ABSTRACT

INTEGRATED MICRO THERMOELECTRIC COOLER: THEORY, FABRICATION AND CHARACTERIZATION

by

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The flows of heat and electricity in a column-type micro thermoelectric (TE) cooler that uses telluride compounds for the n- and p-type elements, are analyzed by modeling the various interfacial resistances. Electron (barrier tunneling) and phonon (diffuse mismatch) boundary resistances at the TE/metal interface, and thermal non-equilibrium between electrons and phonons adjacent to this interface (cooling length), increase the thermal conduction resistance and decrease the Seebeck coefficient of the TE elements. These in turn reduce the device cooling performance, which is also affected by the thermal and electrical contact resistances at the TE/metal and the metal/electrical-insulator interfaces.

From the device optimization, it is predicted (for an available voltage of 3 V) that a micro TE cooler with 50 TE pairs (Bi$_2$Te$_3$ and Sb$_2$Te$_3$ high performance TE films), column thickness of 4 µm (limited by the current fabrication process), and column cross-section area of 7 µm × 7 µm, should produce a temperature drop of 10 K with a cooling load of 10 mW. This device will operate with a current of 11 mA and will require a power of 34 mW. The coefficient of performance is 0.3.
Co-evaporated Bi-Te and Sb-Te films were fabricated at various deposition conditions (evaporation rate of individual species and substrate temperature), and their TE properties (Seebeck coefficient, electrical resistivity, and carrier concentration) were measured, in search of optimal TE performance. The deposition rates were controlled such that the tellurium atomic composition changed from 48 to 74%, and the substrate temperature ranged from 130 to 300°C. The chemical composition and crystal structure of the films were recorded (using a microprobe and a X-ray diffractometer, respectively), analyzed, and compared with standard Bi$_2$Te$_3$ and Sb$_2$Te$_3$ single crystal samples. High performance TE films had a tellurium atomic concentration around 60% and were deposited at a substrate temperature between 260 and 270°C.

Due to degradation of the photoresist used for patterning the TE films, in the first-generation device, they were deposited with a maximum substrate temperature of 130°C. The TE columns were connected using Cr/Au/Ti/Pt layers at the hot junctions, and Cr/Au layers at the cold junctions. A device with 60 TE pairs and column width of 40 µm (finer device structures had limited yield) was tested using infrared thermometry. The average cooling achieved was about 1 K, which was close to the predicted value.

A future-generation device is proposed, where high performance TE films can be patterned with optimized geometries (high density micro TE coolers), allowing these devices to fulfill the requirements for a wireless environmental monitor application.
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by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Mechanical Engineering) in the University of Michigan 2005

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José Paulo
Acknowledgements

I am thankful, above of all, to God, for being with me and my loved ones, and
to all that directly and indirectly contributed to this work. They are, in special, my
advisor, Professor Massoud Kaviany, who gave me unconditional support and motiva-
tion through these years. He taught me great things, through examples of kindness,
patience, wisdom, dedication, and through his commitment to quality, fundamental,
challenge and innovative research. Professor Wise, who shared his expertise in MEMS
and device fabrication, and provided the financial support for this research through
the Engineering Research Center of WIMS. Professor Uher, who friendly took me
as a member of his Laboratory, and taught me about fabrication and characteriza-
tion of thermoelectric films. Professor Kurabayashi, who was always supportive and
helped with suggestions on device analysis and characterization. Professor Douglas
McGregor, now at KSU, who first introduced me to the challenges on deposition of
thermoelectric films. Professor Mehdi Asheghi and Mr. Yizhang Yang, at CMU, who
helped me with device performance measurements and suggestions for improvements
on device fabrication. My mentor in the SSEL, Dr. Andrew DeHennis, who walked
me through MEMS design and fabrication, teaching me with dedication and patience.
My mentor in Physics, Professor Jeffrey Dyck, who introduced me to thermoelectric properties measurements. Xiangchun Zhang, who helped with the thermoelectric film fabrication during the last couple of months. Jason Burr, Kevin Pakravan, Stephen Newhouse and Stephanie Bezilla, who assisted this project as part of their research oriented class ME490. John Mansfield and Carl Henderson, staff members at EMAL, who helped with the characterization and analyses of the thermoelectric films. The SSEL staff, Ning Gulari, Aaron Glatzer, Kimberly Appel, Katharine Beach and Terre Briggs, who helped with discussions and suggestions on device processing, as well as expediting the work in the clean room. The ME staff, Lynn Buege and Kent Pruss, who helped with their engineering expertise on design, fabrication and restoration of support equipments and structures used in this work. Cynthia Quann-White, Kelly Perrington and Jeanne Jaeger, who were a constant source of help on administrative issues. All my current and former lab-mates in ME, Physics and SSEL, who made these years more enjoyable, in particular, Darryl Taylor, Alan Mcgaughey and Xiulin Ruan. The Brazilian government, who financed my Ph.D. studies through CNPq - Conselho Nacional de Desenvolvimento Científico e Tecnológico. And finally, my family, who has given me continuous support and encouragement. My parents, João and Vera, despite the distance, have been always present. My husband, José Paulo, lived and shared with me each day of this journey with patience, understanding and love.
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Nomenclature

\( a \)  \hspace{1em} \text{hexagonal unit cell dimension (m), side length (m)}

\( a_R \)  \hspace{1em} \text{rhombohedral unit cell dimension (m)}

\( \text{at} \)  \hspace{1em} \text{atomic}

\( A_k \)  \hspace{1em} \text{cross-sectional area of the thermoelectric element (m}^2\text{)}

\( A_{j=1,4} \)  \hspace{1em} \text{constants in the electron and phonon temperature equations [Eqs. (2.19) and (2.20)]}

\( B \)  \hspace{1em} \text{emission constant (A/m}^2\text{-K}^2\text{), magnetic field (T)}

\( B_{j=1,10} \)  \hspace{1em} \text{constants in} \text{ } A_j \text{ [Eqs. (2.26)]}

\( c \)  \hspace{1em} \text{unit cell dimension (m)}

\( C_{j=1,15} \)  \hspace{1em} \text{constants in} \text{ } A_j \text{ [Eqs. (2.26)] and} \text{ } B_j \text{ [Eqs. (2.27)]}

\( \text{COP} \)  \hspace{1em} \text{coefficient of performance}

\( d \)  \hspace{1em} \text{side width (m), barrier thickness (m)}

\( e_c \)  \hspace{1em} \text{electronic charge }1.6022 \times 10^{-19} \text{ C}

\( e_e \)  \hspace{1em} \text{electric field (V/m)}

\( E \)  \hspace{1em} \text{electron energy (J)}

\( E_c \)  \hspace{1em} \text{energy at bottom of conduction band (J)}

\( E_F \)  \hspace{1em} \text{Fermi energy (J)}
\( E_g \)  band gap energy (J)

\( E_o \)  potential barrier height (J)

\( E_v \)  energy at top of valence band (J)

\( F \)  arbitrary function (e.g., \( \alpha_s, \rho_e, R_H \))

\( f \)  frequency (Hz)

\( h_p \)  Planck constant \( 6.6261 \times 10^{-34} \) J-s

\( J_e \)  electrical current (A)

\( j_e \)  electrical current density (A/m\(^2\))

\( k \)  thermal conductivity (W/m-K)

\( k_B \)  Boltzmann constant \( 1.3806 \times 10^{-23} \) J/K

\( L \)  length (m), Lorenz number (V\(^2\)/K\(^2\))

\( L_{te} \)  thermoelectric film thickness (m)

\( m_{e,o} \)  electron mass in free space \( 9.1096 \times 10^{-31} \) kg

\( m_{e,te} \)  electron/hole effective mass in the thermoelectric element (kg)

\( n \)  number density of primitive cells (m\(^{-3}\))

\( n_c \)  electron/hole concentration in the thermoelectric element (m\(^{-3}\))

\( N \)  donor/acceptor atom concentration (m\(^{-3}\))

\( N_{te} \)  number of thermoelectric pairs

\( P \)  density of states (s/rad-m\(^3\)), tunneling probability

\( P_e \)  electrical power (W)

\( q \)  heat flux (W/m\(^2\))

\( Q \)  heat flow rate (W)
\( R_e \) electrical resistance (\( \Omega \))
\( R_H \) Hall coefficient (m\(^3\)/C)
\( R_k \) conduction resistance (K/W)
\( \dot{S}_e \) energy conversion rate (W)
\( T \) temperature (K)
\( T_{ctc} \) center-of-thermal-conductivity temperature (K)
\( u \) velocity (m/s)
\( V_b \) built-in potential energy (J)
\( w \) width (m)
\( W \) depletion width (m)
\( Z_e \) figure of merit (1/K)

Greek symbols

\( \alpha_s \) Seebeck coefficient (V/K)
\( \gamma \) \( k_e/k_p \)
\( \gamma_R \) rhombohedral unit cell dimension (m)
\( \delta \) electron-phonon cooling length (m)
\( \Delta F \) uncertainty of function F
\( \Delta \varphi \) voltage (V)
\( \epsilon_o \) free-space permittivity \( 8.8542 \times 10^{-12} \) C\(^2\)/J-m
\( \epsilon_r \) relative permittivity
\( \mu \) electron/hole mobility (m\(^2\)/V-s)
\( \rho_e \) electrical resistivity (\( \Omega \)-m)
\( \tau \) transmission coefficient

\( \tau_e \) electron/hole energy relaxation time (s)

\( \tau_m \) electron/hole momentum relaxation time (s)

\( \phi \) work function (J)

\( \chi \) electron affinity (J)

\( \omega \) angular frequency (rad/s)

Subscripts

\( b \) boundary

\( c \) cold, contact

\( cc \) cold connector

\( D \) Debye

\( e \) electron

\( h \) hot

\( hc \) hot connector

\( j \) phonon mode

\( J \) Joule

\( l \) load

\( m \) metal

\( mc \) metal connector

\( n \) \( n \)-type thermoelectric material

\( opt \) optimum

\( p \) \( p \)-type thermoelectric material, phonon
Peltier

\( sub \) substrate

\( te \) thermoelectric element

\( \infty \) ambient

Superscripts

\( * \) dimensionless

Abbreviations

AMM acoustic mismatch model

DMM diffuse mismatch model

DOS density of states

GEN-1 first-generation device

IR infrared

PR photoresist

SEM scanning electron microscope

TE thermoelectric

XRD X-ray diffraction
Chapter 1

Introduction

With realization of micro and nano fabrication on the rise, it is desirable to miniaturize thermoelectric (TE) coolers to achieve localized or microsystem cooling. The size and boundary effects in phonon and electron transport, and the TE film and device fabrications, have provided the initial motivations for this study. The emergence of the Engineering Research Center for Wireless Integrated Microsystems, at the University of Michigan, created an opportunity to develop the micro TE cooler for a wireless environmental monitor, which required all devices fitting in a volume of 1 in$^3$, and powers on the order of mW. Thermoelectric cooling was found to be suitable for this application, since it does not require any moving parts and can be microelectronically integrated. This is the first combined theoretical and experimental study of such device.

Telluride compounds are the TE materials chosen for the fabrication of a micro TE cooler, since they currently have the highest cooling performance for applications around room temperature. The device design is dependent, among other factors, on
the film thickness. Thin films (700 nm) of tellurium compounds have been deposited by co-evaporation, by Zou et al. [1, 2]. Min et al. [3] proposed a micro TE cooler where the TE thin films are grown on a very thin, low thermal conductivity SiC membrane (PECVD) to minimize the heat leakage effect. In their design, the electrical current and heat flow parallel to the film plane. Thick films (10-30 µm) of tellurium compounds have been deposited by electroplating to fabricate TE coolers, where the current and heat flow perpendicular to the film plane (column-type design) [4, 5]. Yao et al. [6] investigated the influence of geometry and material properties on the performance of this design and showed that local deep cooling (up to 60 K) can be achieved if heat spreading (substrate) materials are properly chosen. Böttner et al. [7] have also deposited such thick layers (10-20 µm) by co-sputtering to fabricate column-type micro coolers.

This conventional column-type TE devices have not been fabricated with thin films (less than 1 µm) due to the parasitic conduction heat transfer between the hot and cold junctions, and the thermal and electrical contact resistances. These problems can be minimized, if thicker films (2 to 10 µm) are used. Here, this design is considered for cooling a chemiresistance vapor sensor of the wireless environmental monitor, as shown in Figure 1.1, where the TE films (Bi₂Te₃ and Sb₂Te₃), grown based on the vapor deposition technique of Zou et al. [2], are limited to 4 µm thick. The goal for the cooler is to lower the temperature of the sensor 10 K below ambient in less than 30 seconds, while using minimal power with a 3 V battery.
Figure 1.1: Rendering of micro TE cooler used with a micro vapor sensor. The column-type design and various energy conversion rates $\dot{S}_{e,i}$, and heat transfer rates $Q_i$, are also shown.

1.1 General Concepts

The micro cooler device is formed by a series of TE pairs, as the one enlarged in Fig. 1.1, where the $n$- and $p$-type semiconductor elements are joined by metallic connectors at the top and bottom. Whenever a dc current $J_e$ flows through one of these TE/metal contacts, heat is either released or absorbed in the contact region, depending on the direction of $J_e$.

As represented in Fig. 1.1, electrons are flowing from the $p$-type element to the top
metal connector, and then to the n-type element (direction opposite to $J_e$), and are absorbing heat at these junctions [Peltier cooling, $(\dot{S}_{e,p})_c$]. As they flow through the bottom connectors, heat is released at the junctions with the semiconductors [Peltier heating, $(\dot{S}_{e,p})_h$]. Therefore, heat is transferred from the load ($Q_c$), which is attached to the cold (top) connector, to the heat sink ($Q_h$), which is the substrate for the hot (bottom) connectors.

The undesirable heat transfer from the hot to the cold connector, $Q_{k,h-c}$, is minimized by increasing the TE element thermal resistance $R_{k,h-c}$, which is directly proportional to the ratio of the thickness $L_{te}$ and the cross-sectional area $A_k$ ($= d_{te}^2$) of the TE element, and inversely proportional to the number of TE pairs $N_{te}$. On the other hand, the resistance to the flow of electrons in the semiconductor $R_{e,h-c}$, which is proportional to $N_{te}L_{te}/A_k$, should be minimized. This resistance causes the undesirable Joule heating $(\dot{S}_{e,J})$, which also occurs in the metal connectors and at their contacts with the TE elements. It becomes then evident that an optimum geometry can be found based on $N_{te}$ and $d_{te}$ ($L_{te}$ is limited to about 4 $\mu$m by the fabrication process), with respect to the power and performance requirements.

The TE properties of the n- and p-type elements, i.e., Seebeck coefficient $\alpha_S$, electrical resistivity $\rho_e$, and thermal conductivity $k$, also affect the energy conversion mechanisms $\dot{S}_e$ and heat transfer $Q$, as shown by the relations

$$\dot{S}_{e,p} \propto \alpha_S,$$

$$\dot{S}_{e,J} \propto R_{e,h-c} \propto \rho_e,$$

$$Q_{k,h-c} \propto R_{k,h-c}^{-1} \propto k.$$
An ideal TE film would then present high $\alpha_S$, and low $k$ and $\rho_e$. However, $k$ and $\rho_e$ are competing against each other, as $k_e$, the electronic contribution to $k$ ($= k_e + k_p$, where $k_p$ is the phonon contribution), is inversely proportional to $\rho_e$. These properties must therefore be optimized. They will vary with fabrication conditions and composition of the TE films.

Note that, these are considered bulk TE properties, and their described macroscopic behavior is well known. With the decrease of $L_{te}$, the transport of heat and electricity in a micro TE cooler will be influenced by the phonon and electron boundary resistances ($R_{k,b,pp}$ and $R_{k,b,ee}$, respectively), and by the electron-phonon nonequilibrium adjacent to the TE/metal interfaces (characterized by the cooling length $\delta$). These interfacial effects are introduced into $\alpha_S$ and $R_{k,h-c}$. Thermal and electrical contact resistances ($R_{k,c}$ and $R_{e,c}$, respectively), which are originated in the fabrication process, are found in all device interfaces. Their effects in reducing the device performance becomes more pronounced, also with the decrease of $L_{te}$.

### 1.2 Approach

The various parameters that can affect the micro TE cooler performance (discussed above), are summarized below.

- **Geometrical parameters**: $L_{te}, d_{te}, N_{te}$
- **TE properties**: $\alpha_S, \rho_e, k$
- **Interfacial effects**: $R_{k,b,ee}, R_{k,b,pp}, \delta, R_{e,c}, R_{k,c}$
The approach taken for evaluation of these parameters, aiming for the design, fabrication and characterization of optimized micro TE cooler devices, is shown in Fig. 1.2. The interfacial effects are first described, and an optimal geometry \((N_{te, opt}, d_{te, opt})\) is predicted using the TE properties reported in [2]. In parallel with the device fabrication, the TE films deposition over various substrates (material and crystal structure), substrate temperatures \(T_{sub}\), and composition, are studied, seeking optimal \(n\)- and \(p\)-type telluride films.

The wafers containing the micro TE coolers fabricated and characterized in the first-generation of devices, did not have a good yield for the smaller (optimal) geometries (limited by the photolithograph process in the cold connector fabrication). Also, due to photoresist temperature limitation, high performance TE films could not be deposited. A future-generation device is proposed, where the high performance TE films fabricated and characterized here, can be patterned, and an optimal device geometry \((d_{te, opt})\) can be achieved. This micro TE cooler will be able to satisfy its application requirements of power and performance.

Further discussions on the physics of micro TE coolers (size effects), telluride family film deposition and characteristics, as well as device fabrication and characterization, as outlined in Fig. 1.2, are reported in the following sections.

1.2.1 Physics

Considerations are given on how the small size of the columns may affect the thermal and electrical transport (electron, phonon and energy conversion) through
Figure 1.2: Thesis outline. Accomplishments and future challenges are indicated in the device fabrication.
the interfaces between the TE and metal films, and thus the performance of the
device. Boundaries hinder the phonon heat flow differently than the electronic heat
flow, and along with the Joule heating associated with electrons, the two subsystems
can be out of thermal equilibrium [8]. As the thickness of the TE film $L_{te}$ decreases
and becomes comparable to the carrier cooling length $\delta$, this electron-phonon non-
equilibrium becomes significant, and influences the TE properties of the device.

The phonon and electron boundary resistances and the phonon-electron non-
equilibrium adjacent to the interfaces of the TE elements have been described by
others [8-14]. Molecular dynamics, lattice dynamics, Boltzmann transport equation,
and Monte Carlo methods, have all been used as tools to understand heat conduc-
tion mechanisms and to simulate the nanoscale transport process [15, 16]. Here,
the phonon boundary resistance is estimated by the Diffuse Mismatch Model using
the measured phonon density of states [9, 10]. The electron boundary resistance is
estimated assuming electron tunneling and using the Wiedemann-Franz law at the
boundaries [8]. The electron and phonon temperature distributions in the TE ele-
ments are obtained from a simplified form of the coupled Boltzmann transport equa-
tions for the electron and phonon subsystems [8, 11, 14]. In addition, the thermal
and electrical contact resistances (due to defects in the crystal structure, variation of
surface roughness, etc., originated in the fabrication process) are estimated from the
experimental results reported in the literature [17-23].

Based on these interfacial effects, which are reported in Chapter 2, the flows of
heat and electricity in the micro cooler are modeled. An optimal geometry is then
obtained, and the overall device performance is predicted in Chapter 3.
1.2.2 Thermoelectric Films

Telluride compounds have been extensively studied in the past decades because of their high TE figure of merit $Z_e T$ at room temperature. In bulk materials, a $Z_e T$ of 0.75 in $p$-BiSb$_2$Te$_3$, at 300 K, was reported about 40 years ago. Since then, there has been modest progress in increasing $Z_e T$ near room temperature. The highest value reported appears to be 1.14 for the $p$-(Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.72}$(Sb$_2$Se$_3$)$_{0.03}$ alloy [24].

In Fig. 1.3, TE properties of telluride films (0.7 to 20 µm thick) are reported at room temperature, for various deposition methods, substrate temperatures and materials. Zou et al. [2] deposited $n$-Bi$_2$Te$_3$ and $p$-Sb$_2$Te$_3$ films by co-evaporation, at $T_{sub}$ of 260 and 230°C, respectively, which had $Z_e T$ of approximately 0.3 ($k$ of 1.5 W/m-K was assumed). Lim et al. [5] used electroplating. The $n$-Bi$_2$Te$_3$ films exhibited significant low performance compared with that reported by others. The properties of the $p$-Bi$_{2-x}$Sb$_x$Te$_3$ films were not fully characterized, due to poor reproducibility. Böttner et al. [7, 25], used co-sputtering, followed by annealing, to improve the TE properties.

Several approaches have been proposed to enhance $Z_e T$ in thin film TE materials. Using quantum-confinement effects, which allows the manipulation of $\alpha_S$ by enhancing the density of states near the Fermi energy, $Z_e T$ ranging from 1.3 to 1.6, at 300 K, was reported for PbSeTe/PbTe quantum dot superlattice structures [26, 27]. Venkatasubramanian el al. [24], showed $Z_e T$ of 2.4 for $p$-type nanostructured superlattices of Bi$_2$Te$_3$/Sb$_2$Te$_3$ at room temperature. These are phonon-blocking/electron-transmitting superlattices, which are produced by alternately depositing thin (1 to
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
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<tr>
<td>Fabrication Method</td>
<td>Co-Evaporation</td>
<td>Electroplating</td>
<td>Co-Sputtering</td>
</tr>
<tr>
<td>Substrate Material</td>
<td>Glass</td>
<td>Au</td>
<td>N/R</td>
</tr>
<tr>
<td>TE Film Material</td>
<td>$p$-$\text{Sb}_2\text{Te}_3$</td>
<td>$n$-$\text{Bi}_2\text{Te}_3$</td>
<td>$p$-$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$</td>
</tr>
<tr>
<td>$T_{sub}$ (°C)</td>
<td>230 260</td>
<td>190 230</td>
<td>N/A N/A</td>
</tr>
<tr>
<td>$\alpha_S$ (µV/K)</td>
<td>171 -228</td>
<td>160 -200</td>
<td>N/R -60</td>
</tr>
<tr>
<td>$\rho_e$ (µΩ·m)</td>
<td>10.4 13.0</td>
<td>31.2 12.9</td>
<td>N/R 10.0</td>
</tr>
<tr>
<td>$\alpha_S^2/\rho_e$ (mW/K²·m)</td>
<td>2.80 3.99</td>
<td>0.82 3.1</td>
<td>N/R 0.36</td>
</tr>
<tr>
<td>$L_{te}$ (µm)</td>
<td>0.7 0.7</td>
<td>0.7 0.7</td>
<td>20 20</td>
</tr>
<tr>
<td>Device Performance</td>
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<td>Thermocouple $\Delta T_{max} = 15.5$ K</td>
<td>TE Cooler $\Delta T_{max} = 2$ K</td>
</tr>
<tr>
<td>Comment</td>
<td>Optimum films; TE properties used in predictions reported in Chapter 3</td>
<td>$p$-type film with higher $T_{sub}$ degrades quality of $n$-type film deposited initially</td>
<td>Poor reproducibility of $p$-type films</td>
</tr>
</tbody>
</table>

Figure 1.3: Performance of the $n$- and $p$-type telluride films reported by other authors. Here, N/A and N/R designate Not/Available and Not/Reported.
4 nm) films of Bi$_2$Te$_3$ and Sb$_2$Te$_3$. For $n$-type Bi$_2$Te$_3$/Bi$_2$Te$_2.83$Se$_{0.17}$, $Z_eT$ was 1.4.

