

THERMOELECTRIC MICRO CONVERTERS FOR COOLING AND ENERGY SCAVENGING SYSTEMS

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Abstract — This paper describes the fabrication process of thermoelectric microconverters, based on *n*-type bismuth telluride (Bi_2Te_3) and *p*-type antimony telluride (Sb_2Te_3) thin films. Materials are fabricated by thermal co-evaporation with thermoelectric properties comparable to those reported for the same materials in bulk form (used in conventional macro-scale Peltier modules). Absolute value of Seebeck coefficient in the range 150-250 μVK^{-1} and in-plane electrical resistivity of 7-15 $\mu\Omega\text{m}$ were obtained. Influence of fabrication parameters on thermoelectric properties is reported. The films were then patterned by photolithography and wet-etching techniques, using HNO_3/HCl -based etchants. Influence of composition and concentration of etchants in the process is reported. A microcooler was fabricated and analysed by infrared thermal image.

Key Words: Thermoelectric, Microcooler, Energy harvesting, Telluride, Bi_2Te_3 , Sb_2Te_3 .

I INTRODUCTION

Tellurium alloys (*n*-type Bi_2Te_3 and *p*-type Sb_2Te_3) are well-established thermoelectric materials for operation near room temperature, widely used in the thermoelectric industry (macro-scale conventional Peltier modules), since they have a high Seebeck coefficient, low electrical resistivity and relatively low thermal conductivity.

The fabrication of efficient solid state thermoelectric microdevices, for local cooling and thermoelectric energy scavenging, requires thin-film deposition processes, patterning and easy integration with standard Si technology. Thermoelectric energy scavenging microsystems fabricated with tellurium alloys can power small electronic devices (up to units of milliwatt) under temperature differences below 10 °C. This type of energy converters can also be used in human-body power generators, to obtain energy from temperature differences between body ($\approx 37^\circ\text{C}$) and room temperature. Peltier microcoolers can achieve temperature differences up to 60 °C, between hot and cold side. Despite the range of exciting applications, only few approaches to manufacture

thermoelectric devices with small dimensions were reported up to now [1,2,3].

Tentative deposition of thin-films by direct evaporation of the bulk materials (Bi_2Te_3 and Sb_2Te_3) proved to be impossible due to the large differences in vapour pressure of Bismuth, Antimony and Tellurium, resulting in a compositional gradient along the film thickness [4]. Other deposition techniques have been reported in the literature for the deposition of telluride thin-films. Co-sputtering, electrochemical deposition, metal-organic chemical vapour deposition or flash evaporation, are some examples.

In the present work, co-evaporation is applied in the fabrication of thermoelectric thin-films, and the influence of growing parameters is studied in detail.

Respecting the use of patterning techniques on thermoelectric films, few approaches have been reported in the literature. Silva et al [2] uses lift-off, with SU-8 photoresist, to create vertical columns of thermoelectric materials. But due to the maximum working temperature of SU-8 photoresist ($\approx 180^\circ\text{C}$), thermoelectric properties of Bi_2Te_3 and Sb_2Te_3 films incorporated in the devices are worst than those obtained in bulk materials, since 200-300 °C of substrate temperature is required to fabricate high quality thermoelectric films. Bottner et al [1] use dry etching to pattern thermoelectric devices. Shafai [6] reports on the possibility of patterning these films by wet etching but no details are given of the process. In the present work, low cost wet-etching techniques are further investigated and details presented.

II FABRICATION PROCESS

Fig. 1 shows the fabrication process of thermoelectric converters. Metallic contact pads

are deposited and patterned on the surface of kapton substrate (a). P-type Sb_2Te_3 film is deposited by thermal co-evaporation (b). Photoresist (PR) is spun and patterned by photolithography (c). Thermoelectric film is patterned by wet-etching in $\text{HNO}_3:\text{HCl}$ etchant (d) and PR is removed. N-type film is then deposited by co-evaporation (e). PR is applied and patterned by photolithography (f). N-type film is etched in HNO_3 etchant (g) and PR removed (h). In the last step, a protection layer of Si_3N_4 is deposited by low-temperature Hot-wire chemical vapor deposition (HW-CVD) (i) and patterned if required, depending on the application.

