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Thermal co-evaporation of Sb₂Te₃ thin-films optimized for thermoelectric applications

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ABSTRACT

Antimony telluride (Sb₂Te₃) is a chalcogenide material used in thermoelectric applications. The deposition of thin films of Sb₂Te₃ requires a precisely controlled process to achieve a desirable high thermoelectric figure-of-merit. The optimization of the thermal co-evaporation process for p-type Sb₂Te₃ thin-film onto plastic substrates (Kapton© polyimide) for thermoelectric applications is reported. The influence of deposition parameters and composition on thermoelectric properties was studied, seeking optimal thermoelectric performance. Energy-dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy all confirmed the formation of Sb₂Te₃ thin films. Seebeck coefficient (up to 190 μ VK⁻¹), in-plane electrical resistivity (8–15 μ Ωm), carrier concentration (1 × 10¹⁹–7 × 10¹⁹ cm⁻³) and Hall mobility (120–180 cm²V⁻¹s⁻¹) were measured at room temperature for the best Sb₂Te₃ thin-films.

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1. Introduction

Integration of efficient solid state thermoelectric microdevices with microelectronics is desirable for local cooling and thermoelectric microgeneration. 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 high Seebeck coefficients, low electrical resistivities and relatively low thermal conductivities [1-3]. Despite new approaches to improve on these thermoelectric properties using nanostructured materials [4-6,30], thin films of tellurides are the most widely used materials in thermoelectric micro-devices, both for local cooling and for energy harvesting [31,32]. In this work, thin film planar technology is used in order to scale down conventional bulk thermoelectric devices to micron size. 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 [7,8]. In this paper, the possibility of integration with next-generation flexible electronic devices is also demonstrated.

Previous work from the authors presented deposition and characterization details for n-type Bi₂Te₃ thin films [9]. This paper

focuses only on p-type Sb₂Te₃ thin films. It has been demonstrated previously that the direct evaporation of the bulk materials results in a compositional gradient through the film thickness due to the large differences in the vapor pressures of antimony and tellurium [10]. Other deposition processes have been reported in the literature for the deposition of Sb₂Te₃ thin films. Co-sputtering, electrochemical deposition, metal-organic chemical vapor deposition or flash evaporation are some examples. Silva [11] and Zou [12] fabricated p-type Sb₂Te₃ films and reported the influence, on the electronic properties, of substrate temperature and evaporation rate of the materials during the film growth. Zou's work was based on a small number of samples and no consistent relation could be established between the growth conditions and material performance. In the present work, the influence of growth parameters (evaporation rates of Sb and Te and substrate temperature) was studied in detail and many samples were fabricated in order to seek a correlation between the growth conditions and the thermoelectric properties of the films. Glass, silicon and polyimide were used as substrates, all giving good film-tosubstrate adhesion. However, for thermoelectric applications, 25 µmthick polyimide (Kapton) film was chosen as substrate because of its low thermal conductivity (as low as $0.16 \text{ Wm}^{-1}\text{K}^{-1}$) and appropriate value of thermal expansion coefficient $(12 \times 10^{-6} \text{ K}^{-1})$, which closely matches the thermal expansion coefficient of the telluride films, thus reducing residual stress and increasing adhesion. Flexible substrates like Kapton also endow the composite film-substrate with

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uncommon mechanical properties thereby enabling the integration of such substrates with many types of devices [13–18].

2. Experimental details

Antimony telluride thin-films were deposited [19] using the coevaporation resistive technique in a high-vacuum chamber at 3×10^{-6} mbar. The power applied to each boat was controlled independently, using two PID (Proportional-Integral-Derivative) controllers to maintain the deposition rate at a fixed value during the film growth. The Sb evaporation flow rate (Fr_{Sb}) was maintained at 2 Ås^{-1} and the Te evaporation flow rate (Fr_{Te}) was in the range 3 Ås^{-1} to 9 Ås^{-1} . The evaporation flow ratio (R = Fr_{Te} / Fr_{Sb}) is defined as the amount of Te that arrives to the substrate during deposition divided by the amount of Sb that arrives.