Exploring thermionic emission at interfaces, Vashaee and Shakouri [28] have recently shown that metal-base superlattices with tall barriers can achieve $Z_eT$ larger than 5, at room temperature. A key requirement is the nonconservation of lateral momentum, which allows a higher number of electrons to participate in the thermionic emission process.

Here, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are used in their simplest form (not doped), as the $n$- and $p$-type materials, respectively. Thin films (about 1 $\mu$m thick) of Bi-Te and Sb-Te compounds are deposited by co-evaporation, at various $T_{sub}$ and compositions, seeking films with optimum TE performance. Although it is known that deposition temperatures above 200$^\circ$C are needed for high $Z_eT$ (or high power factor $\alpha^2_S/\rho_e$, as reported in Fig. 1.3), the performance of telluride compound films formed at lower temperatures is also investigated. This is because in our device fabrication, the TE film patterning method limits $T_{sub}$ to values below 170$^\circ$C. The effect of substrate material and crystal structure on the TE properties is also explored. Platinum is used as the substrate for the TE films in the device fabrication (interfacial layer of the hot connectors), and so, it is of particular interest in the investigation of the effect of substrate on TE performance. This study is presented in Chapter 4.

1.2.3 Device

Only a few attempts to manufacture TE devices with small dimensions (fractions of a millimeter), are known so far. The measured performance of column-type TE
coolers, based on 10 to 20 \(\mu\)m thick films of telluride compounds have been reported and are shown in Fig. 1.3. Lim et al. [5] used successive layers of patterned photore sist and electrochemically filled the compound semiconductor materials and metal connectors. A micro TE cooler was built containing 63 TE pairs and with a device area close to \(1.7 \times 1.7\) mm\(^2\). A maximum cooling of 2 K was detected. Böttner et al. [7], depositing the TE compounds by co-sputtering, developed a column-type micro cooler using a "two-wafer" concept (\(n\)- and \(p\)-type materials are first deposited on separated wafers, patterned and then soldered together). This allowed for an optimal post-processing of the \(n\)- and \(p\)-type wafers. A net cooling of 36.7 K has recently been achieved [25]. The details on the fabrication of this device are not available.

Cooling performance of devices based on nano-engineered TE structures have also been reported. One micron thick InGaAsP/InGaAsP superlattice-based thin film thermionic emission coolers, have demonstrated a maximum cooling of 1.15 K, at room temperature [29]. Fan et al. [30], measured a 2.8 K cooling in a SiGeC/Si superlattice micro cooler, at room temperature. Venkatasubramanian et al. [24], showed a net cooling of 32.2 K at room temperature, in a \(p\)-type \(\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3\) superlattice device.

Here, the designed and fabricated TE coolers are based on co-evaporated and photoresist patterned \(n\)-\(\text{Bi}_2\text{Te}_3\) and \(p\)-\(\text{Sb}_2\text{Te}_3\) films. The column thickness was limited to 5 \(\mu\)m, to allow for uniform stoichiometry of the compounds. The major challenges encountered in fabrication are the patterning of high performance TE films, and patterning of high density devices [i.e., realization of TE columns with optimal \(d_{te}\) and their cold (top) connectors]. These, and the results from characterization of the first-
generation micro TE cooler, including predicted and measured device performances, are described and discussed in Chapter 5. There, fabrication improvements are also proposed for future-generation devices.
Chapter 2

Device Performance: Interfacial Effects on Thermal and Electrical Transport

As described in Chapter 1, the micro thermoelectric (TE) cooler considered for the wireless micro system application, has a column-type design, with 4 \( \mu \)m thick TE elements. Here, the boundary and contact resistances at the various interfaces of this structure are described, and it is shown that their significance is related to the thickness of the TE elements. The phonon-electron non-equilibrium near the TE/metal interface is investigated, and its effect on the TE properties, together with the effect of the boundary resistances, are discussed. The results from this study are used in Chapter 3, for the device geometry optimization and performance predictions.
2.1 Thermal and Electrical Transport at Boundaries

The interface of a conductor and a TE material is characterized by a mismatch in bulk properties and by irregularities in the thin region near the boundary. Different thermal and electrical carriers encounter different resistances across this interfacial region.

Phonons (quanta of energy associated with lattice vibrations) are assumed to strike the interface and lose their memory. The probability of being scattered to one side of the interface or the other is related to the density of states (DOS) and the phonon speeds of different modes. The phonon boundary resistance represents the reflected phonons and is considered independent of the interface structure [9].

Electrons are assumed to encounter a potential barrier at the interface (which depends on the band structure of the two interfacial materials), resulting in the electron boundary resistance. For a metal/semiconductor interface absent of surface states, the potential barrier height is a function of the metal work function (energy required to excite an electron from the Fermi level to the vacuum level), the semiconductor electron affinity (energy difference between the highest energy level in the conduction band and the vacuum level) and the semiconductor bandgap (energy gap that separates the conduction band from the valence band) [31]. The potential barrier width (or thickness) depends on the metal work function, and on the semiconductor permittivity, doping density and work function. Depending on the height and thickness of the potential barrier, electrons can tunnel through this barrier or be thermally...
excited over it (thermionic emission) [8].

Phonon and electron boundary resistances at a metal/TE interface cause electron-phonon thermal non-equilibrium near the boundary, which is most significant in the TE material (the transport of heat in the metal is accomplished by the free conduction electrons). The energy conversion mechanisms (Joule heating and Peltier cooling/heating) will also contribute to this non-equilibrium [8]. In crystalline TE materials, electrons will interact with phonons and impurities, and in the polycrystalline state, with phonons, impurities and grain boundaries. These cause the electrons to reach thermal equilibrium with the lattice (phonons), at a distance from the interface known as the cooling length.

The phonon and electron boundary resistances (related to the thermal transport) are present only at the metal/TE interfaces, and their effects are included in the physical properties of the TE elements. Interfacial features not included in the boundary resistances (e.g., surface defects, crystal size and orientation, strain in the materials), depend on the fabrication process. These affect both the thermal and the electrical transport through the interfaces, and are included in the thermal and electrical contact resistances. These contact resistances are present at all interfaces and are directly added to the bulk resistance of the metal connectors.

2.2 Boundary Resistances

Heat is transferred across a continuous solid junction by electrons and phonons. The thermal boundary resistances associated with TE heat transport through metal/
semiconductor interfaces are presented in Fig. 2.1. A phonon wave incident at the interface will be partially transmitted (and partially reflected) due to the mismatch between the properties of the two materials. This phonon wave reflection causes the phonon boundary resistance \((A_k R_k)_{b,pp}\), as shown in Fig. 2.1(a), where \(A_k\) is the cross-sectional area of the TE element, \(R_k\) is the conduction resistance, and the subscript \(b,pp\) stands for the resistance at the boundary in the phonon subsystem. An electronic potential barrier of thickness \(d\) and height \(E_o\), associated with the different band structures of the two materials, is shown in Fig. 2.1(b). This barrier represents a resistance to the electronic heat transport across the interface, i.e., the electron boundary resistance \((A_k R_k)_{b,ee}\). Energy can also be directly exchanged between phonons (on one side of the interface) and electrons (on the other side). The resistance associated with this energy transfer is the mixed boundary resistance \((A_k R_k)_{b,pe}\), or \((A_k R_k)_{b,pe}\), as shown in Fig. 2.1(c).

### 2.2.1 Phonon Boundary Resistance

In the current application, the interface is formed by a TE material (Bi\(_2\)Te\(_3\) or Sb\(_2\)Te\(_3\)) and a conductor (metal connector), which have different DOS, mass density, Debye temperature and frequency, and also different speeds of sound, providing resistance to the flow of phonons at the interface.

Two theories have been applied to the prediction of the phonon boundary resistance [9]. The first is the acoustic mismatch model (AMM), which assumes no phonon scattering (i.e, a perfect, planar interfaces with specular reflection). The second one
Figure 2.1: Thermal boundary resistances associated with phonon and electron heat transport at the metal/TE interface: (a) Phonon boundary resistance, (b) Electron boundary resistance, (c) Mixed boundary resistances.

is the diffuse mismatch model (DMM), which assumes that all phonons incident on the interface will scatter (i.e., a rough interface with diffuse reflections). In the AMM, the transport is controlled by the difference in the acoustic impedance of the materials (product of the mass density and the phonon velocity). The assumption that no scattering occurs at the interface is reasonable at very low temperatures, where the phonon wavelength is longer than other interface length scales such as defects and roughness. As the temperature increases the phonon wavelength decreases, compromising the AMM theory. In the DMM, the transport is controlled by the diffuse
scattering at the interface and the differences in densities of states.

Phelan [10] showed that by using the measured phonon DOS (as compared to the
DOS calculated assuming the Debye model), the DMM predicts the phonon boundary
resistance $R_{k, b, pp}$ in relatively good agreement with the experimental data. Here we
will use the DMM and show that by using our estimated average phonon speed for
the TE material, the measured DOS and that of the Debye model give similar values
of $R_{k, b, pp}$.

The physical system consists of a film (material $te$, TE element) deposited on a
substrate (material $mc$, metal connector). In a typical application, a net heat flux
$q$ is caused by the increase of the film temperature $T_{te}$, relative to the substrate
temperature $T_{mc}$. The heat flux and temperatures are related through

$$
(A_k R_k)_{b, pp} = \frac{T_{te} - T_{mc}}{q}.
$$

(2.1)

Starting with the general expression for the energy transported per unit time from
material $te$ to material $mc$, and assuming that the transmission coefficient $\tau_{te-mc}$ is
independent of the temperature on either side of the interface (only one side of the
interface is considered) [9], Phelan [10] derived an expression for $q$ as a function of
the phonon DOS $P_p$:

$$
q = \frac{h P \tau_{te-mc}}{8 \pi} \sum_j u_{p(te,j)} \int_0^\infty P_p(\omega_p) \omega_p \left[ \frac{1}{\exp\left(\frac{h \omega_p}{2 \pi k_B T_{te}}\right)} - \frac{1}{\exp\left(\frac{h \omega_p}{2 \pi k_B T_{mc}}\right)} \right] d\omega_p.
$$

(2.2)

In Eq. (2.2), $h_P$ is the Planck constant, $j$ is the phonon mode (either longitudinal
or transverse), $u_{p(te,j)}$ is the speed of the phonon of mode $j$ in material $te$, $\omega_p$ is
the phonon angular frequency, and $k_B$ is the Boltzmann constant. The transmission
coefficient is approximated by [9, 10]
\[
\tau_{te-mc} = \frac{\sum_j u_{p(te,j)}^{-2}}{\sum_j u_{p(te,j)}^{-2} + \sum_j u_{p(mc,j)}^{-2}}.
\] (2.3)

Note that Eq. (2.3) is derived for the case where \(T_{te}\) is equal to \(T_{mc}\) [10], whereas here there is a finite heat flow rate through the TE film. So, Eq. (2.3) would give an adequate prediction of the transmission coefficient for small \(T_{te} - T_{mc}\). Our typical heat flow rates give \(T_{te} - T_{mc}\) approximately equal to or less than 1 K. We use \(T_{te} - T_{mc}\) equal to 1 K and Eq. (2.3) in the present study. However, as also reported by Phelan [10], no significant change in the phonon boundary resistance is found above 90 K, for \(T_{te} - T_{mc}\) up to 10 K.

Equation (2.2) is numerically integrated to yield a value for \(q\), which is substituted into Eq. (2.1) to determine \((A_k R_k)_{h,pp}\). Due to the lack of data for material \(te\) (here, either Sb\(_2\)Te\(_3\) or Bi\(_2\)Te\(_3\)), and since the fabricated films can be polycrystalline (verified by X-ray diffraction, and discussed in Chapter 4), we have assumed that the three phonon wave speeds (two transverse and one longitudinal) are equal, i.e.,
\[
\sum_j u_{p(te,j)}^{-2} = \frac{1}{u_{p(te,t)}^2} + \frac{2}{u_{p(te,t)}^2} = \frac{3}{u_{p(te)}^2}.
\] (2.4)

The phonon speed \(u_p\) is related to the Debye temperature \(T_D\), and to the Debye angular frequency \(\omega_D\), through the expressions
\[
T_D = \frac{h_p \omega_D}{2\pi k_B} \quad \text{and} \quad \omega_D = \left(6\pi^2 u_p^3 n\right)^{1/3},
\] (2.5)
where \(n\) is the ratio between the number of primitive cells and the unit cell volume.

For Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\), the non-primitive hexagonal unit cell with dimensions \(a\) and \(c\) (shown in Fig. 4.1) contains three lattice points and has three times the
Table 2.1: Bulk properties of \( n \)- and \( p \)-type TE elements.

<table>
<thead>
<tr>
<th>Property</th>
<th>Reference</th>
<th>( \text{Bi}_2\text{Te}_3 )</th>
<th>( \text{Sb}_2\text{Te}_3 )</th>
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<tr>
<td>( T_D ), K</td>
<td>[33]</td>
<td>165</td>
<td>160</td>
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<tr>
<td>( a ), m</td>
<td>[33]</td>
<td>( 4.38 \times 10^{-10} )</td>
<td>( 4.25 \times 10^{-10} )</td>
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<tr>
<td>( c ), m</td>
<td>[33]</td>
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<td>( 29.96 \times 10^{-10} )</td>
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<td>171</td>
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<td>[8]</td>
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</tr>
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<td>( k_p ), W/m-K</td>
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<td>( \rho_e ), ( \Omega )-m</td>
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<td>( n_e ), m⁻³</td>
<td>[2]</td>
<td>( 6.5 \times 10^{25} )</td>
<td>( 3.4 \times 10^{25} )</td>
</tr>
</tbody>
</table>

volume of the primitive rhombohedral cell [32]. The numerical values of the lattice parameters \( a \) and \( c \), as well as the Debye temperature [33] used for determining the average phonon speed and the transmission coefficient of material \( te \) are given in Table 2.1. The material \( mc \), assumed to be copper\(^*\), has longitudinal and transverse phonon speeds equal to 4,760 m/s and 2,325 m/s respectively [34]. The results obtained from Eqs. (2.3) and (2.5) are presented in Table 2.2. Bulat [35] has assumed that for bismuth compounds the sound velocity is 2,100 m/s, which is approximately 30%.

\(^*\) Later, in the TE film and device fabrications, it was verified that the TE elements did not present a good adhesion to Cu. Platinum was an acceptable substitute, and was used as the interfacial layer of the hot connectors, as described in Section 5.1.1. Taking the longitudinal and transverse phonon speeds for Pt, which are equal to 3,260 and 1,730 m/s, respectively [34], the transmission coefficients increased only by about 20% (compared with reported values in Table 2.2), and the phonon boundary resistance decreased only by about 20%, at both \( n \)- and \( p \)-type interfaces. Since assuming Cu as the metal connector is a conservative design (as can be inferred from Fig. 3.4), it was used.

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Table 2.2: Microscale properties of n- and p-type TE elements.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bi$_2$Te$_3$</th>
<th>Sb$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$, $m^{-3}$</td>
<td>$5.95 \times 10^{27}$</td>
<td>$6.40 \times 10^{27}$</td>
</tr>
<tr>
<td>$\omega_D$, rad-s$^{-1}$</td>
<td>$2.16 \times 10^{13}$</td>
<td>$2.09 \times 10^{13}$</td>
</tr>
<tr>
<td>$u_p$, m-s$^{-1}$</td>
<td>3.058</td>
<td>2.888</td>
</tr>
<tr>
<td>$\tau_{te\rightarrow mc}$</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>$\tau_m$, s</td>
<td>$2.5 \times 10^{-14}$</td>
<td>$9.8 \times 10^{-14}$</td>
</tr>
<tr>
<td>$\tau_e$, s</td>
<td>$1.0 \times 10^{-11}$</td>
<td>$2.7 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

lower than the values predicted here.

The measured [36] and the Debye phonon DOS, $P_p$ (THz$^{-1}$), as a function of the phonon frequency $f_p$ (THz) for the TE materials Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are shown in Fig. 2.2. To establish $P_p$ as a function of the angular frequency $\omega_p$ and on a per unit volume basis [i.e., $P_p$ given in (s/rad-m$^3$)], as required by Eq. (2.2), the values shown in the graph are divided by $2\pi$ and multiplied by the factor $n$, defined after Eq. (2.5). The Debye DOS $P_{p,D}$ (s/rad-m$^3$) is given by

$$P_{p,D} = \frac{\omega_p^2}{2\pi^2 u_p^3}. \quad (2.6)$$

From the areas under the curves of the Fig. 2.2, we have predicted the boundary resistances using the Debye ($f_p < f_{p,D} = 3.3$ THz) and the measured DOS (0.1 THz $\lesssim f_p \lesssim 5.2$ THz), and have found similar values, as shown in Fig. 2.3. The difference in the resistances reported by Phelan [10] may be due to the lack of agreement between the areas under the curves (for YBa$_2$Cu$_3$O$_{7-\delta}$ used there). In that analysis, $\omega_D$ is to the left of the measured mean frequency, i.e, $\omega_D = 5.4 \times 10^{13}$ rad/s and the measured DOS ranges from $1 \times 10^{13}$ rad/s to $14 \times 10^{13}$ rad/s. The increase in
Figure 2.2: Variation of the phonon DOS, $P_p$, of $n$- and $p$-type TE elements with respect to phonon frequency $f_p$. 

- $\text{Bi}_2\text{Te}_3$ [Debye Model]
  - $P_{p,\text{max}} = 0.90 \text{ THz}^{-1}$ at $f_{p,D} = 3.32 \text{ THz}$
- $\text{Sb}_2\text{Te}_3$ [Debye Model]
  - $P_{p,\text{max}} = 0.88 \text{ THz}^{-1}$ at $f_{p,D} = 3.44 \text{ THz}$

- $\text{Bi}_2\text{Te}_3$ [Experimental, (Rauh et al., 1981)]
- $\text{Sb}_2\text{Te}_3$ [Experimental, (Rauh et al., 1981)]
Figure 2.3: Variation of the phonon boundary resistance \((A_kR_k)_{b,pp}\) of \(n\)- and \(p\)-type TE elements with respect to the temperature \(T_{te}\). The markers are to guide the eye.

The boundary resistance with increase in temperature (at high temperatures) has also been reported by Prasher and Phelan [37]. They developed a new model that incorporates near boundary scattering (due to non-uniformities) in the basic AMM. The thermal boundary resistance at higher temperatures is successfully predicted using an empirical Umklapp scattering parameter. Since no experimental boundary resistance data is available for \(Bi_2Te_3\) and \(Sb_2Te_3\), this model is not used here. It should also be mentioned that the observed minimum in Fig. 2.3 moves to the right, as the Debye temperature increases, and then a plateau behavior is reached, as shown in [9].

In order to assess the effect of any uncertainty in \(u_{p(te)}\) on \(R_{k,b,pp}\), \(\pm 25\%\) variation is allowed in \(u_{p(te)}\) of \(Sb_2Te_3\). In Fig. 2.3, it is shown that \(R_{k,b,pp}\) decreases \(33\%\) and increases \(82\%\) (at \(T_{te} = 300\) K) when \(u_{p(te)}\) increases and decreases \(25\%\) respectively.

For \(T_{te}\) equal to 300 K, the phonon boundary resistances at the \(Bi_2Te_3/Cu\) and
Sb$_2$Te$_3$/Cu interfaces, determined using the experimental DOS, are $9.2 \times 10^{-8}$ K/(W/m$^2$) and $8.0 \times 10^{-8}$ K/(W/m$^2$), respectively. These resistances have the same order of magnitude of the resistances measured by Stoner and Maris [38] [$1.0 \times 10^{-8}$ to $3.2 \times 10^{-8}$ K/(W/m$^2$) at 300 K] between diamond and several metals.

### 2.2.2 Electron Boundary Resistance

When a metal is in contact with a semiconductor, the Fermi energy levels in the two materials must be the same at thermal equilibrium. In addition, the vacuum level must be continuous. These two requirements determine a unique energy band diagram for the ideal metal-semiconductor contact [39]. The energy band diagrams of a metal with work function $\phi_m$, and of $n$- and $p$-type semiconductors with work functions $\phi_n$ and $\phi_p$, and electron affinities $\chi_n$ and $\chi_p$, are shown in Fig. 2.4(a), for $\phi_p > \phi_m > \phi_n$.

When the solids come into contact [Fig. 2.4(b)], the more energetic electrons in the conduction band (CB) of the $n$-type semiconductor will diffuse into the metal in search of lower empty energy levels (just above the metal Fermi energy $E_{F,m}$) and accumulate near the surface of the metal. Electrons flowing from the semiconductor leave behind an electron-depleted region of width $W$. In this region, the difference between the energy at the bottom of the conduction band and the Fermi energy of the $n$-type semiconductor ($E_{c,n} - E_{F,n}$) must increase, so that the concentration of electrons $n_{c,n}$ decreases {$n_{c,n} \sim \exp[-(E_{c,n} - E_{F,n})/k_B T]$} [40]. The bands must bend to increase $E_{c,n} - E_{F,n}$ toward the junction. The potential barrier for electrons
moving from the metal to the $n$-type semiconductor is $E_{o,n} = \phi_m - \chi_n$, and is greater than the built-in potential energy $V_{b,n}$ (energy needed to take an electron from the $n$-type semiconductor to the metal). Eventually this built-in potential reaches a value that prevents further accumulation of the electrons at the metal surface and an equilibrium is reached. Similarly, electrons in the metal will cross the junction to the $p$-type semiconductor searching for lower energy levels around $E_{v,p}$ (energy at the top of the valence band of the $p$-type semiconductor). To show the decrease of hole concentration $n_{c,p}$ near the junction, the $p$-type semiconductor energy bands are
bent downward to increase $E_{F,p} - E_{v,p}$, \( \{n_{e,p} \sim \exp[-(E_{F,p} - E_{v,p})/k_B T]\} [40] \). The potential barrier for electrons moving from the metal to the p-type semiconductor is $E_{o,n} = E_{g,p} - (\phi_m - \chi_p)$, where $E_g$ is the band gap energy.

