied to each boat was controlled independently, using two computed PID controllers to maintain each deposition rate at a fixed value, during the deposition. Bi evaporation rate was maintained at 1 Å/s in all depositions and Te evaporation rate was varied in the range 1–5 Å/s. Each PID controller read the deposition rate from a thickness monitor and was designed to real-time compute the power necessary to apply to the corresponding evaporation boat in order to achieve the user-defined constant evaporation rate. Each thickness monitor, consisting of a quartz crystal oscillator, was carefully placed inside the chamber in order to receive material only from the boat it was monitoring. A metal sheet was placed between the two boats to partially separate the flows from the two evaporants and fully prevent mixing of both materials to occur at the quartz crystals (see Fig. 1). Large boats (baffled boxes, 4 cm^3 volume) were used, in order to achieve stable evaporation rates. A similar procedure was used to evaporate p-type Sb_2Te_3 thin films by replacing Bi with Sb in one of the boats. Substrates were heated to $T_{sub} = 240\,^{\circ}C$, $270\,^{\circ}C$ or $300\,^{\circ}C$ for Bi_2Te_3 deposition and to $T_{sub} = 200\,^{\circ}C$ or $240\,^{\circ}C$ for Sb_2Te_3 deposition. A resistive heater was attached to the substrate holder and temperature was measured on the back of the substrate using a thermocouple embedded in the stainless steel substrate holder. Temperature during deposition was kept constant using a PID controller. A small temperature difference can occur, between the value measured on film surface and the temperature read on the back of the substrate due to low thermal conductivity of polyimide substrate. The film chemical composition and structure were obtained by Energy-Dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). In-plane electrical resistivity was measured at room temperature using the conventional four-probe van der Pauw geometry. Seebeck coefficient was measured by connecting one side of the film to a heated metal block at a fixed temperature and the other side to a heat sink at room temperature. Film thickness was around 1 μm for all depositions.

Table 1
Properties of selected Bi_2Te_3 and Sb_2Te_3 films deposited by co-evaporation

Film	Material	Seebeck (μV/°C)	ρ (μΩ m)	T_{sub} (°C)	$R = F_{Te}/F_{Bi,Sb}$	Ratio of Te to Bi, Sb (at%)	Composition Te (at%)	P.F. ($\times10^{-3}\,W\,K^{-2}\,m^{-1}$)
#C20	Bi_2Te_3	−153	23.0	240	1.55	1.89	65.4	1.0
#C28	Bi_2Te_3	−189	19.5	270	1.58	1.51	60.2	1.8
#C30	Bi_2Te_3	−111	23.9	270	3.57	2.25	69.2	0.5
#C39	Bi_2Te_3	−141	29.5	300	1.57	1.41	58.5	0.7
#C41	Bi_2Te_3	−195	16.2	300	2.07	1.50	60.0	2.4
#C59	Sb_2Te_3	111	25.7	200	1.67	1.51	60.1	0.5
#C60	Sb_2Te_3	124	20.8	200	1.86	1.61	61.7	0.7
#C45	Sb_2Te_3	137	24.3	240	1.58	1.74	63.5	0.8
#C44	Sb_2Te_3	153	31.5	240	2.72	2.50	71.4	0.7

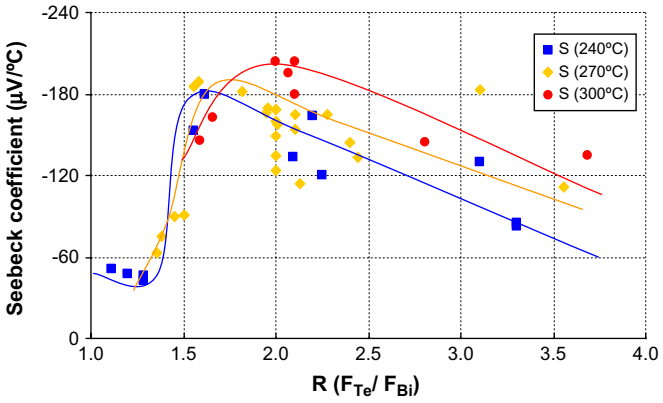

Fig. 3. Seebeck coefficient of Bi_2Te_3 thin films as a function of Te/Bi evaporation rate ratio, R, at $T_{sub} = 240\,^{\circ}C$, 270 °C and 300 °C.