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 [19]. Each thickness monitor, a quartz crystal oscillator, was carefully placed inside the chamber in order to receive material only from the boat that it was monitoring. A metal sheet was placed between the two boats to partially separate the flows from the two evaporants and to fully prevent any mixing of both materials at the quartz crystals. Large boats (baffled boxes, 4 cm³ volume) were used, in order to maintain stable evaporation rates. Substrates were heated to the chosen temperature setpoint (T_{sub}), which was selected in the range 150 °C and 220 °C.

The chemical composition and structure of the films were obtained by energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), particle-induced X-ray emission (PIXE) and Raman spectroscopy.

The SEM equipment is a Leica Cambridge S360 integrated with an Oxford Instruments EDX Link eXLII system. XRD was used for structure investigations using copper K_{α} radiation ($\lambda = 1.54051$ Å) in θ -2 θ geometry with Philips PW1710. The XPS measurements were carried out using monochromatic Al-K α radiation (h ν = 1486.92 eV) with an VG Escalab 250 iXL ESCA instrument (VG Scientific), Photoelectrons were collected from a take off angle of 90° relative to the sample surface. The measurement was done in a Constant Analyzer Energy mode (CAE) with a 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra. Surface elemental composition was determined using the standard Scofield photoemission cross sections. The chemical functional group identity was obtained from the high-resolution peak analysis of carbon (C1s), antimony (Sb3d5), tellurium (Te3d5) and oxygen (O1s), envelopes. RBS measurements were done with a 2 MeV He⁺ ion beam impinging on the sample at an angle of 0° and PIXE collected with a 2.150 MeV H⁺ and 1.075 MeV H_2^+ at angles of 22.5° and 45° [20].

For Raman scattering experiments, the 514.5 nm and 488 nm lines of an Ar + laser and the 1064 nm line (NIR) of an Nd:YAG laser were used for excitation. Raman spectra were obtained from the abovestated two visible lines using a Jobin-Yvon T64000 spectrometer (micro-Raman, in the 30–700 cm⁻¹ Raman shift range, with spot size ~1 µm and spectral resolution ~1 cm⁻¹) and from the third infrared line using a Bruker RFS 100/S Raman spectrometer (macro-Raman, 80–2000 cm⁻¹ Raman shift range, spot size ~100 µm and spectral resolution ~2 cm⁻¹). In all cases, Raman spectra were recorded at room temperature, in a backscattering geometry with polarized incident light and without an analyzer.

In-plane electrical resistivity, carrier concentration and Hall mobility were measured at room temperature using the conventional four probe van der Pauw geometry in a 5 mm side square arrangement. A direct current magnetic field of 80 mT was applied for Hall measurements. The Seebeck coefficient, α , 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 kept at room temperature, with a temperature difference between both sides below 10 °C. The dependence of these properties with temperature is also found elsewhere [29]. Thermal conductivity was measured (in a direction parallel to the substrate) using the technique developed in [21]. An additional film of BiSb was deposited onto the bottom side of the substrate. Current was applied through this BiSb film, and heating was measured indirectly by monitoring the resistivity change in this material. Using the value of applied power, the unknown thermal conductivity of the thermoelectric film was calculated. The power factor (PF) was calculated using Eq. (1) and the dimensionless figure of merit parameter (ZT) was obtained with Eq. (2) (α is Seebeck coefficient – VK⁻¹, ρ is electrical resistivity – Ω m and λ is the thermal conductivity – Wm⁻¹K⁻¹).

$$PF = \alpha^2 / \rho \tag{1}$$

$$ZT = \frac{\alpha^2}{\rho\lambda}T$$
(2)