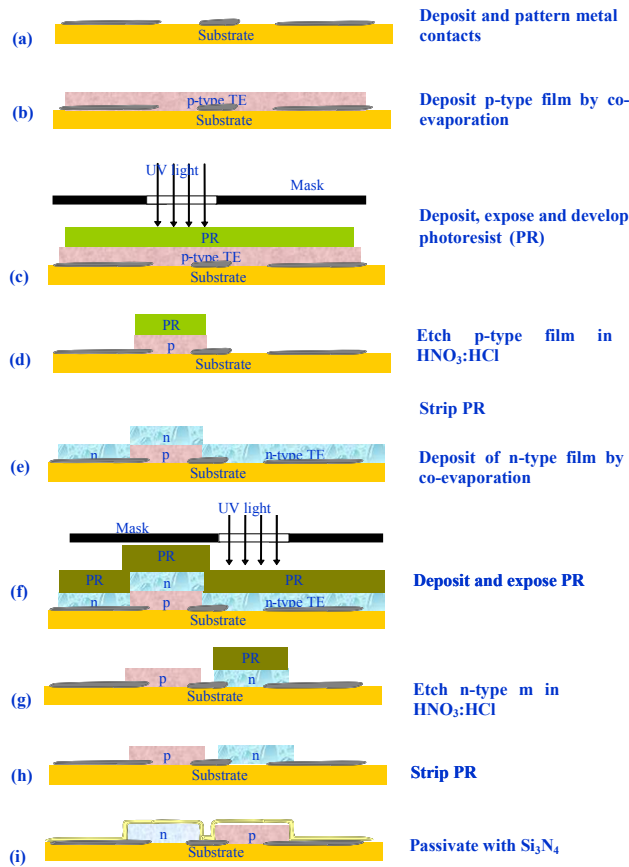


Fig 1: Fabrication steps of thermoelectric converters.

II.1 THIN-FILM DEPOSITION

Thermoelectric films were fabricated by the thermal co-evaporation technique (fig. 2) in a high-vacuum chamber (1×10^{-6} torr) [6]. Two large molybdenum boats (baffled boxes, 4 cm^3 in volume) are used in parallel, one for each of the elementary materials required to produce the desired compound. The power applied to each boat

is controlled independently, using two computed PID controllers to maintain the deposition rate at user-defined constant values, during the deposition process. Two thickness monitors (quartz crystal oscillators) are carefully placed inside the chamber in such a way that each of them receives material only from the boat it is monitoring. To prevent mixing of both materials to occur at the quartz crystal sensors, a metal sheet is placed between the two boats. Substrates are heated to the temperature setpoint (T_{sub}) in the range $150\text{-}270 \text{ }^\circ\text{C}$.

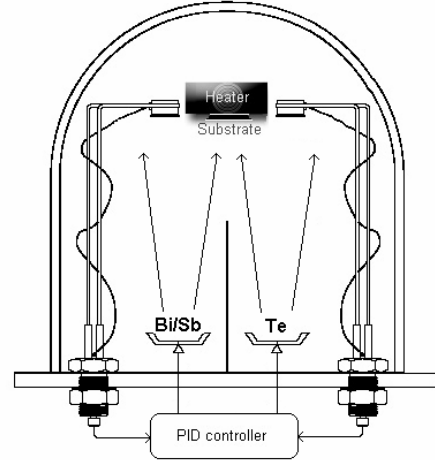


Fig 2: Thermal co-evaporation system.

Table 1 and Table 2 present thermoelectric properties of selected films. Eq. 1 and eq. 2 are used to calculate the power factor, PF , and the figure of merit, ZT , respectively:

$$PF = \alpha^2 / \rho \quad \text{Eq. 1}$$

$$ZT = \frac{\alpha^2}{\rho\lambda} T \quad \text{Eq. 2}$$

α is the Seebeck coefficient in VK^{-1} , ρ is electrical resistivity in Ωm , λ is the thermal conductivity in $\text{Wm}^{-1}\text{K}^{-1}$ and T is the temperature in K. Thermal conductivity of $1.5 \text{ Wm}^{-1}\text{K}^{-1}$ was assumed to calculate ZT [7].