In the present study, the electron boundary resistance is modeled using a potential barrier with a rectangular shape [8], where we take $E_o$ (which can be either $E_{o,n}$ or $E_{o,p}$) as the potential barrier height, and $W/2$ as the potential barrier thickness $d$. The electrons can be transferred across this barrier by tunneling. In analogy with the Wiedemann-Franz law, the electron boundary resistance is given by

$$
\frac{1}{(A_k R_k)_b,ee} = \frac{\pi^2}{3} \frac{T}{(A_k R_e)_b} \left( \frac{k_B}{e_c} \right)^2,
$$

where $(A_k R_e)_b$ is the electrical boundary resistance [8],

$$
\frac{1}{(A_k R_e)_b} = \frac{4\pi e_c^2 m_{e,te} P}{h_p^2} \left[ \frac{h_p^2 E_o}{8\pi^2 m_{e,te} d^2} \right]^{1/2},
$$

$m_{e,te}$ is the effective mass of the electrons/holes in the TE material (given in Table 1), $e_c$ is the electronic charge, and $P$ is the tunneling probability. Tunneling occurs if [8]

$$
\left[ \frac{h_p^2 E_o}{8\pi^2 m_{e,te} d^2} \right]^{-1/2} k_B T \ll 1.
$$

For thick barriers the dominant transport mechanism is thermionic emission. Then, $\pi^2/3$ in Eq. (2.7) is replaced by 2, and the electrical boundary resistance is given by [8]

$$
\frac{1}{(A_k R_e)_b} = \frac{e_c B T e^{-E_o/k_B T}}{k_B},
$$

where $B$ is equal to $120 \times 10^4$ A/m$^2$K$^2$, and $E_o$ is assumed to be much larger than $k_B T$ [31].
In order to choose between tunneling and thermionic emission, $E_o$ and $d$ must be estimated. Mahan and Woods [41] have reported potential barriers between some metals and semiconductors equal to or less than 0.1 eV, including a Bi$_2$Te$_3$/Sb$_2$Te$_3$ interface (0.035 eV). Nagao et al. [42], have reported that ohmic contact characteristics are observed at the Au/Bi$_2$Te$_3$ junction, i.e., no Schottky barrier is formed, so the contact does not limit the current flow. These two results indicate that small barriers can be obtained with such semiconductors. Here, we assume $E_o$ equal to 0.1 eV at the interfaces between the metal and both TE materials. Both Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are narrow-gap semiconductors ($E_{g,n} = 0.15$ eV and $E_{g,p} = 0.2$ eV) [43, 44], and the assumed value (0.1 eV) is lower than their energy gaps. This same relation was verified by the comparison with reported values of $E_o$ for various other metal/semiconductor interfaces [31, 45] and $E_g$ of the respective semiconductors [31].

The barrier thickness $d$ is estimated from the depletion width $W$ ($d = W/2$), which can be approximated (for zero applied voltage) as [39]

$$W = \left(\frac{2\varepsilon_r\varepsilon_o E_o}{\varepsilon_e N}\right)^{1/2},$$

(2.11)

where $\varepsilon_r$ is the relative permittivity of the semiconductor, which is equal to 100 for Bi$_2$Te$_3$ [46] and equal to 55 for Sb$_2$Te$_3$ [47], $\varepsilon_o$ is the free-space permittivity (8.8542 $\times 10^{-12}$ C$^2$/J-m) and $N$ is the donor/acceptor atom concentration in the crystal. When $N$ is much larger than the concentration of the intrinsic semiconductor (pure semiconductor crystal in which the electron and hole concentrations are equal), then $N$ is nearly equal the carrier concentration $n_c$ (electrons in the $n$-type semiconductor and holes in the $p$-type semiconductor) [40], which is given in Table 2.1. Assuming
that this is the case here (i.e., $N \approx n_c$), $d$ is found to be 2.06 nm (metal/Bi$_2$Te$_3$) and 2.12 nm (metal/Sb$_2$Te$_3$).

From Eq. (2.9), we verify that tunneling will occur if $d \ll 3.1$ nm and $d \ll 2.4$ nm for the $n$- and $p$-type semiconductor/metal junctions respectively. Although the values of $d$ obtained from Eq. (2.11) are slightly smaller than these obtained from Eq. (2.9), we assume tunneling as the electron transport mechanism here, and therefore, we use Eqs. (2.7) and (2.8) to evaluate the electron boundary resistance.

The tunneling probability is given by [39]

$$P = \left\{1 + \frac{E_o^2 \sinh^2 [8\pi^2 m_{e,te}(E_o - E)d^2/h_p^2]^{1/2}}{4E(E_o - E)}\right\}^{-1}, \quad (2.12)$$

where $E$ is the electron energy (measured from the bottom of the potential barrier), and $E < E_o$. Taking $E = E_o/2 = 0.05$ eV (i.e., $E \approx 2k_B T$), we obtain $P$ values of 0.104 and 0.031 at the metal/Bi$_2$Te$_3$ and metal/Sb$_2$Te$_3$ junctions, respectively.

The resistances $(A_k R_k)_b$ and $(A_k R_k)_{b,ee}$ are then estimated from Eqs. (2.8) and (2.7) respectively, and are $2.6 \times 10^{-12}$ Ω-m$^2$ and $3.5 \times 10^{-7}$ K/(W/m$^2$) at the metal/Bi$_2$Te$_3$ interface, and $6.8 \times 10^{-12}$ Ω-m$^2$ and $9.3 \times 10^{-7}$ K/(W/m$^2$) at the metal/Sb$_2$Te$_3$ interface.

### 2.2.3 Total Boundary Resistance

The total thermal boundary resistance $(A_k R_k)_b$ is given by [8]

$$\frac{1}{(A_k R_k)_b} = \frac{1}{(A_k R_k)_{b,pp}} + \frac{1}{(A_k R_k)_{b,ee}} + \frac{1}{(A_k R_k)_{b,pe}} + \frac{1}{(A_k R_k)_{b,pe}}. \quad (2.13)$$

Assuming for simplicity that there is no direct heat transfer between electron and phonon subsystems across the boundary, i.e., $R_{k,b,pe}$ and $R_{k,b,pe} \to \infty$, the total ther-
mal boundary resistance will be a function of the phonon and electron boundary resistances only. In this case, at the Bi$_2$Te$_3$/Cu and Sb$_2$Te$_3$/Cu interfaces, the total thermal boundary resistances are $7.2 \times 10^{-8}$ K/(W/m$^2$) and $7.4 \times 10^{-8}$ K/(W/m$^2$), respectively.

### 2.3 Phonon-Electron Non-Equilibrium

Because the thermal boundary resistances of the electrons and phonons are not the same, and due to ohmic heating and Peltier cooling/heating, electrons and phonons can have different temperatures adjacent to the interface ($T_e \neq T_p$) and require a distance $\delta$ (the cooling length) to equilibrate. This phonon-electron non-equilibrium region is shown in Fig. 2.5.

#### 2.3.1 Cooling Length

The cooling length $\delta$, which is the distance from the boundary required for electrons and phonons to reach equilibrium, is defined as [11, 35]

$$
\delta = \left[ \frac{\tau_e k_e}{n_e k_B (k_e + k_p)} \right]^{1/2}.
$$

(2.14)

where $\tau_e$ is the electron/hole energy relaxation time, and $k_e$ and $k_p$ are the electron and phonon contributions to the thermal conductivity $k$ ($k = k_e + k_p$). Bartkowiak and Mahan [8] have reported $k_e$ and $k_p$ equal to 0.5 W/m-K and 1.5 W/m-K, respectively, for Bi$_2$Te$_3$. For Sb$_2$Te$_3$, we assume the same phonon contribution (i.e., $k_p = 1.5$ W/m-K) [17, 18], and estimate the electronic contribution using the Wiedemann-Franz law,
Figure 2.5: Schematic phonon-electron non-equilibrium adjacent to the boundary due to the mismatch of the electron and phonon boundary resistances, Joule heating, and Peltier heating/cooling.

\[ k_e = \frac{LT}{\rho_e}, \]
where \( L \) is the Lorenz number and \( \rho_e \) is the electrical resistivity. For \( L \) equal to \( 2.1 \times 10^{-8} \text{ V}^2/\text{K}^2 \) at 300 K [48] and \( \rho_e \) equal to \( 1.04 \times 10^{-5} \Omega\text{-m} \), we have \( k_e \) equal to 0.6 W/m-K.

The electron/hole energy relaxation time is given by [35, 49]

\[ \tau_e = \frac{k_B T}{2m_{e,te}u_p^2} \tau_m, \quad (2.15) \]

where \( u_p \) is the phonon speed estimated in Section 2.2.1, and \( \tau_m \) is the electron/hole momentum relaxation time, which is a function of the electron/hole mobility \( \mu \) [35, 40],

\[ \tau_m = \frac{m_{e,te}\mu}{e_c}. \quad (2.16) \]

The properties of the \( n \)- and \( p \)-type TE elements used to evaluate the relaxation times and cooling length are given in Table 2.1. The results obtained from Eqs. (2.15)
and (2.16) are presented in Table 2.2. The cooling lengths estimated for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are 66 nm and 156 nm, respectively.

### 2.3.2 Phonon and Electron Temperatures

The kinetics of electrons and phonons in an electric field or in a temperature field is described by the coupled Boltzmann equations for electrons and phonons [11]. For a one-dimensional geometry, these equations can be given by

\[-k_e \frac{d^2 T_e}{dx^2} = \frac{\rho_e j_e}{\tau_e} - \frac{n_e k_B}{\tau_e} (T_e - T_p), \quad (2.17)\]

\[-k_p \frac{d^2 T_p}{dx^2} = \frac{n_e k_B}{\tau_e} (T_e - T_p), \quad (2.18)\]

where $j_e$ is the electrical current density. These are the equations of energy balance in the electron and phonon subsystems.

Assuming that $\rho_e$, $n_e$, $\tau_e$, $k_e$, and $k_p$ are constant, the above equations are solved by defining a center-of-thermal-conductivity temperature $kT_{ctc} = k_e T_e + k_p T_p$, [8]. The solution is

\[T_e = A_1 + A_2 \frac{x}{L_{te}} + \frac{\rho_e j_e^2}{k} \left[ \left( \frac{L_{te}}{2} \right)^2 - x^2 \right] + \frac{\rho_e j_e^2 \delta^2}{\gamma k} - \frac{1}{\gamma} \left[ A_3 \cosh \left( \frac{x}{\delta} \right) + A_4 \sinh \left( \frac{x}{\delta} \right) \right], \quad (2.19)\]

\[T_p = A_1 + A_2 \frac{x}{L_{te}} + \frac{\rho_e j_e^2}{k} \left[ \left( \frac{L_{te}}{2} \right)^2 - x^2 \right] - \frac{\rho_e j_e^2 \delta^2}{k} + \left[ A_3 \cosh \left( \frac{x}{\delta} \right) + A_4 \sinh \left( \frac{x}{\delta} \right) \right], \quad (2.20)\]

where $\gamma = k_e/k_p$, and $L_{te}$ is the TE element thickness.

The four unknown constants $A_1$, $A_2$, $A_3$ and $A_4$ are determined by the boundary conditions for the flow of heat by electrons and phonons at the boundaries, as presented in Figs. 2.6(a) and 2.6(b). Note that, as previously discussed, no direct
Figure 2.6: Schematic temperature distribution of electrons and phonons assuming equilibrium in the connectors. (b) Energy conversion mechanisms and heat transfer path of the electron and phonon subsystems.
heat transfer between electrons and phonons across the boundaries is considered, i.e.,

\[ R_{k,b,\text{ep}} = R_{k,b,\text{pe}} \to \infty. \]

Also for simplicity, it is assumed that electrons and phonons are in equilibrium in the connectors, i.e, \( T_{\text{cp}} = T_{\text{ce}} = T_c \) and \( T_{\text{hp}} = T_{\text{he}} = T_h. \)

The phonon boundary conditions are, at \( x = -L_{te}/2, \)

\[ \frac{[T_c - T_p|_{-L_{te}/2}]}{(A_kR_k)_{b,pp}} - k_p \frac{dT_p}{dx}|_{-L_{te}/2} = 0. \]  (2.21)

and at \( x = L_{te}/2, \)

\[ \frac{[T_p|_{L_{te}/2} - T_h]}{(A_kR_k)_{b,pp}} - k_p \frac{dT_p}{dx}|_{L_{te}/2} = 0. \]  (2.22)

The electron boundary conditions are, at \( x = -L_{te}/2, \)

\[ \frac{[T_c - T_e|_{-L_{te}/2}]}{(A_kR_k)_{b,ee}} - k_e \frac{dT_e}{dx}|_{-L_{te}/2} + (\alpha_{S,\text{bulk}} - \alpha_{S,b}) j_e T_e|_{-L_{te}/2} - (A_kR_e)_b \frac{j_e^2}{2} = 0. \]  (2.23)

and at \( x = L_{te}/2, \)

\[ \frac{[T_e|_{L_{te}/2} - T_h]}{(A_kR_k)_{b,ee}} - k_e \frac{dT_e}{dx}|_{L_{te}/2} + (\alpha_{S,\text{bulk}} - \alpha_{S,b}) j_e T_e|_{L_{te}/2} + (A_kR_e)_b \frac{j_e^2}{2} = 0. \]  (2.24)

The first term in the above equations represents the heat flow as defined by the phonon (electron) boundary resistance, and the second term is the heat flow predicted by the Fourier law. The third term of Eqs. (2.23) and (2.24) represents the Peltier cooling and heating, respectively. The Joule heating at the boundaries is represented by the fourth term.

The bulk Seebeck coefficient \( \alpha_{S,\text{bulk}} \) is given in Table 2.1 for the \( n- \) and \( p- \)type TE materials. The boundary Seebeck coefficient \( \alpha_{S,b}, \) assuming that tunneling is the dominant electron transport mechanism across the metal/semiconductor interfaces, is given by [8]

\[ \alpha_{S,b} = \left( \frac{k_B}{e_c} \right) \frac{\pi^2}{3} k_B T \left[ \frac{\hbar^2 E_o}{8\pi^2 m^*_c d^2} \right]^{-1/2}. \]  (2.25)
Taking the values of $E_o$ and $d$ estimated in Section 2.2.2, we find $|\alpha_{S,b}|$ equal to 252 $\mu$V/K and 187 $\mu$V/K for the $p$- and $n$-type semiconductor/metal junctions, respectively. (The sign of $\alpha_{S,b}$ is discussed in Section 2.4.2).

Equations (2.19) and (2.20) were solved analytically with Eqs. (2.21) to (2.24). The resulting expressions for the coefficients $A_j$ are

$$A_1 = T_h - \left( \frac{C_2A_2 - C_3A_3 - C_4A_4 - C_{15}}{C_1} \right), \quad A_2 = \frac{C_1(T_h - T_c) + 2C_4A_4}{2C_2},$$

$$A_3 = \frac{B_7 + B_8 - B_9A_4}{B_{10}}, \quad \text{and} \quad A_4 = \frac{B_1 + B_2 - B_3}{B_4 + B_5 - B_6},$$

(2.26)

where $B_j$ and $C_j$ are given by

$$B_1 = (C_5C_3/C_1 + C_7)(C_5 - C_1C_6/C_2)(T_h - T_c),$$

$$B_2 = (C_5C_3/C_1 + C_7)[C_9(T_h + T_c) + 2C_{13} + 2C_9C_{15}/C_1],$$

$$B_3 = (C_5C_3/C_1 + C_{11})[2C_5C_{15}/C_1 - C_1C_{10}(T_h - T_c)/C_2 + 2C_{14}],$$

$$B_4 = (C_5C_3/C_1 + C_7)(2C_8 + 2C_6C_4/C_2),$$

$$B_5 = (C_9C_3/C_1 + C_{11})(2C_8 + 2C_6C_4/C_2),$$

$$B_6 = 2(C_9C_3/C_1 + C_{11})[(C_8 + C_6C_4/C_2) + (C_{12} + C_4C_{10}/C_2)],$$

$$B_7 = (T_h - T_c)(C_5 - C_1C_6/C_2)/2 + C_9(T_h + T_c)/2 + C_{13} + C_9C_{15}/C_1,$$

$$B_8 = C_5C_{15}/C_1 - C_1C_{10}(T_h - T_c)/(2C_2) + C_{14},$$

$$B_9 = C_{12} + C_8 + C_4(C_{10} + C_6)/C_2,$$

$$B_{10} = C_{11} + C_7 + C_3(C_9 + C_5)/C_1,$$

(2.27)

$$C_1 = \frac{1}{k_p(A_kR_k)_{b,pp}}, \quad C_2 = \frac{1}{L_{te}} + \frac{C_1}{2},$$

$$C_3 = \frac{\gamma}{1 + \gamma} \left[ \sinh \left( \frac{L_{te}}{2\delta} \right) + C_1 \cosh \left( \frac{L_{te}}{2\delta} \right) \right].$$
\[ C_4 = \frac{\gamma}{1 + \gamma} \left[ \frac{\cosh \left( \frac{L_{te}}{2\delta} \right)}{\delta} + C_1 \sinh \left( \frac{L_{te}}{2\delta} \right) \right], \]
\[ C_5 = \frac{1}{k_e(A_k R_k)_{b,ee}}, \quad C_6 = \frac{1}{L_{te}} + \frac{C_5}{2}, \]
\[ C_7 = \frac{\gamma}{1 + \gamma} \left[ \frac{\sinh \left( \frac{L_{te}}{2\delta} \right)}{\delta} + C_5 \cosh \left( \frac{L_{te}}{2\delta} \right) \right], \]
\[ C_8 = \frac{\gamma}{1 + \gamma} \left[ \frac{\cosh \left( \frac{L_{te}}{2\delta} \right)}{\delta} + C_5 \sinh \left( \frac{L_{te}}{2\delta} \right) \right], \]
\[ C_9 = \frac{C_5 C_{13}}{C_9} - \frac{\rho_e j_e^2 L_{te}}{2(k_e + k_p)} - \frac{(A_k R_e)_{b,ee} j_e^2}{2k_e}, \quad C_{10} = \frac{C_9}{2}, \]
\[ C_{11} = \frac{C_9}{1 + \gamma} \cosh \left( \frac{L_{te}}{2\delta} \right), \quad C_{12} = \frac{C_9}{1 + \gamma} \sinh \left( \frac{L_{te}}{2\delta} \right), \quad C_{13} = \frac{C_9}{1 + \gamma} \frac{j_e}{k_e} (\alpha_{S, bulk} - \alpha_{S, b}), \quad C_{14} = \frac{C_9}{1 + \gamma} \frac{j_e^2}{k_e} \frac{L_{te}}{2}, \]
\[ C_{15} = \frac{C_9}{1 + \gamma} \frac{j_e^2}{k_e} \frac{L_{te}}{2}. \]

For electrical current \( j_e \) equal to zero, \( C_9 \) to \( C_{15} \) [Eqs. (2.28)] are also zero, and the coefficients \( A_j \) can be simplified to

\[ A_1 = \frac{T_h + T_c}{2}, \quad (2.29) \]
\[ A_2 = \frac{\gamma L_{te}^* \coth L_{te}^* + \frac{R_e^* R_e^*(1+\gamma)^2}{2R_e^*}}{R_e^* + \frac{R_e^* R_e^*(1+\gamma)^2}{2R_e^*} + \frac{\gamma L_{te}^* \coth L_{te}^*}{(1+2R_e^*)^{-1}} + \frac{R_e^*}{2}}, \quad (T_h - T_c), \quad (2.30) \]
\[ A_3 = 0, \quad (2.31) \]
\[ A_4 = \frac{\gamma^2 R_p^* - \gamma R_e^*}{R_e^* + \frac{R_e^* R_e^*(1+\gamma)^2}{2R_e^*} + \frac{\gamma L_{te}^* \coth L_{te}^*}{(1+2R_e^*)^{-1}} + \frac{R_e^*}{2}} \times \frac{(T_h - T_c)}{2 \sinh L_{te}^*}, \quad (2.32) \]

where the dimensionless parameters (*) are given by

\[ R_e^* = \frac{R_{k,b}}{R_{k,b,ee}}, \quad R_p^* = \frac{R_{k,b}}{R_{k,b,pp}}, \quad R_e^* = \frac{R_{k,b}}{L_{te}^*}, \quad L_{te}^* = \frac{L_{te}}{2}, \quad (2.33) \]

The electron and phonon temperatures for \( J_e \) \( (= j_e A_k, \text{ where } A_k = 7\mu m \times 7\mu m) \) equal to 0, 15 and 30 mA are shown in Fig. 2.7. Note that at the cold junction \( x = -2 \mu m), the electron temperature decreases with Peltier cooling and increases with Joule...
heating [Eq. (2.23)]. At the hot junction ($x = 2 \mu m$), the electron temperature is increased by both of these energy conversions [Eq. (2.24)], which explains the larger deviations of $T_e$ and $T_p$ from the temperature in this junction ($T_h$), compared with the smaller deviations of $T_e$ and $T_p$ from the temperature in the cold junction ($T_c$). The difference between $T_e$ and $T_p$ increases as $j_e$ increases, as expected by inspection of Eqs. (2.19) and (2.20). The distance from the junctions (hot or cold) required for electrons and phonons to reach equilibrium, i.e., where $T_e = T_p$, is larger (for $j_e$ not equal to zero) than the cooling length of 156 nm estimated for Sb$_2$Te$_3$. This is due
to the effects of Joule heating, not considered in the derivation of Eq. (2.14). This difference increases (i.e., \( \delta \) becomes larger) with the increase of \( j_e \).

### 2.4 Effect of Boundary Resistances and Phonon-Electron Non-Equilibrium on Thermoelectric Properties

The efficiency of the \( n \)- and \( p \)-type TE elements is determined by the figure of merit

\[
Z_e = \frac{\alpha_S^2}{\rho_e k_e} = \frac{\alpha_S^2}{R_{e,h-c}/R_{k,h-c}},
\]

where \( R_{e,h-c} \) and \( R_{k,h-c} \) are the electrical and thermal resistances, respectively. A low electrical resistance is desired in order to minimize the Joule heating, \( \dot{S}_{e,J} \), and the electrical power consumption, \( P_e \), of the device. The thermal resistance must be large to minimize the undesirable conduction heat transfer from the hot junction to the cold junction, \( Q_{k,h-c} \), shown in Fig. 1.1. The Seebeck coefficient \( \alpha_S \) is an indicator of the device thermopower, i.e., the Peltier heating/cooling at the junctions, \( \dot{S}_{e,P} \), and should be maximized.