3. Results and discussion

Several films of Sb₂Te₃ were deposited using different flow rate ratios, R, and substrate temperatures, T_{sub} , in order to study the effect of these parameters on the thermoelectric properties of the films. R was set by fixing the Sb evaporation flow rate (Fr_{Sb}) at $2\,\text{\AA s}^{-1}$ and varying the Te evaporation flow rate (Fr_{Te}) in the range 3–9 $\textrm{\AA s}^{-1}$. Due to a detectable non-uniformity of the evaporation rate over the area of the substrate and the absence of substrate rotation, the amount of Te and Sb that reaches the substrate is different at different places. An error of $\pm 10\%$ should be considered for data associated with the evaporation rate measurements, due to the uncertainties both in the positioning of the sensors and the densities of the materials and also because of deficiency in the thermal contact between substrate and heater (which causes temperature gradients in the film during deposition). Three series of films were fabricated, at $T_{sub} = 150$, 180 and 220 °C. All films were ~1 μ m thick (\pm 30%). Table 1 summarizes the thermoelectric properties of the Sb₂Te₃ films selected for study.

XRD (a typical result is shown in Fig. 1) reveals the polycrystalline structure of Sb₂Te₃. The peaks agree with the powder diffraction pattern for polycrystalline Sb₂Te₃ (file no. 15–874 from [22]) and similar results from XRD analysis can also be found in the literature [11]. The differences in XRD patterns from the two films analyzed could be due to differences on composition and substrate temperature. The substrate temperatures and tellurium contents for the films is presented in Table 1. The planes with the higher XRD intensities obtained with films deposited at T_{sub} = 220 °C are not the same as those from films deposited at T_{sub} = 150 °C or from bulk Sb₂Te₃. The substrate temperature during deposition influences both the

Table 1		
Properties of selected	Sb ₂ Te ₃	films

Film	T _{SUB} ℃	$R = Fr_{Te} / Fr_{Sb}$	%Te by EDX	$lpha$ $\mu V K^{-1}$	ρ μΩm	n 10 ¹⁹ cm ⁻³	$\begin{array}{c} \mu \\ cm^2 \ V^{-1} \\ s^{-1} \end{array}$	$PF \times 10^{-3}$ WK ⁻² m ⁻¹
#1	150	1.47	54.5%	91	7.6	12.5	65.5	1.09
#2	150	1.67	61.4%	140	14.0	2.4	185.8	1.40
#3	150	2.13	64.7%	191	31.2	2.0	174.3	1.17
#4	150	2.35	64.4%	137	43.6	4.6	31.1	0.43
#5	180	1.85	60.4%	134	24.4	9.0	28.4	0.74
#6	180	2.02	59.1%	158	30.3	1.44	143.2	0.82
#7	180	2.35	62.4%	156	39.1	2.0	78.8	0.62
#8	220	1.67	54.9%	81	10.5	25.3	23.5	0.63
#9	220	2.13	61.2%	133	10.0	3.6	174.3	1.78
#10	220	2.50	67.3%	156	9.2	4.1	166.4	2.66
#11	220	3.18	73.5%	188	12.6	4.3	115.2	2.81

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Fig. 1. XRD diffractograms of films #8, #2 and #10.

structure and the orientation of Sb₂Te₃ thin-films. An elemental tellurium phase is also detected in films with higher Te content. SEM cross-sectional and surface (plan) images of the material also reveal the polycrystalline structure of the films and the effect of substrate temperature on polycrystalline morphology (Fig. 2). Grains with dimensions greater than 500 nm occurred in films deposited at higher temperature (Fig. 2A) whereas grains smaller than 500 nm formed in films deposited at lower temperature (Fig. 2B). This is because surface diffusion and the clustering of adatoms were favored at higher substrate temperatures.

XPS analysis was performed on a Sb_2Te_3 thin-film with a 1 µm thickness (Fig. 3). Ion etching during analysis was performed at low energy, to avoid heating the films and thus changing the original composition, due to the different vapor pressures of Sb and Te. Composition was measured as a function of depth in the film and the results demonstrate the existence of both contamination (carbon) and oxidation of film at and near the surface, up to a depth of 50 nm. Film composition measured at greater depth corresponds to that

2.00µm ⊦

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Fig. 3. Composition as a function of depth from the film surface, obtained by XPS.

obtained by EDX. Composition measurements were also confirmed by the RBS/PIXE technique.