Table 1: Properties of selected Bi_2Te_3 films.

| Film | Temp T_{sub} $^\circ\text{C}$ | $R =$ $F_{\text{Te}} / F_{\text{Bi}}$ | α μVK^{-1} | ρ $\mu\Omega\text{m}$ | PF $\times 10^{-3}$ $\text{WK}^{-2}\text{m}^{-1}$ | ZT @300K |
|-------|--|--|---------------------------------|-------------------------------|---|---------------|
| #302A | 160 | 1.6 | -74 | 5.7 | 0.96 | 0.19 |
| #C36 | 190 | 1.7 | -180 | 16.6 | 1.95 | 0.4 |
| #267A | 230 | 2.1 | -156 | 11.3 | 2.16 | 0.43 |
| #267D | 230 | 3.0 | -152 | 13.4 | 1.72 | 0.34 |
| #273C | 270 | 3.2 | -248 | 12.6 | 4.87 | 0.97 |
| #281D | 270 | 3.9 | -220 | 10.6 | 4.57 | 0.91 |

Table 2: Properties of selected Sb_2Te_3 films.

| Film | Temp T_{sub} °C | $R =$ $F_{\text{Te}} / F_{\text{Sb}}$ | α $\mu\text{V}/^\circ\text{C}$ | ρ $\mu\Omega\cdot\text{m}$ | P.F. $\times 10^{-3}$ $\text{W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$ | ZT @300K |
|-------|--------------------------------|--|--|------------------------------------|--|-------------|
| #195C | 150 | 1.47 | 91 | 7.6 | 1.09 | 0.22 |
| #305A | 150 | 1.67 | 140 | 14.0 | 1.40 | 0.28 |
| #306A | 220 | 2.50 | 156 | 9.2 | 2.66 | 0.53 |
| #306D | 220 | 3.18 | 188 | 12.6 | 2.81 | 0.56 |

Fig. 3 and fig. 4 show the influence of the evaporation rate of each material on the thermoelectric properties of the compounds. The evaporation flow rate ratio ($R = F_{\text{Te}} / F_{\text{Bi,Sb}}$) is defined as the amount (in thickness of deposited film) of Te divided by the amount of Bi (or Sb) that arrives to the substrate during deposition. The highest thermoelectric power factor was obtained with Bi (or Sb) evaporation rate of 2 \AA s^{-1} and Te evaporation rate of $6\text{-}7 \text{ \AA s}^{-1}$ ($R=3\text{-}3.5$). T_{sub} was $\approx 270^\circ\text{C}$ for Bi_2Te_3 and $\approx 220^\circ\text{C}$ for Sb_2Te_3 films. All films were deposited on kapton polyimide foil, $25\mu\text{m}$ thick.

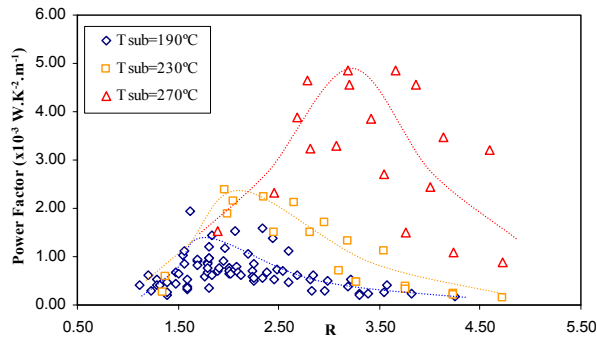


Fig 3: Power factor of Bi_2Te_3 thin-films as a function of Te/Bi evaporation flow rate ratio, R .

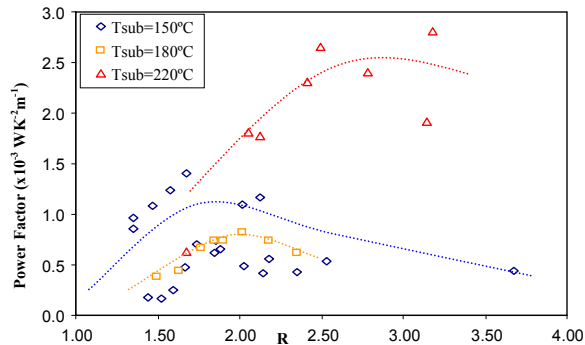


Fig 4: Power factor of Sb_2Te_3 thin-films as a function of Te/Sb evaporation flow rate ratio, R .