Here, as the TE element has a small thickness (\( L_{te} = 4 \mu m \)), its TE properties, and therefore, its efficiency, can be influenced by the boundary effects (phonon and electron boundary resistances and phonon-electron non-equilibrium).
2.4.1 Thermal Resistance of Thermoelectric Element

In the absence of electrical current, the heat flow across the TE element \( i (i = n, p) \) can be calculated as

\[
Q_{k,h-c} (j_e = 0) = \frac{(T_h - T_c)}{(R_{k,h-c})_i}. \tag{2.35}
\]

From the heat flow path shown in Fig. 2.6(b),

\[
Q_{k,h-c} (j_e = 0) = A_k \left[ -k_e \frac{dT_e}{dx} - k_p \frac{dT_p}{dx} \right]_{\frac{L_{te}}{2}} = A_k \left[ -k_e \frac{dT_e}{dx} - k_p \frac{dT_p}{dx} \right]_{\frac{L_{te}}{2}}. \tag{2.36}
\]

Therefore, the thermal resistance of the TE elements is given by

\[
(R_{k,h-c})_i = \left[ \frac{(T_h - T_c)}{A_k \left[ -k_e \frac{dT_e}{dx} - k_p \frac{dT_p}{dx} \right]_{\frac{L_{te}}{2}}} \right] = \left[ \frac{L_{te} (T_h - T_c)}{A_k k_1} \right]_i, \tag{2.37}
\]

or, introducing Eq. (2.30) into Eq. (2.37),

\[
\frac{(R_{k,h-c})_i}{A_k k_1} = \left[ \frac{R_e^* \frac{k_e^* R_e^* (1+\gamma)^2}{2 R_k^*} + \gamma L_{te}^* \coth L_{te}^* + R_p^* \gamma^2}{\gamma L_{te}^* \coth L_{te}^* + \frac{k_e^* R_e^* (1+\gamma)^2}{2 R_k^*}} \right]_i. \tag{2.38}
\]

Note that \( R_{k,h-c} \) is greater than the bulk resistance \( L_{te}/(A_k k) \) due to the thermal boundary resistances and the phonon-electron non-equilibrium. This increase in \( R_{k,h-c} \) reduces the undesirable heat conduction from the hot to the cold junctions.

For \( L_{te} \) much greater than \( 2\delta \), Eq. (2.38) becomes

\[
\frac{(R_{k,h-c})_i}{A_k k_1} = \left[ 1 + \frac{2R_{k,b}}{L_{te}/A_k k_1} \right]_i. \tag{2.39}
\]

The effect of the cooling length and the phonon and electron boundary resistances on the thermal resistance \( R_{k,h-c} \), which is obtained from Eqs. (2.38) and (2.39), is shown in Fig. 2.8(a), for cases (i) to (iv) described below. The increase in \( R_{k,h-c} \), compared to the bulk resistance, is only 7.2% for (i) the predicted resistances \([(A_k R_k)_b,pp\]
Figure 2.8: Variation of (a) thermal resistance, $R_{k,h-c}$, obtained from Eqs. (2.38) and (2.39), and (b) Seebeck coefficient of the TE element, $\alpha_S$, obtained from Eqs. (2.43) and (2.44), with respect to the cooling length $\delta$, and electron $(A_k R_k)_{b,ee}$ and phonon $(A_k R_k)_{b,pp}$ boundary resistances.
$= 9.2 \times 10^{-8} \text{K}/(\text{W/m}^2)$ and $(A_k R_k)_{h,ee} = 3.5 \times 10^{-7} \text{K}/(\text{W/m}^2)$] and cooling length $(\delta = 66 \text{ nm})$ of the Bi$_2$Te$_3$ TE element. An increase of these resistances by an order of magnitude (iv), increases $R_{k,h-c}$ in 72%. Note that $\delta$ can significantly affect $R_{k,h-c}$ only when $R_{k,b,pp}$ (iii) or $R_{k,b,ee}$ (ii) are individually increased, and $\delta \gtrsim 100 \text{ nm}$. The thermal resistance of the TE element is more sensitive to the increase of $R_{k,b,pp}$ (iii). In this case, $R_{k,b,pp}$ is greater than $R_{k,b,ee}$, and the total thermal boundary resistance [Eq. (2.13)] is dominated by the electron contribution. The shaded region in the graph marks the range in which the cooling length is varied as a function of the phonon speed of Bi$_2$Te$_3$ ($u_{p,te}$ estimated in Section 2.2.1 is equal to 3,058 m/s).

2.4.2 Seebeck Coefficient of Thermoelectric Element

The Seebeck coefficient of the TE element $i$ ($i = n, p$) is given by

$$\alpha_{S,i} = \frac{\Delta \varphi_{h-c}}{T_h - T_c}, \tag{2.40}$$

where $\Delta \varphi_{h-c}$ is the voltage drop between the cold and hot interfaces of the element due to the bulk and boundaries Seebeck effects, i.e.,

$$\Delta \varphi_{h-c} = \alpha_{S,b} [T_h - T_e |\frac{L_{te}}{2}] + \alpha_{S,bulk} [T_e |\frac{L_{te}}{2} - T_e |\frac{L_{te}}{2}] + \alpha_{S,b} [T_e |\frac{L_{te}}{2} - T_c]. \tag{2.41}$$

Therefore, Eq. (2.40) becomes

$$\alpha_{S,i} = \left[ \alpha_{S,b} + \frac{T_e |\frac{L_{te}}{2} - T_e |\frac{L_{te}}{2}}{T_h - T_c} (\alpha_{S,bulk} - \alpha_{S,b}) \right]_i, \tag{2.42}$$

or, after evaluating $T_e$ at the cold and hot interfaces [Eq. (2.19)],

$$\alpha_{S,i} = \left[ \alpha_{S,b} + \frac{R_e^* + \frac{R_e^* R_p^* (1+\gamma)^2}{2 R_k^*} + \gamma L_{te}^* \coth L_{te}^* - R_p^* \gamma}{R_e^* + \frac{R_e^* R_p^* (1+\gamma)^2}{2 R_k^*} + \frac{\gamma L_{te}^* \coth L_{te}^*}{(1+2R_k^*)^{-1}} + R_p^* \gamma^2} (\alpha_{S,bulk} - \alpha_{S,b}) \right]_i. \tag{2.43}$$
For $\delta \ll L_{tc}/2$,

$$\alpha_{S,i} = \left[ \alpha_{S,b} + \frac{1}{2k(A_kR_k)_b} + 1 \left( \alpha_{S,bulk} - \alpha_{S,b} \right) \right]_i. \tag{2.44}$$

Note that for $j_e$ equal to zero, $[T_e|_{L_{tc}/2} - T_e|_{-L_{tc}/2}]$ is less than or equal to $(T_h - T_c)$, as shown in Fig. 2.7. Therefore, it is implied from Eq. (2.42) that $|\alpha_{S,i}| \leq |\alpha_{S,bulk}|$. This defines the sign of the boundary Seebeck coefficients obtained from Eq. (2.25), i.e., $\alpha_{S,b}$ is equal to $-252 \mu V/K$ and $187 \mu V/K$ for the $p$- and $n$-type semiconductor/metal junctions, respectively.

The effect of the cooling length and the boundary resistances on the Seebeck coefficient, which is obtained from Eqs. (2.43) and (2.44), is shown in Fig. 2.8(b), for the same four cases discussed in Section 2.4.1 [also indicated in Fig. 2.8(a)]. The effective Seebeck coefficient is lower than the bulk Seebeck coefficient, indicating an undesirable reduction on the TE energy conversion of the device. For the predicted boundary resistances (i) $[(A_kR_k)_{b,pp} = 9.2 \times 10^{-8} \text{ K/(W/m}^2\text{)}$ and $(A_kR_k)_{b,ee} = 3.5 \times 10^{-7} \text{ K/(W/m}^2\text{)}$] and cooling length ($\delta = 66 \text{ nm}$) of the Bi$_2$Te$_3$ TE element, a reduction of $13\%$ is found in $\alpha_S$. This proportion is increased to $77\%$ when both electron and phonon boundary resistances are increased by an order of magnitude (iv). For $\delta < 10 \text{ nm}$, the Seebeck coefficient is more sensitive to the increase in $R_{k,b,pp}$ [$\alpha_S$ is reduced by $37\%$, (iii)], than to the increase in $R_{k,b,ee}$ [$\alpha_S$ is reduced by $15\%$, (ii)], as observed for the thermal resistance of the TE element. However, for larger cooling lengths, the increase in the individual resistances cause opposite effects. While $\alpha_S$ is drastically decreased in case (ii), it is increased in case (iii), where the electron contribution to the total boundary resistance is dominant.
From Figs. 2.8(a) and 2.8(b), it is observed that for $R_{k,b,ee} < R_{k,b,pp}$ (iii), a larger cooling length would result in higher TE efficiency [Eq. (2.34)], due to the increase in both the conduction resistance and the Seebeck coefficient of the TE elements. For $\delta$ equal to 66 nm, any increase in the boundary resistances results in opposite effects on $R_{k,h-c}$ and $\alpha_S$, i.e., the conduction resistance is increased and the Seebeck coefficient is decreased. In Chapter 3, where the results from the device optimization are discussed, the device cooling performance will be investigated as a function of these combined effects. A decrease in the performance with an increase in the boundary resistances is expected, since the efficiency of the TE element is more sensitive to the reduction of $\alpha_S$, than to the increase of $R_{k,h-c}$ [Eq. (2.34)].

2.5 Contact Resistances

The thermal $(A_k R_k)_c$ and electrical $(A_k R_e)_c$ contact resistances are a result of impurities, variations in the crystal size and orientation, defects, etc., at the interface, which are created in the fabrication process. When a semiconductor is grown on top of a metal (or vice versa) there is often no gap at the interface. But the different lattice parameters of the materials allow strain between the layers, which may cause the dislocation of atoms and the formation of defects. Variation in the stoichiometry of the TE compounds, as well as diffusion of the metal into the semiconductor, can also occur. These surface features (not considered in the thermal boundary resistances) affect the transport of heat and electricity through the interfaces. Their effects must be included in the model for prediction of the micro cooler performance, and here this
is done through the introduction of \( (A_k R_k)_c \) and \( (A_k R_e)_c \). Both resistances cause a reduction of the device performance. Thermal and electrical contact resistances are present at the metal/TE interfaces, and thermal contact resistances are present at the metal/electrical-insulator interfaces of the micro cooler. The effect of the thermal contact resistance is a discontinuity of temperature at the interface in the presence of a heat flow. An electrical contact resistance increases the total electrical resistance of the device, and generates Joule heating at the junctions. In practice, annealing (heat treatment) is used to reduce both the thermal and electrical contact resistances.

### 2.5.1 Thermal Contact Resistance

Lahmar et al. [19] performed an experimental investigation on the thermal contact resistance between a gold coating and ceramic substrates, and showed that thermal treatment significantly increases the adhesion and reduces the thermal contact resistance between these materials. The contact resistance decreased from \( 10^{-7} \) K/(W/m\(^2\)) to less than \( 10^{-8} \) K/(W/m\(^2\)) after heat treatment.

Orain et al. [20] have developed a measurement technique for determining the thermal conductivity of dielectric thin films. It was reported that for films thicker than 1 \( \mu \)m, the film thermal conductivity is equivalent to the value for the bulk material. For thinner films, a drop in the conductivity was observed, revealing the importance of the film/substrate contact (and boundary) resistances. The effect of the layering technique and the nature of the metal and substrate on the contact resistance was also presented. Contacts of Au/Al\(_2\)O\(_3\) and Au/SiO\(_2\) formed by evaporation had
resistances estimated on the order of 1 to $2 \times 10^{-7}$ K/(W/m$^2$). Based on these results [19, 20] a thermal contact resistance $(A_k R_k)_c$ of $10^{-7}$ K/(W/m$^2$) is assumed.

Note that, when interfacial thermal resistances are measured, the contributions of the contact and boundary resistances are difficult to distinguish. Therefore, the experimental results are for the dominant resistance, which we assume to be the contact resistance. If this is not the case, the predicted device performance will be lower than the expected (i.e., we have chosen the conservative side), as will be discussed in Section 3.

### 2.5.2 Electrical Contact Resistance

In macroscopic TE devices, electrical contact resistance between the semiconductor and metal electrodes has been reported to typically be between $10^{-8}$ and $10^{-9}$ Ω-m$^2$, when standard techniques for making a junction (such as soldering or hot pressing) are used [17, 21]. However, films with micron or submicron thickness are produced using thin-film growth techniques (e.g., evaporation or sputtering), and the resistances are expected to be much smaller. Jaeger [22] has reported electrical contact resistances for a variety of aluminum-silicon systems, which range from $10^{-5}$ to $10^{-10}$ Ω-m$^2$ as a function of annealing temperature.

If it is assumed that there is no gap at the contact zone, then the electrical contact resistance $(A_k R_e)_c$ is that between the two materials at the interface [for example, Bi(Sb)-Te/metal]. Choosing the highest electrical resistivity between these materials, which is $1.3 \times 10^{-5}$ Ω-m (for Bi$_2$Te$_3$, as presented in Table 2.1), and estimating the
length of the contact equal to 100 nm, results in \((A_kR_e)_c\) equal to \(1.3 \times 10^{-12} \ \Omega \cdot m^2\).

The relation between the thermal (electronic contribution) and electrical resistances: \((A_kR_k)_{b,ee}\) and \((A_kR_e)_b\) when used for boundary resistances, or \((A_kR_k)_{c,e}\) and \((A_kR_e)_c\) when used for contact resistances, is given by Eq. (2.7). As indicated in Section 2.3.1, for Bi\(_2\)Te\(_3\), the electron thermal conductivity \(k_e\) is 25% of the bulk thermal conductivity \(k\) [8]. Assuming the same contribution for the thermal contact resistances, we have \((A_kR_k)_{c,e} = 0.25 (A_kR_k)_c\). Then, from Eq. (2.7), for \(T = 300\) K, \((A_kR_e)_c\) is equal to \(1.8 \times 10^{-13} \ \Omega \cdot m^2\).

Under well-controlled laboratory conditions, measured electrical contact resistance between Si and Pt has been reported to be \(5 \times 10^{-12} \ \Omega \cdot m^2\), and between Si and Al, 1 to \(2 \times 10^{-11} \ \Omega \cdot m^2\) [23]. Si/metal is not a type of electrical contact found in the TE cooler, but this is considered a good indication that the electrical resistivity of the Bi(Sb)-Te/metal contact can be less than or equal to \(2 \times 10^{-11} \ \Omega \cdot m^2\), since the electrical resistivity of Si (\(10^{-4} \ \Omega \cdot m\)) is higher than that of the TE elements. Based on these results, \((A_kR_e)_c\) equal to \(2 \times 10^{-11} \ \Omega \cdot m^2\) is assumed.

### 2.6 Summary

In order to predict the performance of micro TE coolers, various aspects of the electron and phonon transport have been addressed in this study.

The phonon boundary resistances estimated by the DMM theory, using the measured and Debye DOS, are similar, and have the same order of magnitude as the experimental values reported in the literature (for interfaces between diamond and
several metals). For Bi$_2$Te$_3$/Cu and Sb$_2$Te$_3$/Cu interfaces, the phonon boundary resistances are found to be $9.2 \times 10^{-8}$ K/(W/m$^2$) and $8.0 \times 10^{-8}$ K/(W/m$^2$), respectively. The electron boundary resistance is estimated as a function of the thickness and height of the electronic potential barrier, which is associated with the difference in the band structures of the two materials at the junction. Assuming electron tunneling and using the Wiedemann-Franz law at the boundaries, the electron boundary resistance is found to be $3.5 \times 10^{-7}$ K/(W/m$^2$) and $9.3 \times 10^{-7}$ K/(W/m$^2$) at the n- and p-type semiconductor/metal interfaces, respectively. The cooling lengths of 66 nm (Bi$_2$Te$_3$) and 156 nm (Sb$_2$Te$_3$) are estimated using the available electron/hole mobility, phonon speed, and electron/hole concentration. The thermal and electrical contact resistances, estimated using the available experimental results in the literature, are $10^{-7}$ K/(W/m$^2$) and $2 \times 10^{-11}$ Ω-m$^2$, respectively.

Since the predicted values of cooling length $\delta$ are more than one order of magnitude smaller than the TE element thickness, the electron-phonon non-equilibrium does not significantly influence the thermal resistance and the Seebeck coefficient of the TE elements, as shown in Fig. 2.8.

The electron and phonon temperature distributions are obtained as a function of the predicted cooling lengths, electron and phonon boundary resistances, Peltier heating/cooling, and Joule heating.
Chapter 3

Device Geometry Optimization

The flows of heat and electricity in the micro thermoelectric (TE) cooler are modeled here, for device geometry optimization and performance prediction, based on the interfacial effects evaluated in Chapter 2. The energy conservation equations for the hot and cold junctions are solved using SOPHT (Solver for Principles of Heat Transfer) [50].

A device, with 4 $\mu$m thick TE elements, is required to reduce the temperature of a chemiresistance vapor sensor 10 K below ambient (load of 10 mW), using minimum power with a 3 V battery. The optimum number of pairs, column width, and operating condition of such device are estimated, and the effects of contact and boundary resistances on its performance are predicted.
3.1 Thermoelectric Model

The heat flow path in the micro thermoelectric TE cooler is shown in Fig. 1.1 and the various parameters used in the model are indicated in Fig. 3.1. Surface convection and radiation heat transfer between the heat sink and the vapor sensor are neglected as the conduction resistances of the films are much smaller than the surface radiation resistance and the air convection resistance (all in parallel). The Joule heating in the TE material is equally split between the top and bottom bounding surfaces. So, at the cold junction we have [50]

\[ Q_c + Q_{k,c} = (\dot{S}_{e,T})_c + (\dot{S}_{e,J})_{cc} + (\dot{S}_{e,P})_c, \]  

and at the hot junction,

\[ Q_h + Q_{k,h} = (\dot{S}_{e,T})_h + (\dot{S}_{e,J})_{hc} + (\dot{S}_{e,P})_h. \]  

\( Q_{k,h-c} \) is the heat transferred from the hot to the cold surface by conduction,

\[ Q_{k,h-c} = \frac{T_h - T_c}{R_{k,h-c}} = -Q_{k,c-h}. \]  

The thermal resistance \( R_{k,h-c} \) is given by

\[ \frac{1}{R_{k,h-c}} = N_{te} \left[ \frac{1}{(R_{k,h-c})_p} + \frac{1}{(R_{k,h-c})_n} \right], \]  

where \( N_{te} \) is the number of TE pairs, and \( (R_{k,h-c})_n \) and \( (R_{k,h-c})_p \) are given by Eq. (2.38) as a function of the boundary resistances and cooling lengths estimated in Sections 2.2 and 2.3, respectively.
Figure 3.1: Various parameters of the micro TE cooler. The total boundary resistance $R_{k,b}$ (described in Section 2.2.3) at the TE/metal interfaces, and the contact resistances $R_{k,c}$ and $R_{e,c}$ (described in Section 2.5) at the TE/metal and metal/electrical-insulator interfaces are indicated.

$Q_c$ and $Q_h$ are the heat transferred from the load (vapor sensor) to the cold surface and from the hot surface to the heat sink respectively:

$$Q_c = -\frac{T_l - T_i}{R_{k,c-l}} \quad \text{and} \quad Q_h = \frac{T_h - T_\infty}{R_{k,h-\infty}}.$$  \hspace{1cm} (3.5)

At the cold side,

$$\frac{1}{R_{k,c-l}} = N_{te} \frac{1}{R_{k,c1} + R_{k,cc} + R_{k,c2}},$$  \hspace{1cm} (3.6)

and at the hot side,

$$\frac{1}{R_{k,h-\infty}} = N_{te} \frac{1}{R_{k,c3} + R_{k,hc} + R_{k,c4} + R_{k,sink}}.$$  \hspace{1cm} (3.7)

Note that the thermal contact resistances between the TE elements and connectors are $(R_{k,c1})^{-1} = (R_{k,c3})^{-1} = 2A_k(k/L)_{contact}$ and between the connectors and the electrical
insulator films are \((R_{k,c2})^{-1} = A_{cc}(k/L)_{contact}\) and \((R_{k,c4})^{-1} = A_{hc}(k/L)_{contact}\), where \((k/L)_{contact}\) was assumed equal to \(10^7 \text{ (W/m}^2\)/K\, as discussed in Section 2.5.1. The thermal resistances of the connectors are \((R_{k,i})^{-1} = (A_{k/L})_i\), where \(i = cc, hc\), and the thermal resistance of the heat sink (including the electrical insulator film), which was assumed an infinite solid, is \((R_{k,sink})^{-1} = \ln(4a_{hc}/d_{hc})/(\pi k_{sink}a_{hc})\) [50].

\((\dot{S}_{e,P})_c\) is the Peltier cooling at the cold junction and \((\dot{S}_{e,P})_h\) is the Peltier heating at the hot junction, given by

\[
(\dot{S}_{e,P})_c = -N_{te}\alpha_S J_e T_c \quad \text{and} \quad (\dot{S}_{e,P})_h = N_{te}\alpha_S J_e T_h,
\]

where \(J_e\) is the electric current flowing along the TE elements and metal connectors, and \(\alpha_S = \alpha_{S,p} - \alpha_{S,n}\) is the sum of the Seebeck coefficients of the \(n\)– and \(p\)–type materials, which are given by Eq. (2.43).