Bulk Sb₂Te₃ under normal conditions has a rhombohedral crystal structure belonging to space group $R \ 3m (D_{3d}^5)$. Group theory predicts Raman active modes corresponding to irreducible representations A_{1g} and E_g. These are upper and lower modes of each type, in 6 in total (Eg modes are 2 times degenerate). Their frequencies have been determined experimentally and also calculated by Richter et al. [23]; recently they were re-calculated using density functional perturbation theory [24].

Fig. 4 shows typical Raman spectra of the Sb_2Te_3 films and bulk sample [http://www.alfa-chemcat.com (Catalogue Item 14488)], obtained with different excitation wavelengths. The two upper curves were obtained under Nd:YAG laser excitation of wavelength 1064 nm





Fig. 2. Surface and cross-sectional SEM images of Sb₂Te₃ films deposited on glass, T_{sub} = 220 °C and *R* = 2.8 (A); and T_{sub} = 150 °C and *R* = 1.9 (B).

Fig. 4. Typical Raman spectra from Sb2Te3 films obtained at room temperature under 1064 nm (a and b) and 514.5 nm (c and d) excitation lines. The Raman spectrum from the bulk Sb2Te3 is also shown. Vertical lines are the calculated (solid line) and experimental (dotted line) frequency values for the bulk. [24].

and the lower ones were recorded under Ar^+ laser excitation (488 nm or 514.5 nm). In a set of several randomly selected films, grown under different conditions, no significant changes were seen in the positions of the peaks under NIR excitation. The peak frequencies and their full widths at half maximum (FWHM) were determined by fitting each peak with a Lorentzian function. The two strong peaks seen in the spectra (a) and (b) are located at 165 cm⁻¹ (FWHM~9 cm⁻¹) and 112 cm⁻¹ (FWHM ~12 cm⁻¹). Very close values were calculated by Sosso et al. [24]: 166 cm⁻¹ (upper A_{1g}) and 113 cm⁻¹ (upper E_g). An extra broad contribution centered at 149 cm⁻¹ is present in the spectra (see fitting curves in Fig. 4). This peak can be attributed to the lattice vibration of Te in Te aggregates [25].

Additionally a low frequency A_{1g} mode was detected under Ar^+ laser excitation (~69 cm⁻¹). All samples show similar Raman spectra under 488 nm or 514.5 nm laser line excitation. Several extra contributions were also observed at 91, 120, 140, 221, and 260 cm⁻¹, and their frequencies cannot be associated to Sb₂Te₃ neither TeO₂ nor Sb₂O₃ (oxides that could eventually be present in the films). A peak at 267 cm⁻¹ has been assigned by Samal et al. [25] to the Te–O vibration in a thin oxide layer. Different examined areas present different Raman peak intensities from either film or bulk (see Fig. 4b) and c)).

The Raman spectrum obtained from a fresh polished surface of a bulk Sb₂Te₃ is also shown in Fig. 4. Most of the extra peaks seen in this spectrum vanished after a soft polishing. The positions of fundamental peaks agree well with those found in the literature for Sb₂Te₃ Raman modes. These facts lead us to the conclusion that the properties of the near-surface region of bulk and thin films of Sb₂Te₃ are different after a normal exposure to atmospheric air.

All three excitation wavelengths correspond to photon energies well above the band gap energy of Sb₂Te₃ (~0.3 eV). Still, there is an approximately two-times difference in the energy of photons emitted by the Nd-YAG and Ar⁺ lasers, and the corresponding spectra are quite different in terms of the relative intensity of the A_{1g} and E_{g} modes. We reckon that it is most likely due to the different penetration lengths of the photons with wavelengths of about 500 and 1000 nm. In the former case, a very thin near-surface layer is probed, which can be enriched with defects (e.g. Te precipitates), possibly responsible for the extra modes seen in the spectra taken with Ar⁺ laser excitation. However, another possibility should not be completely excluded. As known, in many cases dipole-forbidden Raman scattering by polar optical phonon modes is observed under resonance excitation conditions [26]. This happens due to the very strong electron coupling to the electric field produced by LO phonons. In Sb₂Te₃ crystals, the polar (IR-active and Raman-inactive) A_{1u} and E_{1u} modes are possible candidates to produce this effect. In particular, LO phonons corresponding to the lower E_{1u} mode (128 cm⁻¹) [24] can be responsible for the strong peak overlapping with the E_g one (112 cm^{-1}) thus producing the apparent blue shift of this Raman band in the spectra (c) and (d), relative to (a) and (b). It is tempting to explain in a similar way the Raman peak seen near 140 cm^{-1} only in the spectra (c) and (d), however, the calculated frequency of the upper A_{1u} mode (154 cm⁻¹) [24] is probably too high to make this assignment. The lowest frequency-mode Eg, predicted at 46 cm⁻¹ [24], was not detected in our Raman spectra neither was it observed in the previous work [23].