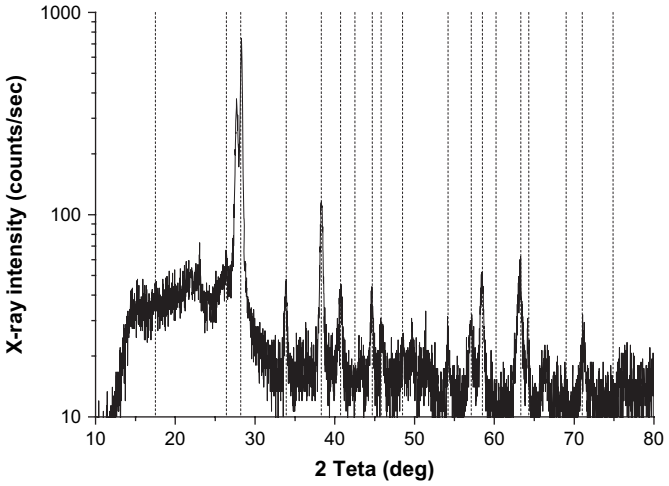

Fig. 5. XRD analysis of a p-type Sb_2Te_3 thin film. The peaks agree with the powder diffraction spectrum for Sb_2Te_3 (dashed lines).

3. Results and discussion

Table 1 summarizes the deposition conditions and measured properties of selected Bi_2Te_3 and Sb_2Te_3 thin films. The evaporation flow ratio, R, is defined as the evaporation rate of Te divided by the evaporation rate of Bi or Sb ($R = F_{Te}/F_{Bi,\ Sb}$). The results show that Te-atom% content is in the range 55–70%, with some films close to stoichiometry (60% Te and 40% Bi/Sb).

3.1. Bi_2Te_3

In order to find the deposition parameters which result in films with best thermoelectric properties, three series of Bi_2Te_3 films were deposited. Bi evaporation rate was 1 Å/s in all evaporations and Te evaporation rate was varied in the range 1–4 Å/s. Fig. 2 shows a typical X-ray diffraction spectrum of an optimized film that reveals its polycrystalline structure. The peaks agree with the powder diffraction spectra for polycrystalline Bi_2Te_3. Fig. 3 shows the Seebeck coefficient of all Bi_2Te_3 films, for the three different substrate temperatures used – 240 °C, 270 °C and 300 °C – as a function of the Te/Bi evaporation ratio R.

For the same R-value films have higher Seebeck coefficient for higher substrate temperature (300 °C) than for lower substrate temperature (270 °C, 240 °C). At $T_{sub} = 300\,^{\circ}C$ the optimal evaporation rate of Te is 2.0 times higher than the evaporation rate of Bi, while at $T_{sub} = 240\,^{\circ}C$, R is only 1.6. This could be attributed to re-evaporation of Te from the substrate as discussed in next paragraph.

In Fig. 4, the value of the Bi_2Te_3 film composition (number of Te atoms divided by number of Bi atoms) obtained by EDX is plotted against R for different substrate temperatures (240 °C, 270 °C and 300 °C). It can be seen that film composition is always lower in Te than the corresponding fraction of evaporated Te, R. This effect is more important as T_{sub} increases from 240 °C to 270 °C and to 300 °C. At 300 °C, the vapour pressure of Te, taken from literature, is 10^5 higher than the vapour pressure of Bi. Therefore, it is possible to conclude that re-evaporation of Te from the substrate at a higher rate than Bi explains why it is necessary to use a higher value of R than the desired ratio of atoms of Te/Bi in the film final composition. In order to quantify this effect several evaporations of pure Te were made at 300 °C on polyimide and the conclusion is that, at this T_{sub}, Te re-evaporation rate can be as-high-as 2 Å/s.

If one looks at the optimized values of Seebeck coefficient as a function of film composition it can be seen (Table 1) that the best films are those whose composition is close to stoichiometry.

3.2. Sb_2Te_3

A similar procedure to the one used to optimize Bi_2Te_3 films was adopted for Sb_2Te_3. Two deposition series were made at $T_{sub} = 200\,^{\circ}C$

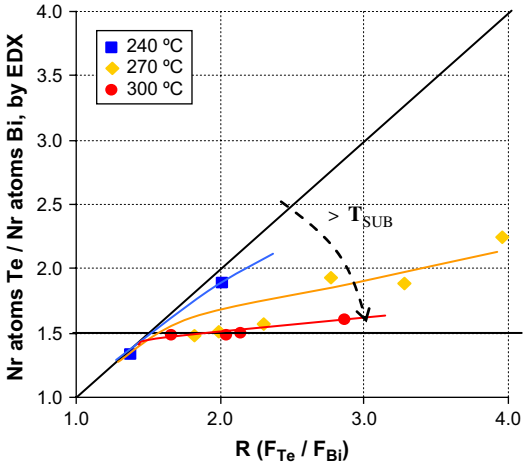

Fig. 4. Ratio of Te/Bi number of atoms in the films as a function of Te/Bi evaporation rate ratio, R, for $T_{sub} = 240\,^{\circ}C$, 270 °C and 300 °C.

