

Optimization of thermoelectric thin-films deposited by co-evaporation on plastic substrates

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Abstract

The optimization of the thermal co-evaporation process for n-type Bismuth Telluride and p-type Antimony Telluride onto plastic substrates (Kapton© polyimide) for thermoelectric applications is reported.

Films were co-evaporated from Bismuth and Tellurium or Antimony and Tellurium to obtain Bi₂Te₃ or Sb₂Te₃, respectively. The evaporation rate of each material was monitored using a crystal oscillator sensor and the power applied to each boat was controlled with a PID algorithm, in order to achieve a precise user-defined constant evaporation rate. The influence of substrate temperature (150 - 300 °C) and evaporation rate (2 Å/s - 9 Å/s) on the electronic properties of the films was studied and optimized to maximize the thermoelectric figure-of-merit.

Energy-dispersive X-ray spectroscopy, X-ray diffraction and Fourier-transform infrared spectroscopy confirmed the formation of Bi₂Te₃ and Sb₂Te₃ thin films. Seebeck coefficients (up to 250 µV/°C), in-plane electrical resistivity (5-40 µΩ.m), Hall mobility (20-100 cm².V⁻¹.s⁻¹) and carrier concentration (10¹⁹-10²¹cm⁻³) were measured at room temperature in films fabricated with different process parameters.

Thermoelectric p-type and n-type thin films with high figures of merit, suitable for the fabrication of lateral Peltier coolers and thermal micro-generators, were obtained.

Introduction

Efficient solid state thermoelectric microdevices are desirable for local cooling and thermoelectric microgeneration specially if they lend themselves to integration with microelectronic circuits. Tellurium alloys (n-type Bi₂Te₃ and p-type Sb₂Te₃) are well-established room-temperature thermoelectric materials, widely used in the thermoelectric industry, since they have a high Seebeck coefficient, low electrical resistivity and relatively low thermal conductivity [1]. In this work, thin film planar technology is used in order to scale down to the micron size the conventional bulk thermoelectric devices. Thin-film technology allows for an enlarged choice of the substrate, the possibility of patterning the devices to micro or submicro dimensions and the easy integration with standard Si technology.

Tentative deposition of Bi₂Te₃ 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 in the literature for the deposition of Bi₂Te₃ thin films. Co-sputtering, electrochemical deposition, metal-organic chemical vapour deposition or flash evaporation are some

examples. Recent work with superlattice materials reports improved figure-of-merit values [3].

Zou [4] fabricated stoichiometric n-type Bi₂Te₃ and p-type Sb₂Te₃ films, and reported the influence of substrate temperature and evaporation rate of the materials during the film growth on the electronic properties. Their work was based on a small number of samples, and no consistent relation could be established between growing conditions and material performance. Silva et al. [2] reported the fabrication of a micro-cooler with co-evaporated films, but due to limitations on fabrication process, optimal growing conditions could not be achieved.

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 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 (12×10⁻⁶ 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 [5].

Experimental

Bi₂Te₃ films were fabricated using the co-evaporation resistive technique in a high-vacuum chamber. The power applied to each boat was controlled independently, using two computed PID controllers to maintain the deposition rate at a fixed value during the deposition. Bi evaporation flow rate (Fr_{Bi}) was maintained at 2 Å/s, and Te evaporation flow rate (Fr_{Te}) was in the range 3 Å/s to 9 Å/s. The evaporation flow ratio ($R = Fr_{Te} / Fr_{Bi,Sb}$) is defined as the amount of Te divided by the amount of Bi (or Sb) that arrives to the substrate during deposition. 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, 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 cm³ volume) were used, in order to maintain stable evaporation rates. A similar procedure was used to evaporate p-type Sb₂Te₃ thin films by replacing Bi with Sb in one of the boats.

Substrates were heated to the temperature setpoint (T_{sub}) which was varied between 150 °C and 300 °C.

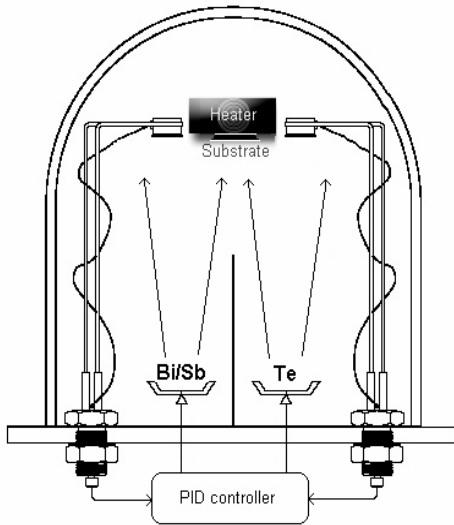


Fig. 1: Co-evaporation system.