II.2 PATTERNING TECHNIQUES

Thermoelectric Bi_2Te_3 thin-films ($1 \mu\text{m}$ thick) were deposited on the kapton substrate. Transene's PKP negative photoresist was applied on the surface and test structures were patterned by wet-etching in $\text{HNO}_3\text{:HCl:H}_2\text{O}$ etchant. Fig 5 shows the

influence of etchant composition on the etch rates. Higher percent of HCl ($\% \text{HCl} / \% \text{HNO}_3 > 0.3$) induces cracking of the film and peeling occurs. Fig 6 shows the influence of etchant dilution (in water) on the etch rate. Dilution above 85% cause peeling to occur. For dilutions below 65%, etching occurs too fast and end-of-process is difficult to control. Best results are obtained with etchant of composition in the range $10\text{:}0\text{:}25$ to $10\text{:}2\text{:}40$ $\text{HNO}_3\text{:HCl:H}_2\text{O}$.

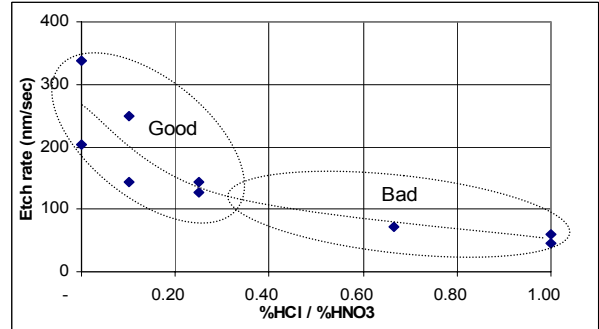


Fig 5: Etch rate of Bi_2Te_3 film in $(1-x)\text{HNO}_3\text{:}(x)\text{HCl}$ solution (diluted 70% in water, in volume).

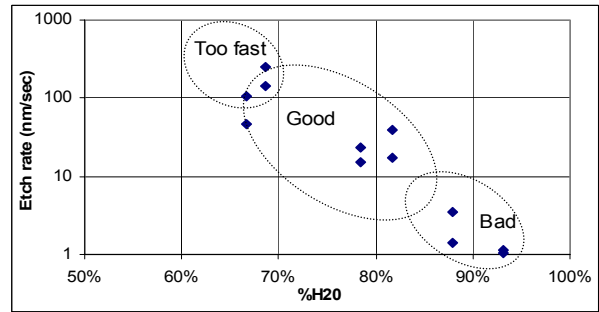


Fig 6: Etch rate of Bi_2Te_3 film in $10\text{:}1 \text{HNO}_3\text{:HCl}$ solution, as a function of dilution in water (in volume).

Fig 7 shows the influence of the etchant composition on the etching process of Sb_2Te_3 thermoelectric films. Cracking and peeling of the film occurs when high percentage of HCl is present in the etchant ($\% \text{HCl} / \% \text{HNO}_3 > 0.3$), as was observed for Bi_2Te_3 films. The etch rate of Sb_2Te_3 films in diluted HNO_3 was about 50 times smaller when compared with the etch rate of Bi_2Te_3 films in the same etchant. This is important in terms of the selectivity of the process in the presence of both materials. Influence of etchant dilution in the etch rates of Sb_2Te_3 films is shown in fig. 8. Best results are obtained with etchant of composition in the range $10\text{:}1\text{:}20$ to $10\text{:}2\text{:}40$ $\text{HNO}_3\text{:HCl:H}_2\text{O}$. Etch rates below $0.1\text{nm}/\text{sec}$ were observed for chromium and aluminum metals, for all the etchant compositions studied. Both Bi_2Te_3 and Sb_2Te_3 are etched with aluminum etchant ($16\text{:}1\text{:}1\text{:}2$

phosphoric acid, nitric acid, acetic acid and water) or Cr etchant (Sigma Aldrich 651826).