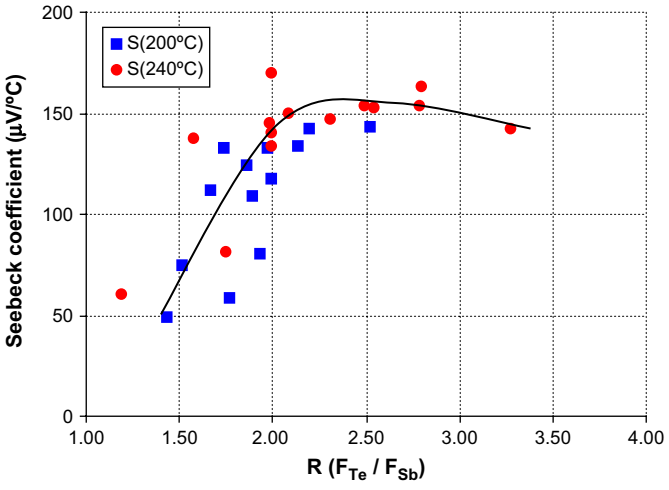

Fig. 6. Seebeck coefficient of Sb_2Te_3 films fabricated at different Te/Sb evaporation fluxes ratio and different substrate temperatures.

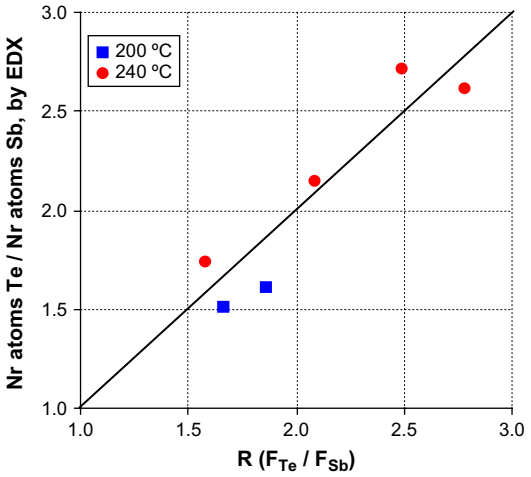

Fig. 7. Composition ratio of Te/Sb number of atoms in the film as a function of R, for $T_{sub} = 200\,^{\circ}C$ and $240\,^{\circ}C$.

and 240 °C. In both T_{sub}-series Sb evaporation rate was fixed at 1 Å/s and Te evaporation rate was varied in the range 1–4 Å/s. Fig. 5 shows a typical X-ray diffraction spectrum of an optimized film that reveals its polycrystalline structure. The peaks agree with the powder diffraction spectra for polycrystalline Sb_2Te_3. Fig. 6 shows the Seebeck coefficient measured in films deposited at different R = Te/Sb evaporation ratios, for $T_{sub} = 200\,^{\circ}C$ and 240 °C. The higher Seebeck coefficients are obtained for $R = 2.0$–2.5. However, in this case and contrary to what was observed for Bi_2Te_3, temperature of substrate in the range studied has little or no influence on Seebeck coefficient. Also, the re-evaporation effect of Te from the substrate is much less important or is totally absent here, as can be seen in Fig. 7 where film composition roughly reproduces the evaporation ratio R used for deposition. This could also be related to the lower T_{sub} used for Sb_2Te_3 than for Bi_2Te_3 deposition. Sb_2Te_3 films with higher Seebeck coefficient are slightly rich in Te (no. atoms Te/no. atoms Sb = 2–2.5).

4. Conclusions

State-of-the-art Bi_2Te_3 and Sb_2Te_3 materials were deposited by co-evaporation, in the form of thin films. EDX results show that Bi_2Te_3 films with high Seebeck coefficients are obtained when the composition of film is stoichiometric (60% Te and 40% Bi). With lower substrate temperatures (240 °C), best films are obtained with Te/Bi evaporation flow ratio of 1.6, but at higher substrate temperatures (300 °C) the evaporation flow ratio should be increased to 2.0, due to re-evaporation of Te from the heated substrate. The best Sb_2Te_3 films are obtained with Te/Sb evaporation flow ratio in the range 2.0–2.5. Substrate temperature, in the range 200–240 °C, has no major influence on Sb_2Te_3 Seebeck coefficient.

Since small deviations on evaporation rates result in large differences in material properties, an accurate calibration of thickness monitor parameters should be done, adjusting the density, Z-factor and tooling factor. Use of as-high-as possible temperature of substrate is also recommended, since the excess of Tellurium will be easily re-evaporated. Substrate temperature above 300 °C becomes impracticable, due to excessive re-evaporation of Tellurium from substrate.

Compatibility with flexible electronics was demonstrated by the use of a 25 μm-thick polyimide foil as substrate, due to its low thermal conductivity and high upper working temperature. Thermoelectric properties achieved on Bi_2Te_3 and Sb_2Te_3 thin films deposited on polyimide in this work are suitable for the fabrication of Peltier microcoolers and thermoelectric microgenerators.

Acknowledgments

One of the authors (L.M. Goncalves) thanks the Portuguese Foundation for Science and Technology (SFRH/BD/18142/2004).

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