The film chemical composition and structure was obtained by Energy-Dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). In-plane electrical resistivity, carrier concentration and hall mobility were measured at room temperature using the conventional four probe van der Pauw geometry. A magnetic field of 80 mT was applied for Hall measurements. Seebeck coefficient was measured by connecting one side of the film to an heated metal block at a fixed temperature and the other side to a heatsink at room temperature, with temperature difference of 10 °C between both sides. Power factor was calculated by eq. 1 (α is Seebeck coefficient $-V/^\circ\text{C}$ and ρ is electrical resistivity $-\Omega\cdot\text{m}$).

$$PF = \alpha^2 / \rho \quad [\text{eq. 1}]$$

Results – Bi_2Te_3 films

Several films of Bi_2Te_3 were deposited with different flow rate ratios, R , and substrate temperatures, T_{sub} , in order to study the effect of this parameters on the thermoelectric properties of the films. R was set by fixing the Bi evaporation flow rate (F_{rBi}) at 2 $\text{\AA}/\text{s}$ and varying the Te evaporation flow rate (F_{rTe}) in the range 3-9 $\text{\AA}/\text{s}$. Three series of films were fabricated, at $T_{\text{sub}} = 190, 230$ and 270 °C. All films were ~ 1 μm thick ($\pm 30\%$).

Table 1: Properties of selected Bi_2Te_3 films.

Film	Temp. T_{sub} °C	$R =$ $F_{\text{rTe}} / F_{\text{rBi}}$	Seebeck α $\mu\text{V}/^\circ\text{C}$	Resist. ρ $\mu\Omega\cdot\text{m}$	P.F. $\times 10^{-3}$ $\text{W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$
#187A	190	1.5	-62	5.7	0.67
#C36	190	1.7	-180	16.6	1.95
#267A	230	2.1	-156	11.3	2.16
#267D	230	3.0	-152	13.4	1.72
#273C	270	3.2	-248	12.6	4.87
#281D	270	3.86	-220	10.6	4.57

Table 1 summarizes the thermoelectric properties of selected Bi_2Te_3 films. X-ray diffraction (XRD) reveals the

polycrystalline structure of Bi_2Te_3 , as shown in fig 2. The peaks agree with the powder diffraction spectra for polycrystalline Bi_2Te_3 . Similar results from XRD analysis can be found in literature [6].

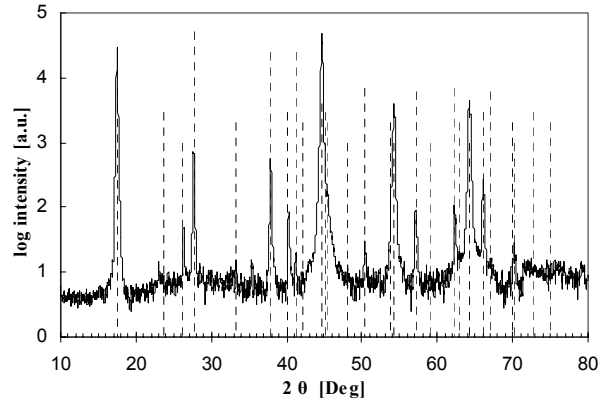


Fig. 2. XRD diffractogram of an n-type Bi_2Te_3 thin film.

The SEM cross-sectional and surface images of the material reveal the presence of grains with dimensions higher than 500 nm (fig.3).

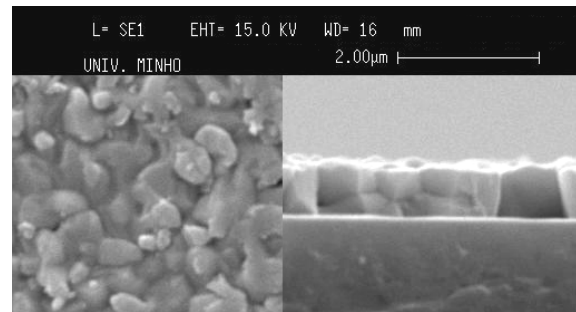


Fig 3: Surface and cross-sectional SEM images of a Bi_2Te_3 film deposited on glass, $T_{\text{sub}} = 270$ °C and $R=3.2$.