The film composition is always poorer in Te than the corresponding fraction of evaporated Te, *R*. This effect is more noticeable as T_{sub} increases. At 220 °C, the vapor pressure of Te is 10^3 higher than the vapor pressure of Sb. Therefore, it is possible to conclude that re-evaporation of Te from the substrate proceeds at a higher rate than Sb. This explains why it is necessary to use a higher value of *R* than the desired atomic ratio of Te/Sb for the final film composition. Since the Te percentage in the films is always smaller than the corresponding percentage of evaporated Te and it also depends on substrate temperature, it is difficult to obtain the desired

stoichiometry. The evaporation rate of tellurium must be adjusted to overcome these factors, in order to obtain the desired final stoichiometry.

Fig. 5 shows the dependence of the flow rate ratio (*R*) on the Seebeck coefficient, resistivity, carrier concentration and power factor for films deposited at different substrate temperatures (150 °C, 180 °C and 220 °C). No dependence of the value of Seebeck coefficient on the substrate temperature (T_{sub}) was noted but the value of this coefficient increases as R is increased. However, there is a strong dependence of electrical resistivity on T_{sub} . Lower electrical resistivity (ρ <15 $\mu\Omega$ m) is obtained with a substrate temperature above 220 °C. Films with compositions in Te richer than stoichiometric have lower carrier concentration ($n < 5 \times 10^{19} \text{ cm}^{-3}$), higher mobility ($\mu > 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), and higher Seebeck coefficient (α >150 μ VK⁻¹), leading to a higher power factor (PF> 1.5×10^{-3} WK⁻²m⁻¹). High mobility is also obtained with R between 2 and 3. At each T_{sub} the maximum value of PF is also obtained at a value of R that depends on T_{sub} (Fig. 5). Maximum PF was obtained at R = 2 for $T_{sub} = 150$ °C or $T_{sub} = 180$ °C. For $T_{sub} = 220$ °C, maximum *PF* is obtained with R = 3, due to re-evaporation of Te from substrate. In thin-films, resistivity and Seebeck coefficient values are higher than these on bulk single crystal, respectively $\rho_{11} \approx 1.9 \,\mu\Omega m$ and $\alpha_{11} = 83 \,\mu\text{VK}^{-1}$ [27]. On the other hand, both carrier concentration and Hall mobility were lower than the values for bulk Sb₂Te₃, $n = 10.6 \times 10^{19} \text{ cm}^{-3}$ and $\mu = 313 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ respectively [27]. The influence of substrate temperature and film composition (measured by EDX) on power factor is shown in Fig. 6. Comparable results obtained by Silva [11] and Zou [12] on the same thin-film materials and from Sb₂Te₃ bulk crystal [27] are also presented. The highest value of $PF = 2.8 \times 10^{-3} \text{ WK}^{-2} \text{m}^{-1}$ was obtained with films deposited at $T_{\rm sub} = 220$ °C with Sb evaporation rate of 2 Ås⁻¹ and Te evaporation rate of 6.4 Ås⁻¹ (R = 3.2). These evaporation parameters resulted in a tellurium-rich composition of the compound with 25-35% of Sb and 65-75% of Te. The value of PF measured on films deposited by co-evaporation at low substrate temperature is lower than PF obtained for bulk materials. But for substrates deposited at $T_{sub} = 220$ °C, the value of *PF* is close to values obtained for bulk Sb₂Te₃.