\((\dot{S}_{e,J})_c\) and \((\dot{S}_{e,J})_h\) are the portions of the Joule heating (generated in the TE elements) assigned to the cold and hot junctions respectively. Note that the Joule heating generated at the metal/TE contacts is also considered, so that

\[
(\dot{S}_{e,J})_c = (\dot{S}_{e,J})_h = \frac{1}{2} J_e^2 R_{e,h-c} + \frac{1}{2} J_e^2 R_{e,c}.
\]

The electrical resistance of the TE elements is

\[
R_{e,h-c} = N_{te} \left( \frac{\rho_{e,p}L_{te}}{A_k} + \frac{\rho_{e,n}L_{te}}{A_k} \right).
\]

The contact electrical resistance is

\[
R_{e,c} = \frac{4N_{te}(A_k R_e)_c}{A_k},
\]

where \((A_k R_e)_c\) is taken to be equal to \(2 \times 10^{-11} \Omega\text{-m}^2\, as discussed in Section 2.5.2.
\((\dot{S}_{e,1})_{cc}\) and \((\dot{S}_{e,1})_{hc}\) are the Joule heating generated in the cold and hot connectors respectively, given by

\[
(\dot{S}_{e,1})_i = J_e^2 R_{e,i}, \quad \text{where } i = cc, hc ,
\]  

(3.12)

\[
R_{e,cc} = N_{te} \left( \frac{\rho_e a}{dL} \right)_{cc}, \quad \text{and } R_{e,hc} = N_{te} \left( \frac{\rho_e a}{dL} \right)_{hc} + R_{e,pads},
\]

(3.13)

Note that \(R_{e,pads}\) is the electrical resistance between the contact pads and the initial TE structures of the cooler device. Based on measurements of preliminary fabricated structures, we have estimated \(R_{e,pads}\) to be 50 \(\Omega\). Therefore, the total electrical resistance of the device can be expressed as

\[
R_e = R_{e,\text{h-c}} + R_{e,cc} + R_{e,hc} + R_{e,c}.
\]

(3.14)

and the total power consumed as

\[
P_e = R_e J_e^2 + (\dot{S}_{e,P})_h + (\dot{S}_{e,P})_c = \Delta \varphi J_e,
\]

(3.15)

where \(\Delta \varphi\) is the total voltage required.

The coefficient of performance is given by

\[
\text{COP} = -\frac{Q_c}{P_e},
\]

(3.16)

The calculations were performed with the thermal and electrical properties of the TE materials given in Table 2.1.

### 3.2 Results and Discussion

The current and voltage required as a function of the number of TE pairs are shown in Fig. 3.2, for \(T_i - T_\infty = 10\) K, \(Q_c = -10\) mW, \(L_{te} = 4\) \(\mu m\), and \(d_{te} = 7\),
Figure 3.2: Variation of required (a) voltage $\Delta \phi$, and (b) current $J_e$, with respect to number of TE pairs $N_{te}$. The shaded region indicates the range of operating conditions for $\Delta \phi$ equal to or smaller than 3 V.

9 and 11 $\mu$m ($A_k = d_{te}^2$). For $\Delta \varphi = 3$ V, the micro cooler will need 30 to 60 TE pairs, as indicated by the shaded area. For $d_{te} = 7$ $\mu$m, the device operating current is lower than 20 mA. Note that the values of $T_l - T_{\infty}$ (10 K), $Q_c$ (-10 mW) and $\Delta \varphi$ (3 V) are requirements of a specific application (cooling of a micro chemiresistor vapor sensor), as indicated in Fig. 1.1. The height of the columns $L_{te}$ (4 $\mu$m) is a result of preliminary fabrication studies. In Chapter 5, where the device fabrication
is reported, $L_{te}$ ranges from 4 to 5 μm. The minimum dimension of $d_{te}$ (7 μm) has been chosen due to the limitations on the minimum feature size (3 μm) obtained in our micro fabrication process.

The device power requirement and coefficient of performance, as a function of the number of TE pairs, are shown in Fig. 3.3. For $d_{te} = 7$ μm, the minimum power consumed $P_{e,\text{min}}$ is equal to 26 mW, which corresponds to a maximum coefficient of performance COP$_{\text{max}}$ of 0.38. Typical COP values of commercially available TE modules are between 0.4 and 0.7 (for $L_{te} > 1$ mm). For devices with shorter TE elements, the performance is expected to be lower [51], as predicted here. The decrease in the device performance is due to the increase of both conduction heat transfer (from the hot to the cold junction) and resistance to the flow of electrons (which causes the undesirable Joule heating) with the increase of $N_{te}$. The selection of the cross-sectional area of the TE elements (i.e., $d_{te}^2$) is a compromise between reducing the conduction (a small area is desirable) and reducing the Joule heating (a large area is desirable).

For a given load $Q_c$, as the number of pairs increases, the current needed to achieve the desirable $(T_\infty - T_i)$ is decreased, since each TE pair receives a smaller portion of the load. This has a positive effect on the reduction of the power required [Eq. (3.15)], which when combined with the negative effect of the electrical resistance, results in the minimum power and the maximum coefficient of performance observed in Fig. 3.3.

Having defined the number of pairs as a function of the voltage $[(N_{te} = 50 \text{ pairs is chosen from Fig. 3.2(a)}]$, and the side width of the columns for optimum performance
Figure 3.3: Variation of (a) power requirement $P_e$, and (b) coefficient of performance COP, with respect to number of TE pairs $N_{te}$. The shaded region indicates the range of operating conditions for $\Delta\varphi$ equal to or smaller than 3 V.

[(d_{te} = 7 \mu m is chosen from Fig. 3.3], the effect of the phonon boundary resistance $(A_k R_k)_{b,pp}$ and the electron boundary resistance $(A_k R_k)_{b,ee}$ on the reduction of the vapor sensor temperature is investigated. The results are shown in Fig. 3.4. The device cooling performance $(T_\infty - T_i)$ decreases with the increase of $(A_k R_k)_{b,ee}$, due to the reduction of the Seebeck coefficient, as presented in Fig. 2.8(b) [case (ii)], indicating that this effect is more pronounced on the performance than the increase
Figure 3.4: Variation of the load temperature drop, \( T_\infty - T_l \), with respect to phonon boundary resistance \( (A_k R_k)_{b,pp} \). The shaded region indicates the uncertainty in \( (A_k R_k)_{b,pp} \) as a function of the phonon speed of the TE element \( u_{p,te} \). The dashed lines indicate the operating condition, based on the values of electron and phonon boundary resistances estimated in Section 2.2., and thermal and electrical contact resistances estimated in Section 2.5.

of the thermal resistance shown in Fig. 2.8(a). As \( (A_k R_k)_{b,ee} \) decreases, \( (T_\infty - T_l) \) becomes less sensitive to the increase of \( (A_k R_k)_{b,pp} \). The effects of the electron thermal transport [which dominates when \( (A_k R_k)_{b,pp} \gg (A_k R_k)_{b,ee} \)] on the boundary and bulk Seebeck coefficients, need to be further investigated.

Note that the variation in \( (A_k R_k)_{b,ee} \) from \( 10^{-7} \) to \( 10^{-5} \) K/(W/m²) in Fig. 3.4, corresponds to a variation in the potential barrier height \( E_o \) from approximately \( 0.5E_o \) to \( 1.5E_o \). The shaded area indicates the uncertainty in \( (A_k R_k)_{b,pp} \) as a function of the phonon speed \( u_{p,te} \). The dashed line indicates the operating condition, based on the values of the electron and phonon boundary resistances estimated in Section 2.2.

From the region defined by the shaded area and the curves, a minimum value for the
device cooling performance \((T_\infty - T_l)\) of 7 K can be predicted.

In Fig. 3.5(a), the effect of the thermal contact resistance \((A_k R_k)_c\) on \((T_\infty - T_l)\) is presented. The value of \((A_k R_k)_c\) equal to \(10^{-7}\) K/(W/m\(^2\)), which was estimated in Section 2.5.1, is indicated by the dashed line. An increase in \((A_k R_k)_c\) by one order of magnitude would reduce the cooling performance to zero. Note that this result is comparable with the effect of the thermal boundary resistances shown in Fig. 3.4, for the two cases with higher electron boundary resistance. In the Fig. 3.5(b), it is shown that increasing the electrical contact resistance \((A_k R_e)_c\) by one order of magnitude \([\,(A_k R_e)_c = 2 \times 10^{-11}\, \Omega \cdot \text{m}^2\) was estimated in Section 2.5.2, and is indicated by the dashed line] would also reduce the cooling performance \((T_\infty - T_l)\) to zero. Both thermal and electrical contact resistances can be diminished by improving the fabrication process and by post-fabrication treatments.

In Fig. 3.6, the effect of the film thickness \(L_{te}\) on the device cooling performance is presented. The optimum values observed are due to the opposite effects of increasing the electrical (undesirable) and conduction (desirable) resistances of the TE elements. The model predictions are based on \(L_{te} = 4\, \mu\text{m}\) (indicated by the dashed line), which has been, so far, a fabrication limit. For \(d_{te} = 7\, \mu\text{m}\), which results in higher COP and lower power (as shown in Fig. 3.3), the maximum cooling performance can be reached when \(L_{te} = 10\, \mu\text{m}\). Based on this result, we will work towards increasing the TE film thickness.

In Fig. 3.7, the temperature distribution in the various films (Sb\(_2\)Te\(_3\) is the TE material) that form the TE cooler is shown for \(J_e = 11\, \text{mA}\), which is obtained for \(\Delta \varphi = 3\, \text{V}\), \(Q_c = -10\, \text{mW}\) and \(N_{te} = 50\, \text{pairs}\). The thicknesses of the films are not to
Figure 3.5: Variation of the load temperature drop, $T_\infty - T_l$, with respect to (a) thermal contact resistance $(A_kR_k)_c$ and (b) electrical contact resistance $(A_kR_e)_c$. The dashed lines indicate the operating condition, based on the value thermal and electrical contact resistances estimated in Section 2.5.
Figure 3.6: Variation of the load temperature drop, $T_\infty - T_l$, with respect to TE element length $L_{te}$. The dashed line indicates the value of $L_{te}$ (4 $\mu$m) used in the model for prediction of the micro TE cooler operating condition.

scale. The temperature drop observed at the cold and hot interfaces (load/connector and connector/TE element) is a result of the thermal contact resistance ($A_k R_k)_c$ (estimated in Section 2.5.1). On the cold side (amplified region I), $(T_l - T_c) = 0.25$ K, and on the hot side (amplified region II), $(T_h - T_\infty) = 1.22$ K. In the TE element, the distributions of phonon temperature $T_p$ and electron temperature $T_e$ are shown, and the phonon-electron non-equilibrium near the boundaries is evident. This non-equilibrium depends on the phonon and electron boundary resistances, Peltier cooling/heating and Joule heating, as discussed in Section 2.3.2. At the cold junction $(T_p - T_e)$ is 5.98 K, and at the hot junction $(T_e - T_p)$ is 6.86 K. These large temperature differences indicate the importance of the thermal and electrical transport at the metal/TE interfaces when thin TE films are considered (here, $L_{te} = 4 \mu$m). The length of the non-equilibrium region is about 500 nm, which is much greater than
Figure 3.7: Temperature distribution in the TE cooler. The film thickness (vertical axis) is not to scale.
δ = 156 nm obtained from Eq. (2.14). This indicates that a more accurate estimation of the cooling length is needed.

### 3.3 Summary

It is predicted (for Δϕ equal to 3 V) that a micro TE cooler with number of pairs $N_{te}$ of 50, $L_{te}$ of 4 µm, and $d_{te}$ of 7 µm, should deliver a load $Q_c$ of 10 mW with temperature of 11 K below the ambient. This device will require a power $P_e$ of 34 mW, an electrical current $J_e$ of 11 mA, and will have a coefficient of performance COP of 0.3.

The distance from the junctions (hot or cold) over which electrons and phonons reach equilibrium are found to be larger than the predicted cooling length δ. This is due to the Joule heating, not considered in the derivation of Eq. (2.14), and indicates that a more accurate model for predicting the cooling length is required. Also, from the temperature distribution shown in Fig. 2.14, a difference between the phonon and electron temperatures as high as 6.8 K is observed (and could be larger with an increase in current). The phonon-electron non-equilibrium at the metal/TE interface is evident, and indicates the importance of the thermal transport in the electron subsystem.

Although the phonon and electron boundary resistances reduce the conduction heat transfer along the columns, they also reduce the Peltier heating/cooling through the reduction of the Seebeck coefficient (as discussed in Chapter 2). The combined effect is the reduction of the device cooling capacity when the electron boundary
resistance is larger than $10^{-7} \text{K}/(\text{W/m}^2)$ (which includes the values estimated in Section 2.2.2), as shown in Fig. 3.4. As the electron boundary resistance decreases, the thermal transport becomes dominated by the electron subsystem at the interface, causing the increase of the cooling performance. Based on these results, we believe that a further investigation of the electron boundary resistance and boundary Seebeck coefficient is needed. In addition, the direct heat transfer between electron and phonon subsystems across the boundary (which was assumed negligible, for simplicity, in Section 2.2.3), should be further investigated.

Although the discontinuities of temperature at the interfaces caused by the thermal contact resistances are small (compared to the electron-phonon non-equilibrium), as shown in Fig. 3.7 in the enlarged regions I and II, this resistance is an important factor affecting the device performance, as verified in Fig. 3.5(a). The electrical contact resistance is equally important. Both contact resistances are affected by the fabrication process (as discussed in Section 2.5), which can generate a greater uncertainty than that related to the prediction of the electron and phonon boundary resistances. Thus, we consider the thermal and electrical contact resistances the most critical parameters affecting the device performance.

The length of the TE element $L_{te}$ (4 $\mu$m) has so far been limited by the film deposition method used. From Fig. 3.6, it is found that the aspect ratio $L_{te}/d_{te}$ of the columns should be around 1.5 in order for the micro cooler to provide optimal cooling. As $d_{te}$ is constrained by the fabrication process to be equal to or larger than 7 $\mu$m, the film thickness should then be increased.
Chapter 4

Thermoelectric Films

In Chapter 2, predictions of device geometry and performance were obtained from the thermoelectric (TE) model as a function of optimum TE properties reported in the literature [2]. However, in the device fabrication, the designed, high performance \( n \)- and \( p \)-type elements must first be realized.

In this Chapter, the fabrication and characterization of films in the Bi-Te and Sb-Te system are reported. Seeking optimum power factors, the deposition conditions for the co-evaporated films, namely the material and crystal structure of the substrate, the evaporation rate of the individual species, and the substrate temperature, were varied. The Seebeck coefficient, electrical resistivity, carrier concentration, chemical composition, grain size, and crystal orientation of the films, were measured and analyzed. In Chapter 5, the TE properties reported here are used to predict the performance of the fabricated and proposed future-generation devices.
4.1 Crystal Structure

The crystal structures of bismuth telluride (Bi$_2$Te$_3$) and antimony telluride (Sb$_2$Te$_3$) are rhombohedral with 5 atoms in the primitive unit cell [33, 43, 52], as shown for Bi$_2$Te$_3$ in Fig. 4.1(a). There are tellurium atoms at the vertices of the rhombohedral unit cell (total of 1 tellurium atom) and the remaining atoms (2 tellurium and 2 bismuth atoms) are on the diagonal of the cell through the center. However, it is easier to represent this structure by a hexagonal cell, as shown in Fig. 4.1(b). Quintuple layers of atoms are stacked along the $c$-axis. These atomic layers occur in the sequence Te$_1$-Bi-Te$_2$-Bi-Te$_1$, where Te$_1$ and Te$_2$ are the two types of tellurium atoms in the crystal. Arguments based on the bonding in the crystal distinguish the types of tellurium atoms Te$_1$ and Te$_2$. Their bond lengths are different [53]. The bonding between the atoms within a quintuple layer is of ionic-covalent type, while the interaction between the two neighboring Te$_1$ layers (larger bond length) is of van der Waals type.

The lattice parameters of the hexagonal cell ($a$ and $c$) are presented in Table 2.1 for Bi$_2$Te$_3$ and Sb$_2$Te$_3$. The dimensions of the rhombohedral cell ($a_R$ and $\gamma_R$) can be determined from $a$ and $c$ by

$$a_R = \frac{1}{3} \left(3a^2 + c^2\right)^{1/2}$$ and $$\sin \frac{\gamma_R}{2} = \frac{3}{2 \left[3 + (c/a)^2\right]^{1/2}}.$$ (4.1)

Note that the structures of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are similar. The radii of the Te, Sb and Bi atoms are listed in Table 4.1.
4.2 Deposition

The vacuum chamber used for the TE film deposition is shown in Fig. 4.2(a). The substrate support (for a 4 in wafer) with heater and rotation mechanism are mounted on an 8 in flange [Fig. 4.2(b)], and the dual evaporation source assembly for 17 cc boats (also adjustable for 4 cc boats) is mounted on a 10 in flange with electrical feedthroughs [Fig. 4.2(c)]. These components were specially designed and fabricated for the co-evaporation of the Bi-Te and Sb-Te films. The schematics in Figs. 4.2(b) and (c) are also shown in Fig. 4.3, where their relative position with respect to the
Table 4.1: Atomic, covalent and van der Waals radii (Å) of Te, Sb and Bi atoms, [54].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic</th>
<th>Covalent</th>
<th>Van der Waals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>1.82</td>
<td>1.41</td>
<td>2.20</td>
</tr>
<tr>
<td>Bi</td>
<td>1.55</td>
<td>1.52</td>
<td>2.40</td>
</tr>
<tr>
<td>Te</td>
<td>1.43</td>
<td>1.37</td>
<td>2.20</td>
</tr>
</tbody>
</table>

substrate shutter and thickness monitors inside the vacuum chamber is indicated.

Each of the elements (Bi, Sb and Te shots are 99.999% pure) of the desired compound (from the Bi-Te or Sb-Te systems) is placed in the 17 cc molybdenum boat, which is connected to an independent power supply (controlled manually). The flux from each source is monitored with separate quartz crystal sensors. The substrates are placed at a distance of 46 cm above the sources, and rotate at a controlled speed. A resistive heater (placed above the substrate) can maintain a constant substrate temperature of up to 300°C, which is measured by a type K thermocouple located at a distance of 5 mm from the substrate edge. The calibration of this thermocouple was established by comparing its temperature with a second thermocouple attached directly at the back surface of the substrate, which was stationary. An additional film thickness monitor is used to measure the overall thickness of the deposited compound.

Vapor pressures and melting point of the elements are listed in Table 4.2. Note that Bi is the only component that will melt before evaporation, which makes its deposition rate easier to control, compared with Sb and Te. The pressure during deposition varied from $1 \times 10^{-6}$ to $4 \times 10^{-6}$ torr. The Bi and Sb deposition rates varied from $1 \pm 0.1$ to $2.5 \pm 0.1$ Å/s, while the Te rate varied from $2.5 \pm 0.5$ to
Figure 4.2: Vacuum chamber used for deposition of the TE films (a). Components specially designed and fabricated for co-evaporation of thick Bi-Te and Sb-Te films on 4 in wafers, (b) and (c).
4.5 ± 0.5 Å/s. All substrates were cleaned prior to the deposition with acetone and isopropanol, and dried with N₂.

4.3 Characterization

4.3.1 Crystal Structure and Composition

The microstructure of the films (grain size and orientation) was examined using a high resolution scanning electron microscope (SEM), which is combined with a focussed ion beam workstation. The latter was used for in-situ preparation and analysis of sample cross-sections. In order to prevent the damage to the surface grains by the ion beam, a platinum patch (1 µm thick) was deposited on top of each
Table 4.2: Temperature $T$ ($^\circ$C) for vapor pressure (torr) and melting point of Te, Sb and Bi [55].

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting Point</th>
<th>$10^{-8}$ torr</th>
<th>$10^{-6}$ torr</th>
<th>$10^{-4}$ torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>631</td>
<td>279</td>
<td>345</td>
<td>425</td>
</tr>
<tr>
<td>Bi</td>
<td>271</td>
<td>347</td>
<td>409</td>
<td>517</td>
</tr>
<tr>
<td>Te</td>
<td>450</td>
<td>155</td>
<td>209</td>
<td>280</td>
</tr>
</tbody>
</table>

TE film, prior to the sectioning.

The orientation of the crystals in the films was determined from X-ray diffraction (XRD) analyses. The patterns were obtained using a Scintag Powder X-ray Diffractometer.

The relative concentration of the elements was measured, with an accuracy of $\pm 2\%$, by an electron microprobe analyzer, and averaged over ten distinct locations for each sample.

4.3.2 Thermoelectric Properties

The Seebeck coefficient $\alpha_S$ was measured at room temperature, under vacuum. In each case, data were collected from two films deposited at the same time on identical substrates, which were mounted as shown in Fig. 4.4. One end of the film (10-20 mm long and 2-4 mm wide) was thermally connected to a heat sink and the other end to a heater. The temperatures of the hot and cold sides ($T_h$ and $T_c$, respectively) were measured with fine copper-constantan thermocouples. The Cu leads of the thermocouples were also used to measure the potential difference, $\Delta\varphi$, across the
Figure 4.4: Probe used for the Seebeck coefficient and electrical resistivity measurements. Two substrates, with the same TE film deposited on them, are held by the heat sink (cold side). The heater is attached to the opposite edge of the substrates (hot side). The electrical resistivity measurements are performed on substrate 2, while Seebeck coefficient are obtained from both substrates.

The Seebeck coefficient was determined by

$$\alpha_s = \frac{\Delta \varphi}{T_h - T_c},$$  \hspace{1cm} (4.2)

and the results were corrected for the thermopower of the Cu leads.

The electrical resistivity was obtained using the standard four probe method, also at room temperature, and under vacuum. It is given by

$$\rho_e = \frac{R_e A_t}{L},$$  \hspace{1cm} (4.3)

where $L$ is the film length (distance between the fine copper wires used for $\Delta \varphi$ measurement when an electrical current $J_e$ is applied), $A_t (= w L_{te})$ is the film cross section area, and $R_e (= \Delta \varphi / J_e)$ is the electrical resistance. The film thickness, $L_{te}$, was obtained from four different locations on the sample, with an accuracy of $\pm 5\%$. 

\hspace{1cm} 70
using a surface profiler.

Hall effect measurements were performed in a cryostat equipped with a superconducting (5 T) magnet. A magnetic field $B$ and current $J_e$ were applied, and $R_e$ (or $\Delta \varphi$) was measured. Data were taken in both magnetic field directions to eliminate effects due to any probe misalignment. The Hall coefficient is given by

$$R_H = R_e \frac{L_{te}}{B},$$

(4.4)

and from that, the carrier concentration $n_c$ and mobility $\mu$ were calculated using

$$n_c = \frac{1}{R_H e_c} \quad \text{and} \quad \mu = \frac{R_H}{\rho_e},$$

(4.5)

where $e_c$ is the electron charge.

### 4.3.3 Error Analysis

The uncertainty $\Delta F$ of a property $F$ was calculated using the relation

$$\Delta F(x_1, x_2, ...) = \left[ \sum_{i=1}^{n} \left( \frac{\partial F}{\partial x} \Delta x_i \right)^2 \right]^{1/2}$$

(4.6)

where

$$F(x_1, x_2, ...) = \alpha_S(\Delta \varphi, T_h, T_c)$$

$$= \rho_e(R_e, w, L_{te}, L)$$

$$= \frac{\alpha_S^2}{\rho_e(\alpha_S, \rho_e)}$$

$$= R_H(R_e, L_{te})$$

$$= n_c(R_H)$$

$$= \mu(R_H, \rho_e).$$
Table 4.3: Uncertainties of measured and calculated properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_S$</td>
<td>± 5%</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>± 12%</td>
</tr>
<tr>
<td>$\alpha^2_S/\rho_e$</td>
<td>± 15%</td>
</tr>
<tr>
<td>$R_H$</td>
<td>± 15%</td>
</tr>
<tr>
<td>$n_e$</td>
<td>± 15%</td>
</tr>
<tr>
<td>$\mu$</td>
<td>± 20%</td>
</tr>
</tbody>
</table>

The results are shown in Table 4.3.