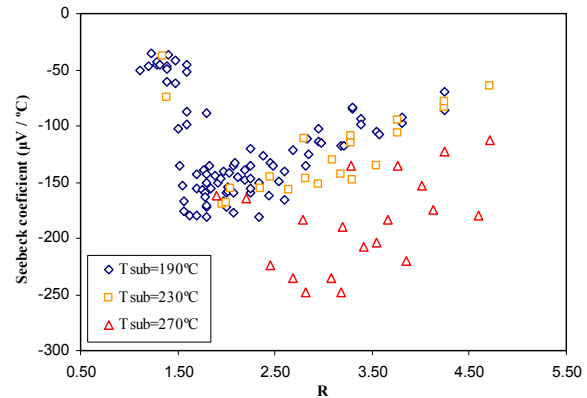


Fig 4: Seebeck coefficient of Bi_2Te_3 thin films as a function of Te/Bi evaporation flow ratio, R .

Fig. 4 shows the dependance of the Seebeck coefficient on the flow rate ratio (R), for films deposited at different substrate temperatures (190 °C, 230 °C and 270 °C). At each T_{sub} the maximum value of Seebeck coefficient is obtained at a value of R that depends on T_{sub} and decreases monotonically with T_{sub} . The film composition is always poorer in Te than the corresponding fraction of evaporated Te, R . This effect is

more important as T_{sub} increases. At 300 °C, the vapour pressure of Te is 10^5 higher than the vapour pressure of Bi. Therefore, it is possible to conclude that re-evaporation of Te from the substrate proceeds at a higher rate than Bi. This explains why it is necessary to use a higher value of R than the desired atomic ratio of Te/Bi in the final film composition. Fig 5 shows the electrical resistivity of Bi_2Te_3 films as a function of R for different T_{sub} .

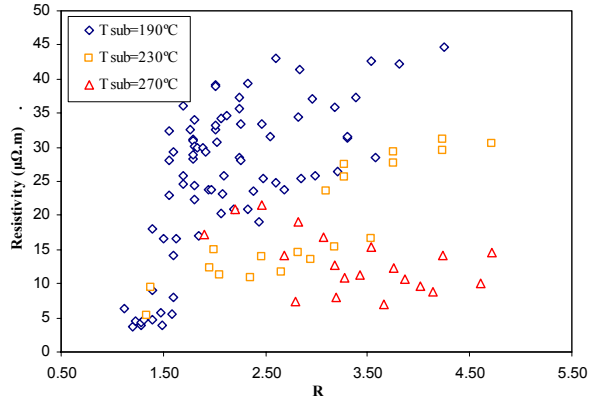


Fig 5: Electrical resistivity of Bi_2Te_3 as a function of Te/Bi evaporation flow rate ratio, R .

The best power factor obtained at each substrate temperature is shown in fig 6. The highest PF was obtained at $T_{\text{sub}} = 270$ °C. For $T_{\text{sub}} > 290$ °C films with high mechanical stress and/or poor adhesion were obtained due to the degradation of the polyimide substrate.

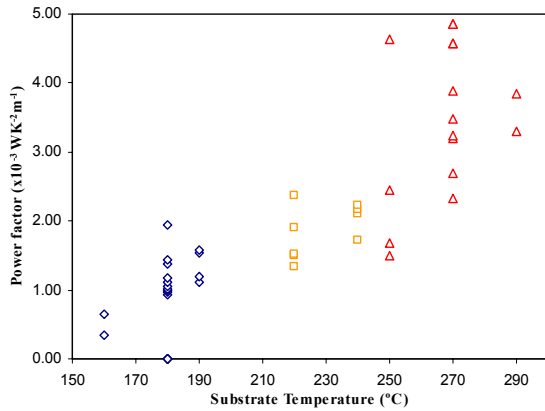


Fig 6: Power factor of selected Bi_2Te_3 films plotted as a function of substrate temperature.

A thermoelectric $PF = 4.9 \times 10^{-3} \text{ W K}^{-2} \text{ m}^{-1}$ was obtained in films deposited at $T_{\text{sub}} = 270$ °C with Bi evaporation rate of 2 Å/s and Te evaporation rate of 6 Å/s ($R = 3$). This evaporation parameters resulted in a near-stoichiometric composition (by EDX analysis) of the material with 35-40% of Bi and 65-60% of Te.