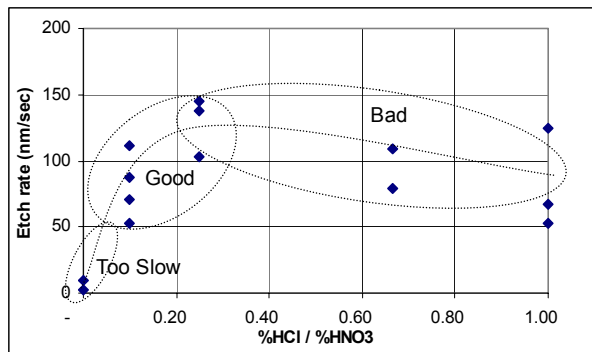


Fig 7: Etch rate of Sb_2Te_3 film in $(1-x)HNO_3:(x)HCl$ solution (diluted in 70% water, in volume).

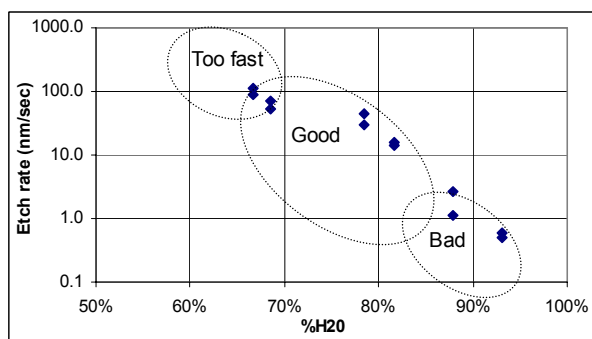


Fig 8: Etch rate of Sb_2Te_3 film in 10:1 $HNO_3:HCl$ solution, as function of dilution in water (in volume).

III DEVICES

A planar in-plane thermoelectric converter, with 8 pairs of thermoelectric elements was fabricated on top of a $25\mu m$ thickness kapton foil. An electric current of 4 mA was supplied to the device, to work as a microcooler. Using an infrared microscope, a thermal image of the device was acquired. A temperature difference of $5^\circ C$ was measured between the hot and the cold sides, under vacuum (fig. 10).

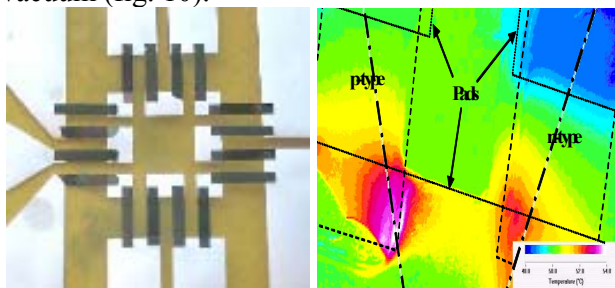


Fig 10: Photo of thermoelectric microcooler (left) and thermal image map of two thermoelectric legs (right), obtained by infrared microscope, when 4 mA are applied through the device.

IV CONCLUSIONS

Thermoelectric thin-films with high figure of merit (≈ 0.97 in n-type film and ≈ 0.56 in p-type film) were obtained by thermal co-evaporation deposition. Best films were fabricated with Bi (Sb) evaporation rate of 2 \AA s^{-1} and Te evaporation rate of $6-7 \text{ \AA s}^{-1}$. Substrate was heated to the temperature of $270^\circ C$ and $220^\circ C$ respectively for Bi_2Te_3 and Sb_2Te_3 films. The influence of the deposition parameters on the thermoelectric properties of the films was reported. Films were patterned by wet-etching in $HNO_3:HCl:H_2O$ and influence of the etchant composition in the etch rate and pattern quality were investigated. Best wet-etching results were obtained in 10:1:30 $HNO_3:HCl:H_2O$, with an etch rate of 100-200 nm/sec. Etch rate below 0.1 nm/sec was observed on aluminum and chromium films, allowing a selectivity higher than 1000. Bi_2Te_3 can also be etched in 30% HNO_3 etchant, with selectivity higher than 50 to Sb_2Te_3 films. This fabrication process was successfully applied in the fabrication of a thermoelectric microcooler, and a temperature difference of $5^\circ C$ was achieved.

V ACKNOWLEDGMENTS

This work was supported by ADI (MPYROM) and FCT (SFRH/BD/18142/2004). Thermal image analysis was performed in Cardiff University, UK.

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