For $\alpha_S$, which was obtained from two samples of the same film that were mounted side-by-side in the probe [Fig. 4.4], variations in repeatability were also taken into account. The Seebeck coefficient was measured on each sample after heating and waiting 20 to 30 minutes for steady-state, and also after cooling. So, data were collected twice for each sample, totaling four measurements for each film. The difference between the maximum and minimum value of these four measurements was calculated in terms of a fraction of the averaged $\alpha_S$. This was compared with the result from Eq. (4.6), and the larger value was taken as the uncertainty in $\alpha_S$.

The accuracy of the $\rho_e$ was limited by the uncertainties in $A_t$ and $L$, while for $R_H$, the limit was found by drifts in $R_e$ (or $\Delta\varphi$). Measurements of $R_H$ were not completed when drifts were above 10%, which limited the data collection to only few points in the Bi-Te system. The electrical contacts, which were made with silver paint, were suspected to be causing this problem. Metallic (Cu or Au) contacts can be patterned prior to or after the TE film deposition, for future measurements.
4.4 Optimum Power Factor: Bi-Te System

4.4.1 Effect of Substrate Temperature on Thermoelectric Properties of Bi-Te Films

One micron thick Bi-Te films with Te concentration around 60% were deposited on glass substrate at temperatures varying from 130 to 280°C. In Fig. 4.5(a), the measured TE properties are shown for the various films, together with the TE properties reported by [2] (listed in Fig. 1.3 and Table 2.1), which were used for the device performance predictions reported in Chapter 3. The Seebeck coefficient is negative indicating that the films are n-type, and its absolute value increases with $T_{sub}$ up to 260°C, where it reaches a plateau. Also, at this temperature $\rho_e$ has a minimum, and the power factor, $\alpha^2_s/\rho_e$, has its optimum value. At higher temperatures, because Te can re-evaporate from the substrate leaving point defects (e.g., a vacancy or an antisite defect) in the crystal structure, $\rho_e$, which is sensitive to these defects, increases sharply.

The lower values of $\alpha_S$ at $T_{sub} < 260^\circ$C can be an indication that other Bi-Te phases co-exist with Bi$_2$Te$_3$. For pure Bi (although it is unlikely to find unreacted Bi in the films), $\alpha_S$ is -50 and -100 $\mu$V/K for directions parallel and perpendicular to the trigonal axis, respectively [56]. The film composition was measured at ten distinct locations on the sample, as previously mentioned, and for an analytical volume of about 1 to 2 $\mu$m$^3$, the at% Te varied from 59.3 to 60.1, for the film deposited at 130°C. Although these values might indicate that the compound is Bi$_2$Te$_3$, they could
Figure 4.5: Effect of $T_{\text{sub}}$ on the TE properties (a), and on the XRD patterns of Bi-Te films deposited on glass, (c) to (i), where the at% Te varied from 59.7 to 60.9. In (b), the pattern of the reference powdered Bi$_2$Te$_3$ single crystal is shown.
Table 4.4: Measured Hall coefficient $R_H$, carrier concentration $n_c$ and mobility $\mu$ of Bi-Te films, at room temperature.

<table>
<thead>
<tr>
<th>$T_{sub}$, °C</th>
<th>at% Te</th>
<th>$R_H$, $10^{-6}$ m$^3$/C</th>
<th>$n_c$, $10^{25}$ m$^{-3}$</th>
<th>$\mu$, $10^{-4}$ m$^2$/V-s</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>60</td>
<td>-0.063</td>
<td>9.9</td>
<td>2</td>
</tr>
<tr>
<td>260</td>
<td>60</td>
<td>-0.355</td>
<td>1.8</td>
<td>125</td>
</tr>
<tr>
<td>280</td>
<td>60</td>
<td>-0.270</td>
<td>2.3</td>
<td>52</td>
</tr>
<tr>
<td>260</td>
<td>59.7</td>
<td>-0.017</td>
<td>37</td>
<td>2.9</td>
</tr>
<tr>
<td>260</td>
<td>57.6</td>
<td>-0.006</td>
<td>96</td>
<td>9.6</td>
</tr>
<tr>
<td>260</td>
<td>54.0</td>
<td>-0.003</td>
<td>196</td>
<td>10.6</td>
</tr>
</tbody>
</table>

be an average of various phases, since the area analyzed with the microprobe covers hundreds of grains for the low-temperature film, as can be inferred from Fig. 4.6(a).

The surface SEM micrograph of the film co-evaporated at 260°C, with at% Te of 60, is shown in Fig. 4.6(b), where grains as large as 0.5 µm are evident. The dashed lines at the cross-sectional view are highlighting the grain boundaries. Voids are observed in the cross-section of the film deposited at 130°C [Fig. 4.6(a)], and the grain boundaries, although appearing to be closer to each other than in the higher $T_{sub}$ films, are not well defined.

In Table 4.4, $R_H$, $n_c$ and $\mu$ are presented for films deposited at $T_{sub}$ of 250, 260 and 280°C. Among the films with 60% of Te, the one deposited at 260°C, which has the highest power factor, also has the highest mobility (presumably because it is very close to a true Bi$_2$Te$_3$ stoichiometry and thus has a minimal number of defects). High mobilities are expected for crystal structures with large grain sizes since they tend to reduce boundary scattering of carriers.
Figure 4.6: SEM micrograph showing top and cross-section of co-evaporated Bi$_2$Te$_3$ films deposited at (a) 130°C and (b) 260°C, both with at%Te of 60, and (c) 260°C with at%Te of 54. The bar on the bottom-right of each SEM micrograph corresponds to a length of 500 nm (on scale). In (b) and (c), the dashed lines at the cross-section views are highlighting grain boundaries.
The diffraction pattern of powdered Bi$_2$Te$_3$ single crystal and of the Bi-Te films are shown in Figs. 4.5(b), and (c) to (i), respectively. The position of the peaks agrees with the associated entries in the Powder Diffraction File for Bi$_2$Te$_3$ [57], and the corresponding reflection planes ($hkl$) are labeled.

The three highest relative intensities, $I/I_o$, reported in [57], correspond to the planes (015) ($I/I_o = 100$), (1.0.10) ($I/I_o = 25$) and (110) ($I/I_o = 25$). For other peaks $I/I_o \leq 8$. Note in Fig. 4.5 that these three strongest peaks are seen in the spectra of the reference powdered Bi$_2$Te$_3$ (b) and of the films deposited at 130 (c), 180 (d) and 230°C (e) (the relative intensities are different). These reflection planes indicate no preferential crystallite orientation of samples (b) to (e), which was expected for (b), since the powdered grains are randomly oriented. We tried to match the X-ray spectra of other possible phases (apart for Bi$_2$Te$_3$) within the Bi-Te system but found no convincing match.

Note that the intensities of the diffraction peaks corresponding to (00$l$) planes (c-axis preferentially oriented, perpendicular to the substrate surface) become significant at $T_{sub}$ of 230°C [Fig. 4.5(e), peaks corresponding to (006) and (0.0.15) planes], and increase at higher temperatures. They are dominant in the film deposited at 260°C [Fig. 4.5(g)], which had the highest power factor [Fig. 4.5(a)].

In Fig. 4.7, the diffraction patterns of the Bi-Te films deposited at 130 and 260°C are enlarged to show the effect of $T_{sub}$ on the line width of the peaks. The smaller line widths observed in Fig. 4.7(b), when compared with (a), indicate an increase in grain size with the increase of $T_{sub}$, and suggest higher crystalline quality. This result is in agreement with Figs. 4.6(a) and (b). Such physical characteristic of the films
4.4.2 Effect of Film Composition on Thermoelectric Properties of Bi-Te Films

Bi-Te films were deposited on glass substrates at various stoichiometries for $T_{sub}$ of 260 and 130°C. The effect of film composition on the TE properties can be seen, at these temperatures, in Figs. 4.8(a) and 4.9(a). The optimum power factors, given in Table 4.5 for both $T_{sub}$, were found for at% Te of approximately 60. Note that in Fig. 4.8(a), films with at% Te > 60 could not be obtained due to the re-evaporation of Te from the substrate.

In the XRD patterns, also presented in Figs. 4.8 and 4.9, no effect of composition on the predominant orientation of the films (c-axis for films deposited at $T_{sub}$ of 260°C, and random for films deposited at $T_{sub}$ of 130°C) was observed.
Table 4.5: Measured optimum TE properties of co-evaporated Bi-Te films deposited at 260°C and 130°C.

<table>
<thead>
<tr>
<th>$T_{\text{sub}}$, °C</th>
<th>$\rho_e$, $\mu\Omega$-m</th>
<th>$\alpha_S$, $\mu$V/K</th>
<th>$\alpha_S^2/\rho_e$, mW/K²-m</th>
<th>at% Te</th>
<th>$L_{ie}$, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>28.3</td>
<td>-228</td>
<td>1.84</td>
<td>60.11</td>
<td>1.0</td>
</tr>
<tr>
<td>130</td>
<td>16.9</td>
<td>-81</td>
<td>0.39</td>
<td>59.99</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Hall coefficients for films deposited at 260°C, given in Table 4.4, indicate a reduction of the carrier concentration $n_c$ with the increase in the Te content. The mobility $\mu$ has a maximum at at% Te of 60. Note that, although $\mu$ is about 10× lower for the film with at% Te of 54, its resistivity $\rho_e$ is also lower compared with the film with 60% of Te, as show in Fig. 4.8(a), due to its higher $n_c$ ($\rho_e$ is inversely proportional to the product between $\mu$ and $n_c$).

The top surface of the films with at% Te of 60 and 54 (both deposited at 260°C) are shown in Figs. 4.6(b) and (c), respectively. The film with larger grain size is richer in Te and has higher carrier mobility. The cross-sections are also presented, where this difference in grain size is clearly indicated by the grain boundaries highlighted with dashed lines.

### 4.4.3 Effect of Substrate Material and Crystal Structure on Thermoelectric Properties of Bi-Te Films

Bi-Te films were co-evaporated on glass (Type II Soda Lime), Al$_2$O$_3$ (0001), MgO (100), mica, and Pt substrates at $T_{\text{sub}}$ of 260°C. The effect of film composition on the TE properties is shown in Figs. 4.10(a) to (c) for all substrates, with the exception...
Figure 4.8: Effect of Te composition on the TE properties (a), and on the XRD patterns of Bi-Te films deposited on glass at \( T_{sub} \) of 260°C, (c) to (i). In (b), the pattern of the reference powdered Bi\(_2\)Te\(_3\) single crystal is shown.
Figure 4.9: Effect of Te composition on the TE properties (a), and on the XRD pattern of Bi-Te films deposited on glass at $T_{sub}$ of 130°C, (c) to (i). In (b), the pattern of the reference powdered Bi$_2$Te$_3$ single crystal is shown.
Figure 4.10: Thermoelectric properties of Bi-Te films deposited at 260°C on glass, mica, MgO and Al₂O₃ substrates. (Lines are used only to guide the eye.)
Table 4.6: Reflection planes of Bi-Te films deposited on various substrates at $T_{\text{sub}}$ of 260°C and for at% Te around 60.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>(00l) + (015)</td>
</tr>
<tr>
<td>Pt</td>
<td>(00l) + (015)</td>
</tr>
<tr>
<td>Mica</td>
<td>(00l) + (015) + (0.2.10)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>(00l) + (015) + (205)</td>
</tr>
<tr>
<td>MgO</td>
<td>(00l) + (015) + (205) + (1.1.15)</td>
</tr>
</tbody>
</table>

of Pt (substrates with high electrical resistivity are required to allow for reliable measurements of TE properties). At a given at% Te, the variation of film composition among the substrates was found to be within ±0.5%. Although the highest power factor was obtained for a film grown on MgO (at% Te of 60.1), this is not the case for other Te compositions. Therefore, to within an uncertainty of 15%, no significant effect of the substrate (material and crystal structure) on the TE film properties is evident. This is an indication that films grown on Pt are likely to present similar performance as the ones reported here.

In the XRD patterns, the position of the peaks agrees with the associated entries in the Powder Diffraction File for Bi$_2$Te$_3$ [57], for all substrates (including Pt), and no significant effect of at% Te on the crystal structure of the films was observed. The reflection planes verified in the films with at% Te around 60, are listed in Table 4.6, where $l$ is equal to 3, 6, 15, 18 and 21. The peaks from (00$l$) planes presented higher intensities. The c-axis is the predominant orientation for the Bi$_2$Te$_3$ crystal structures grown on glass and Pt, while crystals grown on MgO are more randomly oriented.
The XRD patterns of the Bi-Te film deposited on glass and Pt (at 260°C and with at% Te of 60.11), are shown in Figs. 4.11(a) and (b), respectively. In (c) is the spectra of the Pt substrate, which should be subtracted from (b), in order to properly compare (a) and (b). Note that the same (00\(l\)) peaks are detected in both films, and the relative intensities of most of them are similar.

### 4.4.4 Summary

The highest power factors were obtained for Bi\(_2\)Te\(_3\) (at% Te around 60) films deposited at \(T_{\text{sub}}\) of 260°C (2.11 and 1.84 mW/K\(^2\)-m for deposition on MgO and glass, respectively). Comparing this result with the ones given in Fig. 1.3, it is verified that the optimum \(n\)-type film reported by Zou et al. [2], which was also deposited by co-evaporation at 260°C, presented the same value of \(\alpha_S\) listed in Table 4.5. However, \(\alpha_S^2/\rho_e\) is about 2 times lower than in [2], due to differences in \(\rho_e\). The \(n\)-type film reported by Böttner, [25], yielded lower performance.

The crystalline quality of the films reported here, deduced from the line widths of the XRD patterns and from the SEM micrographs, was affected by \(T_{\text{sub}}\). No effect of composition on crystal orientation was seen.

Based on the limited number of tests performed, no significant effect of the substrate material and crystal structure on the TE properties was observed, within an uncertainty of \(\pm 15\%\). This is an indication that Bi-Te films deposited on Pt are likely to have the same performance as the films deposited on glass, Al\(_2\)O\(_3\), MgO or mica. The XRD pattern indicates that Bi\(_2\)Te\(_3\) forms on Pt (at \(T_{\text{sub}}\) of 260°C), which
Figure 4.11: X-ray diffraction patterns of a Bi-Te film deposited on glass (a) and Pt (b) (at 260°C and with at% Te of 60.11), and of the Pt substrate (c).
supports its use in the cold connector of the micro TE cooler. Platinum is the metal that interfaces with the TE elements, as shown in Fig. 5.6(c).

## 4.5 Optimum Power Factor: Sb-Te System

### 4.5.1 Effect of Substrate Temperature on Thermoelectric Properties of Sb-Te Films

The measured Seebeck coefficient and electrical resistivity, and the calculated power factor of Sb-Te films deposited on glass, are shown in Fig. 4.12(a) as a function of $T_{\text{sub}}$. The TE properties given in [2] (also listed in Fig. 1.3 and Table 2.1), which were used in the TE model for predictions of device performance reported in Chapter 3, are also indicated. The tellurium concentration varies from 60.0% to 61.1% among the films, which are approximately 1 $\mu$m thick. The Seebeck coefficient is positive indicating that the films are $p$-type. Note that the maximum $\alpha_S$ and the minimum $\rho_e$ do not occur at the same temperature, as observed for the Bi-Te system in Fig. 4.5(a). The optimum power factor is found at $T_{\text{sub}}$ around 270°C.

For $T_{\text{sub}} < 270^\circ$C, the difference between the maximum and minimum values of $\alpha_S$ is about 15% of their average [Fig. 4.12(a)], while in the Bi-Te system this value increases to 80% [Fig. 4.5(a)]. This lower sensitivity of $\alpha_S$ to $T_{\text{sub}}$ in the Sb-Te system can be due to the higher background carrier density of this system compared with Bi-Te. A weak bond between Sb and Te layers exists, and usually involves antisite defects (the occurrence of Sb atoms occupying Te lattice positions). Due to such
Figure 4.12: Effect of $T_{\text{sub}}$ on the TE properties (a), and on the XRD pattern of Sb-Te films deposited on glass, (c) to (j), where the at% Te varied from 60.0 to 61.1. In (b), the pattern of the reference powdered Sb$_2$Te$_3$ single crystal is shown.
native defects, Sb$_2$Te$_3$ always shows a $p$-type conductivity with the hole concentration on the order of $10^{26}$ m$^{-3}$ (almost one order of magnitude higher than Bi$_2$Te$_3$, which is presented in Table 4.4 for at% Te of 60) [33, 58]. On the other hand, the sensitivity of $\rho_e$ to $T_{sub}$ is comparable in both systems. A possible explanation for this is given in the following paragraph.

A second type of carrier can exist (or can be increased in number), such as minority carriers (electrons, in this case), due to the higher carrier concentration of Sb-Te. They both (holes and electrons) will contribute to the electric current density ($j_e$). These contributions may be expressed in terms of partial electrical resistivities and partial Seebeck coefficients of each carrier (subscripts $e$ and $h$), as [59]

$$j_{e,i} = \frac{1}{\rho_{e,i}} \left( e_e - \alpha_{S,i} \frac{\partial T}{\partial x} \right), \quad (4.7)$$

where $i = e, h$ and $e_e$ is the electric field. If $\partial T/\partial x$ is zero, then

$$j_e = j_{e,e} + j_{e,h} = (\rho_{e,e}^{-1} + \rho_{e,h}^{-1}) e_e, \quad (4.8)$$

and

$$\rho_e^{-1} = \rho_{e,e}^{-1} + \rho_{e,h}^{-1} = e_c [(n_c \mu)_e + (n_c \mu)_h]. \quad (4.9)$$

If $j_{e,i}$ is zero,

$$\alpha_S = \frac{e_e}{\partial T/\partial x} = \frac{(\alpha_S \rho_e^{-1})_e + (\alpha_S \rho_e^{-1})_h}{\rho_e^{-1}}. \quad (4.10)$$

Note that in Eq. (4.9) the contribution of both carriers is additive towards $\rho_e$, while $\alpha_S$, in Eq. (4.10), depends on the relative amount of each carrier ($\alpha_S$ is positive for holes and negative for electrons). Therefore, the extra carriers in the Sb-Te system
may affect the sensitivity of $\alpha_S$ to $T_{sub}$, to a greater extent than they affect $\rho_e$, as demonstrated here when this system is compared with the Bi-Te.

The lower values of $\rho_e$ shown in Fig. 4.12(a), when compared with the results from Fig. 4.5(a), can also be attributed to the higher background carrier density (or higher $n_c$) of Sb-Te films. As defined in Eq. (4.9), $\rho_e$ is inversely proportional to $n_c$.

The surface SEM micrographs of the film co-evaporated at 170 and 270°C are shown in Figs. 4.13(a) and (b), respectively, with magnifications of 60000× and 15000× (where the latter indicates homogeneity in grain structure). The grain size increases with $T_{sub}$, and an increase in carrier mobility $\mu$ is expected as discussed in Section 4.4.1. This is in agreement with the decrease of $\rho_e$ as $T_{sub}$ increases, observed in Fig. 4.12(a), since $\rho_e$ is inversely proportional to $\mu$ [Eq. (4.9)]. At high $T_{sub}$, re-evaporation of Te from the substrate occurs (which creates point defects in the crystal structure), causing the increase of $\rho_e$.

The diffraction pattern of powdered Sb$_2$Te$_3$ single crystal and the Sb-Te films deposited at $T_{sub}$ varying from 170 to 270°C, are also shown in Figs. 4.12(b), and (c) to (j), respectively. The position of the peaks agrees with the associated entries in the Powder Diffraction File for Sb$_2$Te$_3$ [57], and the corresponding reflection planes $(hkl)$ are labeled.

The three highest relative intensities, $I/I_o$, reported in [57], correspond to the planes (015) ($I/I_o = 100$), (1.0.10) ($I/I_o = 35$) and (110) ($I/I_o = 25$). For other peaks $I/I_o \leq 10$. Note that in Fig. 4.12, these three strongest peaks are seen in the spectra of the reference powdered Sb$_2$Te$_3$ (b) and the two highest peaks are dominant in the film deposited at 170°C (c) (the relative intensities are different), as well as in
Figure 4.13: SEM micrograph showing top views of co-evaporated Sb-Te films deposited at (a) 170 and (b) 270°C, both with at%Te around 60, and (c) 270°C with at%Te about 50. Each micrograph on the right shows a larger area of the same film, indicating uniformity of the grain structure.
Figure 4.14: X-ray diffraction patterns of Sb-Te films deposited at 170 (a) and 270°C (b), showing the effect of $T_{\text{sub}}$ on the line widths.

the other films up to $T_{\text{sub}}$ of 260°C. These reflection planes indicate no preferential crystallite orientation of samples (b) to (g), which was expected for (b), since the powdered grains are randomly oriented. No convincing match with X-ray spectra of other possible phases (apart from Sb$_2$Te$_3$) within the Sb-Te system was found.

In the XRD spectra for the film deposited at 270°C [Fig. 4.12(h)], and at higher substrate temperatures, the intensity of the diffraction peaks that correspond to (00$l$) planes increased relative to the other peaks identified in the films deposited at lower $T_{\text{sub}}$. It is evident that as $T_{\text{sub}}$ increases, the Sb-Te crystal structures become more c-axis oriented.

In Fig. 4.14, the XRD spectra of the films deposited at 170 and 270°C are enlarged (for $2\theta$ varying from 37 to 47°) in order to show the difference in line widths between peaks of the two films. As $T_{\text{sub}}$ increases, the line widths decrease (peaks are sharper) suggesting higher crystalline quality. This result is in agreement with the increase in grain size shown in Fig. 4.13, as $T_{\text{sub}}$ increases.
4.5.2 Effect of Film Composition on Thermoelectric Properties of Sb-Te Films

The composition of the Sb-Te films was varied from approximately 50 to 62 at% Te, and 50 to 74 at% Te, for films deposited on glass substrate at 270 and 170°C, respectively. The effect on the TE properties can be seen in Figs. 4.15(a) and 4.16(a). The optimum power factors are given in Table 4.7.