Results – Sb_2Te_3 films

Three series of Sb_2Te_3 films were deposited, at $T_{\text{sub}} = 150$ °C, 180 °C and 220 °C, and R between 1.4 and 3.7. Sb deposition rate (F_{Sb}) was fixed at 2 Å/s for all depositions and Te deposition rate (F_{Te}) was varied in the range 2.8-7.4 Å/s.

Table 2 summarizes the thermoelectric properties of selected Sb_2Te_3 films.

Table 2: Properties of selected Sb_2Te_3 films.

Film	Temp. T_{sub} °C	$R = F_{\text{Te}} / F_{\text{Sb}}$	Seebeck α $\mu\text{V}/^\circ\text{C}$	Resist. ρ $\mu\Omega.\text{m}$	P.F. $\times 10^{-3} \text{ W.K}^{-2}.\text{m}^{-1}$
#195C	150	1.5	91	7.6	1.1
#305A	150	1.7	140	14	1.4
#304D	220	2.1	133	10	1.8
#306A	220	2.5	156	9.2	2.7
#306D	220	3.2	188	12.6	2.8

Fig. 7 shows a typical X-ray diffractogram of an optimized film that reveals its polycrystalline structure. The peaks agree with the powder diffraction spectra for polycrystalline Sb_2Te_3 and with literature [6].

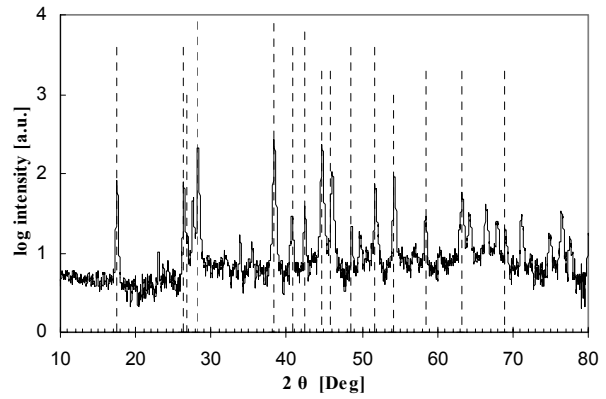


Fig. 7. XRD diffractogram of a p-type Sb_2Te_3 thin film.

The SEM surface and cross-sectional images of a Sb_2Te_3 film deposited by co-evaporation (fig. 8) reveal the presence of grains with dimension ~ 500 nm.

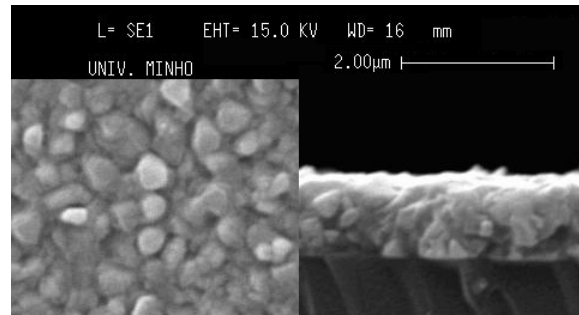


Fig 8: Surface and cross-sectional SEM image of a Sb_2Te_3 film deposited on glass, $T_{\text{sub}}=220^\circ\text{C}$ and $R=2.8$.

Fig.9 shows the values of the measured Seebeck coefficient as a function of flow rate ratio, for $T_{\text{sub}} = 150$ °C, 180 °C and 220 °C. The influence of R and T_{sub} on electrical resistivity of Sb_2Te_3 films can be seen in Fig10. Despite there is no significant change in electrical resistivity of films deposited at 150 °C and 180 °C, there is a major decrease in resistivity when $T_{\text{sub}} = 220$ °C.

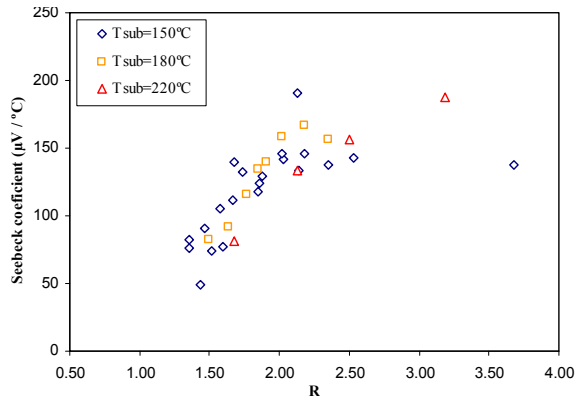


Fig 9: Seebeck coefficient of Sb_2Te_3 films as a function of Te/Bi evaporation fluxes ratio, R .