Thermal conductivity was measured (in film direction) in one Sb₂Te₃ film, using the method described by Völklein [21]. A value of $\lambda = 1.8 \text{ Wm}^{-1}\text{K}^{-1}$ was obtained. This value is comparable to that for bulk Sb₂Te₃ $\lambda \approx 1 \text{ Wm}^{-1}\text{K}^{-1}$, along the c-axis and $\lambda \approx 4 \text{ Wm}^{-1}\text{K}^{-1}$ in the perpendicular direction [27]). Thermal conductivity is due to electron and phonon contribution effects, respectively λ_e and λ_p ($\lambda = \lambda_e + \lambda_p$). The electron contribution could be estimated through the Wiedemann-Franz law, $\lambda_e = \text{LT}/\rho_e$, where L is the Lorentz number, T the temperature and ρ_e is the electrical resistivity. Considering L= $2.1 \times 10^{-8} \text{ V}^2 \text{K}^{-2}$ [28] and $\rho_e = 15 \,\mu\Omega m$, at 300 K, $\lambda_e = 0.42 \text{ Wm}^{-1}\text{K}^{-1}$ and $\lambda_p = 1.38 \text{ Wm}^{-1}\text{K}^{-1}$. Working from the measured value of Seebeck coefficient for this film ($\alpha = 160 \,\mu\text{VK}^{-1}$), the figure of merit value ZT = 0.3 was calculated.

4. Conclusions

P-type Sb₂Te₃ thermoelectric thin films with high figures of merit were fabricated by thermal co-evaporation. The best films have a Seebeck coefficient of 188 μVK⁻¹and a resistivity of 12.6 μΩm, which represents a power factor of 2.8×10^{-3} WK⁻²m⁻¹. Films were deposited onto glass substrates and flexible Kapton substrates, with good adhesion. The influence of evaporation rates and substrate temperature on composition, Seebeck coefficient, electrical resistivity, Hall mobility and carrier concentration is reported. EDX results show that films with high power factor are obtained when the composition of film is tellurium rich (30% Sb, 70% Te for Sb_xTe_{1-x}). The agreement between the results of Raman and XRD analysis for the films studied in this work and the values reported in the literature for bulk Sb₂Te₃ shows that the compositions of the grown films are close to stoichiometry. We have demonstrated in our Raman spectroscopy

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Fig. 5. Seebeck coefficient, resistivity, carrier concentration and power factor of Sb2Te3 thin films as a function of Te/Sb evaporation flow ratio, R.



Fig. 6. Power factor of selected Sb2Te3 films plotted as a function of substrate temperature and as a function of composition, obtained by EDX. Results from other authors for thin-films [11,12] and bulk single crystal [22] are also presented.

results that the 1064 nm wavelength excitation is more appropriate for volume analysis and the 488 nm (or 514.5 nm) line is better for surface studies of materials in the Sb_2Te_3 system.

The highest thermoelectric power factor for Sb₂Te₃ thin films was obtained for those deposited at a substrate temperature around 220 °C, Sb evaporation rate of 2 Ås⁻¹ and Te evaporation rate of 6.4 Ås⁻¹. A thermal conductivity of 1.8 Wm⁻¹K⁻¹ was measured and a figure of merit at room temperature of ZT=0.3 calculated. These results are comparable with the best published results for the same material. The characterization of a n-type Bi₂Te₃ thermoelectric material can also be found in [9].

The flexible electronics concept was demonstrated by the use of a 25 µm-thick polyimide foil as a substrate. Due to its low thermal conductivity ($\lambda \approx 0.16 \text{ Wm}^{-1}\text{K}^{-1}$) and high upper working temperature (>300 °C), polyimide is an adequate choice for thermoelectric device fabrication. The thermoelectric properties achieved for Sb₂Te₃ thin-films deposited on polyimide in this work are suitable for the fabrication of Peltier micro-coolers and thermoelectric micro-generators.

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