At $T_{sub}$ of 270°C, because the measured results [Fig. 4.15(a)] do not follow a smooth curve, each property is plotted separately with error bars in Fig. 4.17, where an approximate best fit line is drawn as a guide to the eye. The optimum power factor is found for a film slightly rich in Te. The peak in Fig. 4.17(c) is located on the right side of the vertical dashed line (which marks the Sb$_2$Te$_3$ stoichiometry), where the resistivity has a minimum [Fig. 4.17(b)]. The peak found for $\rho_e$ at at% Te of 59.5 might be due to a defect structure forming around that composition.

The top surface of the films with at% Te of 60 and 50 (both deposited at 270°C) are shown in Figs. 4.13(b) and (c), respectively. The one richer in Te has larger grain size, again indicating that its mobility is likely to be higher. In contrast to the Bi-Te system, where $\rho_e$ at 60% Te was about $6 \times$ larger than that at 54% [Fig. 4.8(a)], the Sb-Te system does not show significant differences in $\rho_e$ at these compositions [Fig. 4.17(b)]. The difference in carrier concentration should not be as pronounced as the one measured for Bi-Te [Table 4.4], due to the higher background carrier density of the Sb-Te films near stoichiometry.

The power factor of films deposited at 170°C [Fig. 4.16(a)] slightly increases
Figure 4.15: Effect of Te composition on the TE properties (a), and on the XRD pattern of Sb-Te films deposited on glass at \( T_{\text{sub}} \) of 270°C, (c) to (i). In (b), the pattern of the reference powdered Sb\(_2\)Te\(_3\) single crystal is shown.
Figure 4.16: Effect of Te composition on the TE properties (a), and on the XRD pattern of Sb-Te films deposited on glass at $T_{sub}$ of 170°C, (c) to (h). In (b), the pattern of the reference powdered Sb$_2$Te$_3$ single crystal is shown.
Figure 4.17: Thermoelectric properties of Sb-Te films deposited on glass substrate at 270°C. The estimated uncertainties of $\alpha_S$, $\rho_e$ and $\alpha_S^2/\rho_e$ are ±5, 12 and 15%, respectively. (Lines are used only to guide the eye.)

Table 4.7: Measured optimum TE properties of co-evaporated Sb-Te films deposited at 270 and 170°C.

<table>
<thead>
<tr>
<th>$T_{sub}$, °C</th>
<th>$\rho_e$, $\mu\Omega$-m</th>
<th>$\alpha_S$, $\mu$V/K</th>
<th>$\alpha_S^2/\rho_e$, mW/K²-m</th>
<th>at% Te</th>
<th>$L_{te}$, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>12.5</td>
<td>149</td>
<td>1.78</td>
<td>60.53</td>
<td>1.1</td>
</tr>
<tr>
<td>170</td>
<td>25.5</td>
<td>126</td>
<td>0.62</td>
<td>58.85</td>
<td>1.0</td>
</tr>
</tbody>
</table>
around 60% Te, and then reaches a plateau. No effect of composition on the crystal orientation of these films is found [Figs. 4.16(c) to (h)]. They are polycrystalline. For at% Te above 60, note that the peak intensities are comparable to ones in the reference pattern for Sb$_2$Te$_3$ [Fig. 4.16(b)].

For films deposited at 270°C, the XRD patterns shown in Figs. 4.15(c) to (i), indicate that at at% Te about 60 and above it, the intensities of the peaks corresponding to (00l) planes increase significantly [the highest corresponding to (0.0.15)]. Below 60% Te, films are polycrystalline [with the highest peak corresponding to plane (015)].

4.5.3 Effect of Substrate Material and Crystal Structure on Thermoelectric Properties of Sb-Te Films

Additional substrates, such as Pt, Al$_2$O$_3$, MgO and mica (the same type used in the Bi-Te system analysis), were included, together with glass, in each of the co-evaporations of Sb-Te, at $T_{sub}$ of 270°C, discussed in the previous sections.

All films deposited on MgO and mica, and most of the films on Al$_2$O$_3$ had a rather poor quality. The films appeared transparent on these substrates and no electrical continuity was found in them. The exceptions were the films deposited on Al$_2$O$_3$ at 270°C, with at% Te of 58.5, 58.9 and 59.3. However, the thicknesses of these three films on Al$_2$O$_3$ were about 20% smaller than the values measured for the same films grown on glass (around 1 µm). It is evident that there are problems with Sb-Te sticking to these substrates. The crystal structure of Sb$_2$Te$_3$ is very similar to Bi$_2$Te$_3$,
as presented in Section 4.1, and therefore, we would expect no effect of the substrate on the TE properties of Sb-Te films, as verified for the Bi-Te system.

X-ray diffraction analyses show that on Al$_2$O$_3$, the Sb-Te crystal structures were strongly c-oriented, while on Pt, no preferential orientation was detected. Because it was not possible to compare the measured TE properties of the films deposited on glass with the other substrates, and also, because the films deposited on Pt did not have the c-preferential orientation verified for the films with optimum power factor deposit on glass, the question remains if films deposited on Pt will have the same TE properties as the films deposited on glass.

4.5.4 Summary

The higher carrier concentration of Sb-Te films did affect the TE properties. The Seebeck coefficient was found to be less sensitive to $T_{\text{sub}}$ and the electrical resistivities in general were lower, compared with the Bi-Te system.

The highest power factor (1.78 mW/K$^2$-m) was obtained for a film deposited at 270$^\circ$C, with at% Te of 60.5. This result can be compared with the ones reported in Fig. 1.3. In [2], the best $p$-type film was deposited at 230$^\circ$C and had $\alpha_S^2/\rho_e$ of 2.8 mW/K$^2$-m. This difference in performance is mostly due to $\alpha_S$, since the resistivities are comparable, as can be seen in Table 4.7. The $p$-type ternary compound fabricated by co-sputtering [25], which was annealed after deposition, yielded significantly higher $\alpha_S$, but also had a higher $\rho_e$ than the other optimum $p$-type Sb-Te films.

The SEM micrographs and the line widths in the XRD patterns reported here...
indicate an increase in crystalline quality of the films with the increase of $T_{\text{sub}}$. Films deposited at 270°C become preferentially c-oriented for at% Te above 60, while no effect of composition was found for films deposited at 170°C.

Thermoelectric properties were measured only for films on glass substrate due to the poor quality of the Sb-Te films deposited on Al₂O₃, MgO and mica. The films grown on Pt were analyzed by XRD and showed no preferential orientation, while c-orientation was found for optimum films grown on glass. This is an indication that the TE properties of films grown on Pt substrate might also differ from those grown on glass. Due to the limited data, no conclusion can be drawn on the effect of substrate (material and crystal structure) on the TE properties of Sb-Te films. A more extensive investigation is needed.
Chapter 5

Device Fabrication and Characterization

Micro thermoelectric (TE) coolers were designed with the number of pairs $N_{te}$ and the column width $d_{te}$ varying from 3 to 300, and 7 to 40 $\mu$m, respectively, and those include the optimum geometry ($N_{te}$ of 50 and $d_{te}$ of 7 $\mu$m) predicted in Chapter 3. Fabrication challenges and results of the first-generation devices are described and discussed here. The cooling performance of this generation, which was characterized by low performance TE films and large $d_{te}$ (low density devices), was measured and compared with predictions from the TE cooler model.

Fabrication improvements are proposed, which focus on reduction of $d_{te}$, patterning of high performance TE films, and increasing the TE element thickness $L_{te}$. This future-generation of devices will be able to achieve the desired cooling for the wireless micro system application described in Chapter 1.
5.1 Fabrication of First-Generation Device

The column-type structure of the micro TE cooler, as shown in Fig. 1.1, can be divided in three components: hot (bottom) connectors, TE elements, and cold (top) connectors. These are fabricated using integrated-circuit technology, as described in the sections that follow.

5.1.1 Hot Connectors

The fabrication steps of the hot connectors and pads are shown in Fig. 5.1. The silicon (Si) wafer is also the micro cooler heat sink. To provide electrical insulation for the device, an 850 nm silicon dioxide (SiO$_2$) layer is grown on the Si wafer [Fig. 5.1(a)]. Photoresist (PR) 1827 is spun cast [Fig. 5.1(b)], and a lift-off pattern for the hot connectors and electrical connectors (pads) is defined [Fig. 5.1(c)] using mask 1 [Fig. 5.1(f)]. These connectors are Cr/Au/Ti/Pt layers grown by e-beam evaporation [Fig. 5.1(d)]. The Au and Pt layers are 200 nm and 20 nm thick, respectively. The Cr and Ti are 20 nm thick seed layers. The Pt, which has an electrical resistivity about 5 times larger and a thermal conductivity about 5 times smaller than Au, is used for its good adhesion to the columns, while preventing the diffusion of Au into the TE elements. After the PR lift-off [Fig. 5.1(e)], the resulted fabricated structures are shown schematically in Fig. 5.1(g).
Figure 5.1: Fabrication processes and materials of hot connectors and pads. (a) to (e) Fabrication steps. (f) Schematic of mask 1 (dark field). (g) Schematic of fabricated structures.
5.1.2 Thermoelectric Elements

Each column of a TE pair is patterned consecutively using an Omnicoat/SU-8 PR mold, as shown in Figs. 5.2 and 5.3. The $n$-type and $p$-type TE elements are co-evaporated as described in Section 4.2.

A layer of Omnicoat is deposited prior to SU-8 [Figs. 5.2(a) and 5.3(a)] to facilitate the PR lift-off. SU-8, after exposure and post-exposure bake, becomes a highly cross-linked epoxy, which is extremely difficult to remove with conventional solvent-based resist strippers. For Sb-Te films, depositions with a substrate temperature equal to or greater than 210°C resulted in an over hardbaked SU-8, which could not be removed without damaging the TE films. For Bi-Te films, the limiting temperature is 170°C. In the first-generation device (GEN-1), the TE films were deposited with a substrate temperature of 130°C.

The SU-8 and Omnicoat are exposed using the clear field masks shown in [Figs. 5.2(e) and 5.3(e)], and developed [Figs. 5.2(b) and 5.3(b)] using SU-8 developer and O$_2$ plasma, respectively. After the TE film deposition [Figs. 5.2(c) and 5.3(c)] and PR removal [Figs. 5.2(d) and 5.3(d)], the resulted structures are illustrated in Figs. 5.2(f) and 5.3(f). The actual Sb-Te and Bi-Te TE elements deposited on the hot connector pattern are shown in Fig. 5.4. Note that the width of the TE elements is about 7 µm. The yield of such geometry was below 10%. Only devices with TE element cross-sectional area of 40 µm × 40 µm (which presented 90% yield at this point in fabrication) were completed.
Figure 5.2: Fabrication processes and materials of $n$-type column. (a) to (d) Fabrication steps. (e) Schematic of mask 2 (clear field). (f) Schematic of fabricated structures.
Figure 5.3: Fabrication processes and materials of p-type column. (a) to (d) Fabrication steps. (e) Schematic of mask 3 (clear field). (f) Schematic of fabricated structures.
Figure 5.4: Bi-Te and Sb-Te films deposited on Cr/Au/Ti/Pt hot (bottom) connectors. The cold (top) connectors are not shown. (a) SEM micrograph showing a top view of the fabricated structures. This image is the enlarged section "A" indicated in the part (b), top right. (b) SEM micrograph of a device with 50 TE pairs.

5.1.3 Cold Connectors

The final steps of the fabrication process are presented in Figs. 5.5 and 5.6. A contact area is defined on top of each TE element [Fig. 5.5(b)]. After developing and hardbaking the PR (AZ9245), a thin Cr/Au layer (20 nm/20 nm) is deposited by sputtering [Fig. 5.5(c)]. This metallization is necessary to avoid the exposure of the PR in the subsequent photolithography process [Fig. 5.6(a)], which is required to define the area where Au (the metal that forms the cold connectors and closes the
Figure 5.5: Fabrication processes and materials of cold connectors - part I (first metallization). (a) to (d) Fabrication steps. (e) Schematic of mask 4 (dark field).
Figure 5.6: Fabrication processes and materials of cold connectors - part II (second metalization). (a) to (c) Fabrication steps. (d) Schematic of mask 5 (dark field). (e) Schematic of fabricated structures.
electrical circuit of the TE cooler) is deposited [Fig. 5.6(c)]. This structure will be connected to a load.

To ensure a clean electrical contact opening, the PR on top of the columns [Fig. 5.5(b)] is overexposed. This is due to variations in the PR thickness, caused by differences in the height of the TE elements (differences as large as 0.8 µm between the n- and p-type TE elements have been observed).

Using Ti/Cu and Cu for the last two metallizations (hot connector) results in a large increase in the total electrical resistance of the devices with time, which might be due to oxidation of the Cu.

The height of the PR above the columns, indicated by \( h \) in Fig. 5.6(a), ranges from 1 to 2 µm. Due to this surface non-uniformity, two connector deposition techniques have been employed. First one is sputtering, which allows for a good step coverage. The top connector was formed by a 0.3 µm (50 nm/250 nm) layer of Cr/Au, as indicated in Fig. 5.6(c). The second one uses evaporation, and a 2 µm (1500 nm/500 nm) layer of Ti/Au was needed. For Au, a maximum thickness of 500 nm was allowed (process limitation) during a single e-beam evaporation. A thicker layer of Au and a thinner layer of Ti are preferred due to the Au lower electrical resistivity.

In Figs. 5.7 and 5.8, the results of the cold connector fabrication by sputtering and by evaporation are shown, respectively, where the PR layers indicated in Fig. 5.6(b) were successfully removed with lift-off in acetone. Note that in Fig. 5.7 there are undesired residual materials left on the top connectors (which can cause poor thermal contact with the load). This is due to the Cr/Au that is grown on the side walls of the PR mode. Here, there is a compromise between decreasing the PR thickness, and
Figure 5.7: SEM micrograph showing a complete electrically connected device with 3 TE pairs, where the top connector was deposited by sputtering. The cross-sectional area of the TE columns is equal to 40 µm × 40 µm.

allowing enough PR height for the lift-off. In some devices, the Cr/Au layer from the first metallization was not completely lifted-off with the PR, and a swab was used to very gently remove it from the top of the TE pairs (the wafer and swab were immersed in acetone). In other trials for the second metallization, sputtered Cr/Au connectors thicker than 0.3 µm (desirable for reducing the connector electrical resistance) were used, but caused a drastically decrease in the device yield. The ratio between $L_1$ and $L_2$, which are indicated in Fig. 5.6(b), could not be made smaller than 10.

5.2 Characterization of First-Generation Device

The cooling performance of the fabricated micro TE coolers has been evaluated at an ambient temperature $T_\infty$ of 63°C. All devices discussed here were fabricated on the same wafer. The TE properties, composition and crystal structure of the $n$-
Figure 5.8: SEM micrograph showing complete electrically connected devices with (a) 3 and (b) 60 TE pairs. The top connectors were deposited by evaporation. The cross-sectional area of the columns is equal to $40 \, \mu m \times 40 \, \mu m$. 
Table 5.1: Deposition conditions and measured properties of Bi-Te and Sb-Te films, at room temperature.

<table>
<thead>
<tr>
<th>TE Film</th>
<th>Sb-Te</th>
<th>Bi-Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{sub}}$, °C</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>$L_{\text{te}}$, μm</td>
<td>4.2</td>
<td>4.9</td>
</tr>
<tr>
<td>$\rho_e$, μΩ-m</td>
<td>31</td>
<td>36</td>
</tr>
<tr>
<td>$\alpha_S$, μV/K</td>
<td>97</td>
<td>-74</td>
</tr>
<tr>
<td>at%Te/at%(Bi or Sb)</td>
<td>1.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

and $p$-type films that compose these devices were investigated. From the TE cooler model presented in Chapter 3, the cooling performance was predicted and compared with the measured results.

5.2.1 Properties of Bi-Te and Sb-Te Films

The measured substrate temperature during the film deposition ($T_{\text{sub}}$), thickness ($L_{\text{te}}$), electrical resistivity ($\rho_e$), Seebeck coefficient ($\alpha_S$), and stoichiometry (at% element ratio) of the $n$- and $p$-type TE elements are given in Table 5.1. The measurement techniques have been discussed in Section 4.3. In Fig. 5.9, reference diffraction patterns from powdered single crystals of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are compared with the diffraction patterns of the co-evaporated films. The data agree with the associated entries in the Powder Diffraction File [57], and the corresponding reflection planes ($hkl$) are labeled. Although the films are off-stoichiometry (at% element ratio $\neq 1.5$), the positions of the peaks for the films match with the reference spectra. The results show that the films are polycrystalline without a strong preferential orientation, as
Figure 5.9: X-ray diffraction pattern of co-evaporated films and powdered single crystals of (a) Sb$_2$Te$_3$ and (b) Bi$_2$Te$_3$. The measured peaks agree with the powder diffraction file [57].

expected for low $T_{sub}$ [Figs. 4.9 and 4.16]. This justifies using the measured in-plane TE properties as the cross-plane properties in the modelling for prediction of the device cooling performance.

The figure of merit $Z_e$, defined by Eq. (2.34), can also be written as

$$Z_e = \frac{(\alpha_{S,p} - \alpha_{S,n})^2}{[(k\rho_e)^{1/2} + (k\rho_n)^{1/2}]^2},$$

[17], where $k$ is given in Table 2.1. Note that this is a optimized expression for $Z_e$ since it does not include geometric parameters. At room temperature, the dimensionless figure of merit $Z_eT$ was found to be 0.032.
Table 5.2: Base-line properties used in the TE cooler model.

<table>
<thead>
<tr>
<th>TE Film at Interface</th>
<th>$Sb_2Te_3$</th>
<th>$Bi_2Te_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(A_kR_k)_c$, K/(W/m$^2$)</td>
<td>$10^{-7}$</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>$(A_kR_e)_c$, Ω-m$^2$</td>
<td>$2\times10^{-11}$</td>
<td>$2\times10^{-11}$</td>
</tr>
<tr>
<td>$(A_kR_k)_{b,pp}$, K/(W/m$^2$)</td>
<td>$8.0\times10^{-8}$</td>
<td>$9.2\times10^{-8}$</td>
</tr>
<tr>
<td>$(A_kR_k)_{b,ee}$, K/(W/m$^2$)</td>
<td>$9.3\times10^{-7}$</td>
<td>$3.5\times10^{-7}$</td>
</tr>
<tr>
<td>$k$, W/m-K</td>
<td>2.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 5.2.2 Predicted Cooling Performance

In predicting the device cooling performance, consideration was given to the phonon $(A_kR_k)_{b,pp}$ and electron $(A_kR_k)_{b,ee}$ boundary resistances, the phonon-electron thermal non-equilibrium in the regions adjacent to the interfaces of the TE elements, and the thermal $(A_kR_k)_c$ and electrical $(A_kR_e)_c$ contact resistances. These base-line properties, which were estimated in Chapter 2, are summarized in Table 5.2. Using these and the measured ($L_{te}$, $\rho_e$ and $\alpha_S$) properties given in Table 5.1, the performance of a device with the number of TE pairs $N_{te}$ equal to 60 and a cross-sectional area of the columns $A_k$ ($= d_{te}^2$) of 40 μm × 40 μm, was evaluated and is shown in Fig. 5.10. The dashed lines indicate the maximum temperature difference between the heat sink and the top surface of the cold connector*, $(T_\infty - T_l)$ of 0.5 K, for an applied voltage $\Delta\varphi$ of 1.8 V, an electrical current $J_e$ of 36 mA, and under a minimal cooling load $Q_c$ of 0.1 mW (thermobuoyant surface convection and surface radiation). The predicted

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*The temperature difference $(T_\infty - T_l)$ is also referred to here as the device cooling performance. The coefficient of performance, which is given by Eq. (3.16), is nearly zero, since $Q_c$ is minimal. Note also that $T_l$ and $T_2$, which are indicated in Fig. 3.1, are taken to be equal.
device total electrical resistance $R_e$ is 50 $\Omega$ [including a measured $R_{e,pads}$ of 10 $\Omega$, Eq. (3.13)].

### 5.2.3 Measured Cooling Performance

Using an infrared (IR) thermal microscope (InfraScope II) and 5× lens (pixel resolution of 4.8 $\mu$m and accuracy of 5%), the thermal image of a fabricated micro TE cooler ($N_{te}$ of 60 and $d_{te}$ of 40 $\mu$m) operating with $J_e$ of approximately 23 mA was obtained, and is shown in Fig. 5.11. The measured $R_e$ of this device (at room temperature) was 51 $\Omega$. Temperature calibration was performed by measuring the surface emissivity at different temperatures, and fitting a linear function to the measured points [60].

Note that, in the graph of Fig. 5.11, a side-view schematic drawing of the TE pairs
Figure 5.11: Infrared surface thermal image of a device with 60 TE pairs and column width of 40 µm. The top connectors were deposited by sputtering. The layout of the TE elements and connectors along line-trace is represented by the side-view schematic drawing at the temperature graph.
(scaled with respect to pixels) illustrates the position of the line trace in the thermal image. Darker lines, which indicate lower temperatures, are above the TE elements, while the surfaces of the bottom connectors and the substrate (SiO$_2$) are marked by higher temperatures. In this case, $(T_\infty - T_l)$ can be approximated to 1.3 ± 0.5 K, where $T_\infty$ is maintained at about 63°C.

The TE cooling figure of merit can be obtained from [17]

$$Z_e = 2 \frac{(T_\infty - T_l)}{T_l^2}.$$  (5.2)

For $T_l$ equal to 61.7°C, $Z_eT_\infty$ is found to be 0.0078, which is four times smaller than the optimized $Z_eT$ calculated in Section 5.2.1. This is due to effects of geometry ($N_{te}$, $L_{te}$, $d_{te}$), interfacial resistances (listed in Table 5.2), and external conditions ($Q_c$, $T_\infty$), in addition to the TE properties, on the performance of a micro TE cooler device.

In the thermal image, the isolated spots with large temperature gradients indicate fabrication defects. This device had the top connectors deposited by sputtering, and, as shown in Fig. 5.7, there are residual metals not completely removed by the lift-off process. These can cause an electrical short-circuit between the top and bottom connectors. The non-uniform temperatures observed at the top connectors can be due to the TE element surface roughness or oxidation, both of which compromise an efficient thermal contact.