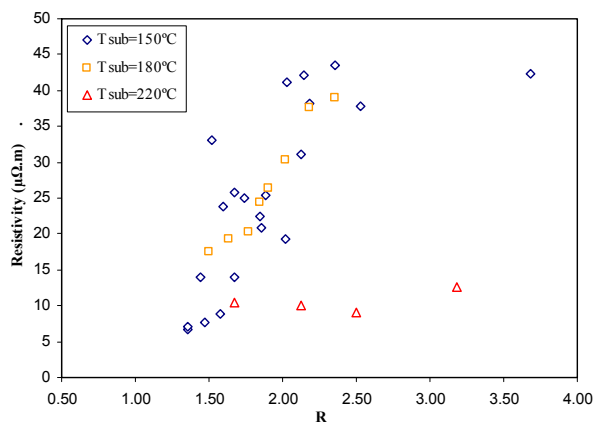


Fig 10: Electrical resistivity of Sb_2Te_3 as a function of Te/Bi evaporation flow rate ratio, R .

Films with higher Seebeck coefficient and lower resistivity (which results in a higher $PF \sim 2.8 \times 10^{-3} \text{ W K}^{-2} \text{ m}^{-1}$) are obtained at $T_{\text{sub}} \sim 220^\circ\text{C}$ and $R = 2.5-3$. The solid state atomic composition of these films is 27-35% Sb, 73-65% Te. Fig.11 shows the power factors obtained for the best Sb_2Te_3 films deposited at each temperature ($T_{\text{sub}} = 150^\circ\text{C}$, 180°C and 220°C).

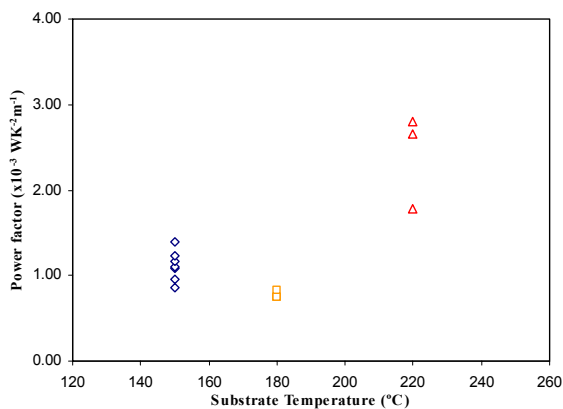


Fig 11: Power factor of selected Sb_2Te_3 films plotted as a function of substrate temperature.

Conclusions

N-type Bi_2Te_3 and P-type Sb_2Te_3 thermoelectric thin films with high figure of merit were fabricated by thermal co-evaporation. The best films have a Power factor of $4.87 \times 10^{-3} \text{ W.K}^{-2}.\text{m}^{-1}$ and $2.8 \times 10^{-3} \text{ W.K}^{-2}.\text{m}^{-1}$ respectively for Bi_2Te_3 and Sb_2Te_3 . These values compare well with the best published results for the same materials. Films were deposited onto glass substrates and flexible Kapton substrates, with good adhesion. The influence of evaporation rates and substrate temperature on Seebeck coefficient and electrical resistivity was reported. EDX results show that films with high Seebeck coefficients are obtained when the composition of film is near-stoichiometric (35-40% Bi, 65-60% Te for $\text{Bi}_x\text{Te}_{1-x}$ and 27-35% Sb, 73-65% Te for $\text{Sb}_x\text{Te}_{1-x}$). The highest thermoelectric power factor for Bi_2Te_3 thin films was obtained at substrate temperature around 270°C , Bi evaporation rate of 2 \AA/s and Te evaporation rate of 6 \AA/s . The highest PF in Sb_2Te_3 films was obtained at $T_{\text{sub}} = 220^\circ\text{C}$, Sb evaporation rate of 2 \AA/s and Te evaporation rate of 6 \AA/s .

The flexible electronics concept was demonstrated by the use of a $25 \mu\text{m}$ -thick polyimide foil as a substrate. Due to its low thermal conductivity and high upper working temperature, polyimide is an adequate choice for device fabrication. The 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 [7].

Acknowledgments

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