A second device, also with $N_{te}$ of 60, $d_{te}$ of 40 µm, and with the top connector deposited by sputtering, was annealed at 200°C for 2 hours in a nitrogen stream. The measured $R_e$ before and after annealing were 51 Ω and 58 Ω, respectively. A thermal image of this device is shown in Fig. 5.12. Observe the difference in the
Figure 5.12: Infrared surface thermal image of a device with 60 TE pairs and column width of 40 µm, which was annealed at 200°C for 2 hours. The top connectors were deposited by sputtering. The layouts of the TE elements and connectors along lines 1 and 2 are represented by the side-view schematic drawings at the temperature graphs.
layout of the TE elements and connectors along lines 1 and 2 (shown by the side-view schematic drawings superimposed on the temperature graphs). The line trace 2 marks the complete extension of the top connectors, where lower temperatures, although not uniform, are evident. In this case, \( (T_\infty - T_i) \) can be approximated as 0.8 ± 0.5 K (where \( T_\infty \) is maintained at about 62.5°C), indicating that annealing (at the conditions mentioned above) did not significantly affect the overall device cooling performance when compared with the first device tested. However, note that this was a preliminary attempt on improving the performance by thermal post-treatment. A more careful investigation on annealing is required for each of the TE films (n- and p-type) aiming at improvement of the TE properties. Also, annealing the device, can reduce the contact resistances. In this regard, the inclusion of a diffusion barrier between the TE elements and metal connectors should be considered.

The micro TE coolers with the top connectors deposited by evaporation presented an overall electrical resistance 1.6 to 1.8 times the \( R_e \) of the devices previously discussed (i.e., devices with top connectors deposited by sputtering), and it increased up to 5 times after annealing at 200°C for 2 hours in a nitrogen stream. These devices produced no detectable cooling, even before annealing, as shown in Fig. 5.13. This might be due to the diffusion of the thick Ti layer (1.5 µm, deposited prior to Au) into the TE elements.
Figure 5.13: Infrared surface thermal image of a device with 60 TE pairs and column width of 40 µm. The top connectors were deposited by evaporation. The layouts of the TE elements and connectors along lines 1 and 2 are represented by the side-view schematic drawings at the temperature graphs.
5.2.4 Comparison between Measured and Predicted Cooling Performances

The characterized devices have an overall electrical resistance about 2% (before annealing) to 16% (after annealing) larger than the predicted resistances. The measured device temperature difference \((T_\infty - T_l)\) was approximately 100% larger than the predicted value. The defects observed as hot spots in the thermal images indicate that improvements can be made in the fabrication of the top connectors, which would increase the disagreement between the measured and predicted performances.

The TE properties and resistance used in the TE cooler model, which are given in Tables 5.1 and 5.2, present uncertainties that can be related to this difference. It is possible that they have changed during the top connector fabrication process, where the wafer was heated to as high as 200\(^\circ\)C. Also, TE properties of films deposited on Pt were not measured, as discussed in Chapter 4. They were assumed to be equal to the ones measured on glass substrates. In Fig. 5.14, the sensitivity of the device overall performance to these properties is shown, for \(\Delta \phi, Q_c, T_\infty, N_{te}\) and \(d_{te}\) equal to 1.8 V, 0.1 mW, 63\(^\circ\)C, 60 pairs and 40 \(\mu\)m, respectively. The TE properties [Fig. 5.14(a)] vary up to \(\pm 50\%\) of their base values for both \(n\)- and \(p\)-type elements, and the resistances [Fig. 5.14(b)] vary from a factor of 0.1 to a factor of 10.

Note that, the relation \(\alpha_2^2/(\rho_e k)\) from Eq. (2.34) is not obeyed in Fig. 5.14(a). This is due to the TE element geometry being far from optimum (\(L_{te}/d_{te}\) around unity). The TE properties most affecting performance are \(\alpha_S\) and \(k\). Zou et al. [2] have assumed \(k\) for \(p\)-Sb\(_2\)Te\(_3\) and \(n\)-Bi\(_2\)Te\(_3\) films as 1.5 W/m-K, while in Chapter 2,
Figure 5.14: Effect of (a) TE properties and (b) resistances used in the TE cooler model on the predicted cooling performance of a device with 60 TE pairs and column width of 40 $\mu$m.

$k$ was estimated to be around 2 W/m-K for both films (as given in Table 5.2). The dashed lines in Fig. 5.14(a) are indicating that this 25% reduction in $k$ would increase $(T_\infty - T_I)$ by about 60%. In Fig. 5.14(b), it is seen that the device performance is less sensitive to the electrical than to the thermal resistances (boundary and contact).
5.3 Proposed Fabrication and Characterization of Future Generations

Developments in the fabrication of a micro TE cooler comprise overcoming the limits encountered with the processes indicated in Fig. 5.15. The first-generation device fabricated and tested, whose results were presented in previous sections, is labeled as GEN-1. In this first generation, a limit on the TE column length $L_{te}$ (indicated in the inclined axis of Fig. 5.15) was reached due to difficulty in controlling the sublimation of the tellurium element. The uncertainty in the deposition rate increases with the depletion of Te inside the evaporation boat. When this fluctuation is greater than $\pm 0.6 \text{ Å/s}$ (for films thicker than $5 \mu\text{m}$), large stoichiometry non-uniformity is generated. Also in GEN-1, the column width of the TE elements (indicated in the vertical axis) was restricted to $40 \mu\text{m}$. Almost no yield of smaller $d_{te}$ devices was obtained, as discussed in Section 5.1. The TE films were deposited at low $T_{sub}$ (indicated in the horizontal axis) to facilitate the PR removal.

The future generations GEN-2 and GEN-3, also shown in Fig. 5.15, are discussed in the following sections.

5.3.1 Second-Generation Device

5.3.1.1 Proposed Fabrication

The second generation of devices, GEN-2, should focus on improvements in the following steps of the device fabrication.
Figure 5.15: Map of device generation aiming at GEN-3. GEN-1 has been completed. GEN-2 is the proposed next generation of devices.

- **Photolitography process that defines the pattern for the TE elements:**
  The objective is to increase the yield of the higher performance (high density) devices by reducing $d_{te}$, since the optimum aspect ratio $L_{te}/d_{te}$ was estimated to be around 1.5, as discussed in Section 3.3 (in GEN-1, $L_{te}/d_{te}$ was equal to 0.11). This can be done by optimizing PR spinning, exposure and development. The lower limit of 7 $\mu$m is due to the minimum feature size (3 $\mu$m) obtainable in the mask fabrication process.

- **TE film deposition:** The TE film performance at $T_{sub} < 170^\circ$C can be maximized by optimizing film stoichiometry, as shown by results reported in Sections
4.4 and 4.5. The limit of 170°C for $T_{sub}$ is related to the maximum temperature that the PR (used for patterning the columns) can be exposed to without over hardbaking (when it can not be removed without damaging the TE elements). The increase in $T_{sub}$ is desired to obtain films with optimum power factors, i.e., $\alpha^2 / \rho_e$ around 1.8 or greater ($Z_e T \gtrsim 0.3$), as reported in Chapter 4.

- **Patterning and deposition of the cold (top) connector**: This has greatly affected the yield and performance of GEN-1, as discussed in previous sections. The cold connector thickness, $L_{cc}$, indicated in Fig. 3.1, should be increased (which can be done by evaporation) to allow for the reduction of $R_e$. Additionally, the introduction of a diffusion barrier between the TE element and connectors, and the removal of the first Cr/Au layer (by using negative PR) used to avoid the exposure of the PR between the columns, are expected to increase the yield and also the performance of the devices.

### 5.3.1.2 Predicted Cooling Performance

In Fig. 5.16, the cooling performance of optimized geometries ($d_{te}$ of 7 µm and $N_{te}$ of 15, 60 and 120, for $L_{te}$ of 4.5 µm) are plotted as a function of the applied voltage $\Delta \varphi$. The TE properties used in these predictions are reported in Tables 4.5 and 4.7, for the lower values of $T_{sub}$.

A decrease of about 2.8 K in the cold connector temperature is expected for $\Delta \varphi$ as low as 0.6 V ($N_{te}$ of 15). The maximum cooling of 3.1 is predicted for the device

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†Because the cold connector area, given by the product of $a_{cc}$ and $d_{cc}$ (Fig. 3.1), is significantly smaller than the hot connector area, $a_{hc}d_{hc}$, the device performance is more sensitive to $L_{cc}$ than to $L_{hc}$.
with 60 pairs, when 2.2 V is applied ($J_e$ of 6 mA), as indicated by the dashed lines.

5.3.2 Third-Generation Device

5.3.2.1 Proposed Fabrication

The breakthrough in cooling performance, i.e., ($T_\infty - T_l$) over 10 K for $Q_c$ of 10 mW (as predicted in Chapter 3), can be achieved in the third-generation device, GEN-3, with high performance TE elements and larger $L_{te}$. The later can be done with larger evaporation boats, shown in Fig. 4.2(c), which minimizes the effect of material depletion on the deposition rate control of the elements (non-uniform stoichiometry). The proposed methods for fabrication of optimum TE elements are given below.

- **Patterning the $n$- and $p$-type high performance TE films**: These are films deposited at optimal conditions, i.e, $260^\circ$C < $T_{sub}$ < $270^\circ$C (indicated in the hori-
ontal axis of Fig. 5.15), by using silicon shadow masks with high precision alignment. The masks are aligned to the substrate (using a mask-aligner adapted for shadow masks) for direct deposition and pattern of the high-performance TE films. Although this is a straight forward solution, it presents a high cost due to the precision required in the fabrication and alignment of the shadow masks.

- **Annealing the PR-patterned low-performance TE films**: These are films deposited at $T_{sub} < 170^\circ$C. Böttner et al. [7] have measured a considerable increase in TE performance of both $n$- and $p$-type materials after annealing at temperatures around 300°C for some hours. This post-processing step requires a series of experiments that will determine the precise time and temperature needed for each TE element to reach maximum TE performance. The deposition conditions of the TE films (initial composition and film structure) are additional variables in this process.

- **Patterning the $n$- (or $p$-type) high performance TE film and annealing the $p$- (or $n$-type) TE element**: The second is a PR-patterned low-performance TE film. A combination of metallic shadow mask (with coarse alignment) and etching is used to define the first TE element (this process can not be repeated for the second element, because the first would not resist to the etching process). Brass or aluminum shadow masks, micro-machined fabricated, can be mechanically aligned to the substrate [61]. Large areas (that will absorb alignment errors) of high performance TE film are deposited, patterned with PR and etched.
The challenge of the last two methods, where annealing/etching are required, is on heat treating (under Te pressure) and etching the TE elements, while protecting the metal connectors [25].

5.3.2.2 Predicted Cooling Performance

In Fig. 5.17, the cooling performance of optimized geometries are presented as a function of $\Delta \phi$, for $L_{te}$ of 4.5 $\mu$m and 8 $\mu$m. The TE properties used in these predictions are reported in Tables 4.5 and 4.7, for the higher values of $T_{sub}$.

At 3 V, the maximum $(T_\infty - T_i)$ for a device with $L_{te}$ of 4.5 $\mu$m is 8.2 K. Increasing $L_{te}$ to 8 $\mu$m, the cooling performance increases to 13 K, but also the power requirement ($P_e$ will be about $4\times$ larger for $L_{te}$ of 8 $\mu$m). Note that the 80% increase in $L_{te}$ is not entirely reflected on improvement of performance (which was increased by 60%) due to differences in $d_{te}$ and $N_{te}$ of these devices. At 6 V, $(T_\infty - T_i)$ can be increased from 10 K to 15 K, with $L_{te}$ varying from 4.5 $\mu$m to 8 $\mu$m, and $P_e$ is not drastically affected (for these optimal geometries), as compared with $\Delta \phi$ of 3 V.

5.3.3 Proposed Improvements in Device Characterization

Two new structures are proposed to improve the thermal characterization of the TE cooler devices. One can be used to measure the thermal conductivity of the TE films, and the other for more precise IR thermometry. Both should be included in the layout of the new set of masks for GEN-2 and GEN-3. A more detailed description of these structures and measurement techniques [60] is given below.
Figure 5.17: Predicted performance of GEN-3 for optimized geometries at 3 and 6 V.

5.3.3.1 Thermal Conductivity Measurement

A thermorelectance setup, which is based on changes in surface optical reflectivity of a metal as its temperature varies due to a transient heating, can be used for thermal conductivity evaluation of the TE films.

The sample with the thermal conductivity to be measured (Bi-Te or Sb-Te film) should be sandwiched between a top metal layer (Cr/Au) and a high thermal conductivity substrate, usually a silicon substrate (here, the TE film samples can be grown on SiO$_2$ and on Cr/Au/Ti/Pt). A nanosecond, pulsed laser heating can establish an initial temperature rise (about 40°C) on the metal surface. A low-power probe laser can monitor the metal surface reflectivity change, which is produced by the temperature decay. By solving the transient multilayer heat conduction for this metal/sample/substrate system (where the exact thickness of each layer is required)
and fitting the result to the measured temperature decay, the thermal conductivity of the TE film sample can be extracted. To satisfy the one-dimensional heating condition, the length and width of the TE film samples can be both 1 mm, which are much larger than the sample thickness (4 to 5 µm). Calibration and uncertainty of this method should be further investigated.

5.3.3.2 Thermometry

Metal bridges with 4 probe accesses, as shown in Fig. 5.18, can be deposited on the oxide film, next to the monitored devices, in order to be in the same field of view during the device performance characterization.

The bridge temperature is determined by measuring its resistance, which is first calibrated at different temperatures by passing small current without induced Joule heating. During the actual measurements, a large current is used causing temperature rise in the bridge. The average temperature is measured by the electrical resistance thermometry and compared with the IR images.
5.4 Summary

The TE properties, geometry, external operating conditions and performance of the devices discussed here and in Chapter 3, are summarized in Fig. 5.19.

In GEN-1, integrated micro TE cooler devices with 60 TE pairs, and thickness and width of columns of approximately 4.5 µm and 40 µm, respectively, were fabricated using co-evaporation for deposition of the TE elements. The Seebeck coefficient and electrical resistivity of the films were measured, and from a micro TE cooler model a net cooling of 0.5 K was predicted for an applied voltage of 1.8 V and a minimal cooling load of 0.1 mW. The predicted total electrical resistance $R_e$ was 50 Ω.

Using an IR camera, thermal images of these devices operating at 23 mA and at an ambient temperature of 63°C were obtained. An average cooling performance of 1.3±0.5 K was verified (measured $R_e$ of 51 Ω). For a device with the same geometry and TE properties, but annealed at 200°C for 2 hours, the cooling performance was 0.8±0.5 K. After annealing, the electrical resistance increased to 58 Ω, which is an indication of the need for a diffusion barrier between the metal connectors and TE elements.

GEN-2 focuses on increasing the ratio $L_{te}/d_{te}$ (0.11 for GEN-1) towards unity. As the TE element length has reached a limit of 5 µm (uniform stoichiometry limit), improvements will be made in the photolithography process to allow for a smaller $d_{te}$. The performance of the TE films will be improved ($\alpha_S^2/\rho_e$ is doubled) by a slight increase in $T_{sub}$, from 130°C in GEN-1 to maximum of 170°C in GEN-2 (limited by the PR removal), as indicated in the horizontal axis of Fig. 5.15, and also by sto-
<table>
<thead>
<tr>
<th>DEVICE</th>
<th>Designed Chapter 3 (GEN-0)</th>
<th>GEN-1</th>
<th>GEN-2</th>
<th>GEN-3</th>
</tr>
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<tr>
<td>TE Properties</td>
<td>From [2] Measured Table 5.1</td>
<td>Measured Tables 4.4 and 4.6 (Lower $T_{sub}$)</td>
<td>Measured Table 4.4 and 4.6 (Higher $T_{sub}$)</td>
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<td>$\alpha_{S,n}$, $\mu$V/K</td>
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<td>0.39</td>
<td>1.84</td>
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<tr>
<td>($\alpha_{S}^{2}/\rho_{e}$)$_{p}$, mW/K$^{2}$-m</td>
<td>2.81</td>
<td>0.30</td>
<td>0.62</td>
<td>1.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Geometry</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{te}$</td>
<td>50</td>
<td>60</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>$d_{te}$, $\mu$m</td>
<td>7</td>
<td>40</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>$L_{te}$, $\mu$m</td>
<td>4</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>$L_{cc}$, $\mu$m</td>
<td>2</td>
<td>0.3</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

| External Condition | | | |
|-------------------| | | |
| $Q_{e}$, mW | -10 | -0.1 | -0.1 | -10 |
| $T_{\infty}$, $^\circ$C | 25 | 63 | 25 | 25 |

<table>
<thead>
<tr>
<th>Performance</th>
<th>Predicted</th>
<th>Measured</th>
<th>Predicted</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>($T_{\infty} - T_{l}$), K</td>
<td>11</td>
<td>0.5</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>$\Delta \varphi$, V</td>
<td>3</td>
<td>1.8</td>
<td>1.18</td>
<td>2.2</td>
</tr>
<tr>
<td>$J_{e}$, mA</td>
<td>11</td>
<td>36</td>
<td>23</td>
<td>6</td>
</tr>
<tr>
<td>$P_{e}$, mW</td>
<td>34</td>
<td>65</td>
<td>27</td>
<td>13</td>
</tr>
<tr>
<td>COP</td>
<td>0.3</td>
<td>0.0015</td>
<td>0.0037</td>
<td>0.008</td>
</tr>
</tbody>
</table>

* Averaged from $L_{te,n}$ and $L_{te,p}$, listed in Table 5.1.
** The total electrical resistance of the device ($R_{e} = 51 \Omega$) was measured at room temperature.
The variables $\Delta \varphi$, $P_{e}$ and COP were calculated as a function of $J_{e}$ and $R_{e}$.

Figure 5.19: Summary of geometry, TE properties, performance and external operating conditions of the device designed in Chapter 3, the fabricated first-generation device (GEN-1), and future generations (GEN-2 and GEN-3).
chiometry optimization. In the cold connector fabrication, the thickness of the second metallization will be increased ($L_{cc} = 2 \, \mu m$) to allow for lower $R_e$. The maximum predicted cooling performance is 3.1 K, for $\Delta \varphi$ of 2.2 V. In the device characterization, new structures should be added to the mask layout to allow for the thermal conductivity measurement of the TE films and for more precise IR thermometry.

GEN-3 will focus on the fabrication of high performance TE elements, either by patterning the high performance TE films, or by post-processing (e.g., annealing) the films deposited at low substrate temperature to improve their TE performance. For $L_{te}$ of 4.5 $\mu m$, $(T_\infty - T_l)$ as high as 10.4 K can be obtained if $\Delta \varphi$ of 6 V is applied. Increasing $L_{te}$ to 8 $\mu m$, this performance can be increased by 42% to $(T_\infty - T_l)$ of 14.8 K.

The optimum device design and performance predicted in Chapter 3, denoted in Fig. 5.19 by GEN-0, can be compared with the device geometry (b) of GEN-3. Both have the constrain of using a battery of 3 V. The lower $(T_\infty - T_l)$ predicted from GEN-3(b), 8.2 K, compared with 11 K for GEN-0, is mostly due to the performance of the TE films. The power factors $\alpha_2^2/\rho_e$ reported in [2] are 60 to 100% larger than the measured $\alpha_2^2/\rho_e$ of the optimum films fabricated here and reported in Chapter 4.
Chapter 6

Conclusion

Using a specially designed vacuum chamber, 4 to 5 $\mu$m thick Bi-Te and Sb-Te films were deposited and patterned, and column-type micro thermoelectric (TE) coolers were fabricated. The TE films were optimized for maximum power factor, by performing experiments-characterizations using various substrate materials, substrate temperatures, and film compositions. The theoretical studies show that, with this TE element height, the size effects (especially the phonon and electron boundary resistances) become important. These effects were included in a TE model for the device geometry optimization. In the first fabrication attempt, the yield for the high density devices (optimal column width around 7 $\mu$m) was rather very low, so it was only possible to test coarser structures (off from optimal geometry), resulting in a minimal cooling effect. Also, using photoresist for patterning the thermoelectric elements, limited the film deposition substrate temperature, and resulted in rather low intrinsic TE properties. The requirements for overcoming these performance limitations are summarized below.
• **Deposition and patterning of high performance TE films**: The substrate temperature and the film composition were found to be the most important parameters affecting the TE film performance. Optimum power factors for \(n\)- and \(p\)-type, Bi-Te and Sb-Te films, respectively, were obtained for substrate temperatures above 250°C and tellurium concentration around 60%. However, these optimal TE films were not compatible with photolitography processes, due to the hardbake of the photoresist at substrate temperatures above 170°C. Patterning the high performance films will require the use of shadow masks. The additional methods discussed in Section 5.3.2.1, have the challenge of protecting the metal connectors during the annealing or etching processes.

• **Fabrication of TE elements with optimal aspect ratio** \(L_{te}/d_{te}\): For optimal cooling, the ratio between the TE element thickness \(L_{te}\) and width \(d_{te}\), was predicted to be around 1.5. Because \(d_{te}\) is constrained by the fabrication process, \(L_{te}\) should ideally range between 10 and 20 \(\mu\)m (mostly due to parasitic heat conduction). This length requirement poses a challenge on fabrication of Bi-Te and Sb-Te films with highest intrinsic TE properties. As \(L_{te}\) increases, the composition uniformity, as well as the TE properties uniformity of the TE films, may become compromised. In the first-generation device, \(L_{te}\) was limited due to large stoichiometry non-uniformity (verified with the depletion of the elements inside the evaporation boats, and difficulty in controlling the deposition rate of the elements).
• **Realization of minimal contact resistances at the device interfaces:** The thermal and electrical contact resistances were found to be critical parameters affecting the device performance, as they can vary with the fabrication process. They can be further minimized by device annealing. For the first-generation device fabricated and tested here, the measured and predicted device performances were in good agreement. Therefore, it appears that the estimated resistances are reasonable.

A future generation of integrated micro TE coolers, able to fulfill these requirements, and satisfy the power and performance needs of the wireless environmental monitor application, is proposed.

Finally, the specific contributions of this work can be summarized as follows.

• Development of a TE model that takes into account the size and interfacial effects on thermal and electrical transport. It provides optimized geometries and can predict with reasonable accuracy the device cooling performance and operating conditions.

• Demonstrating-characterizing that high performance *n*-type Bi-Te films can be formed on Pt, thus allowing for use of this conductor as the metal connector layer that interfaces with the TE elements.

• Verification that polycrystalline structures of *n*-Bi-Te and *p*-Sb-Te, with 60 at% Te, are formed at low substrate temperature (not optimal), which suggests the possibility for improvements in the TE properties of the low performance TE films, by annealing.
• Development of a fabrication process that allows for the manufacture of column-type micro TE coolers on a single substrate (based on photolithography processes and possible introduction of shadow masks), and for their integration into other micro devices.
References


[36] H. Rauh, R. Geick, H. Köhler, N. Nücker, and N. Lehner, Generalized phonon density of states of the layer compounds Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$, (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$, *Solid State Physics*, **14**, 2705-2712, (1981).


