Development of Thermoelectric Thin Films Based on Bi_2Te_3

O. Ben-Yehuda, Y. Sasson, Y. Gelbstein, G. Kimmel and Z. Dashevsky

Department of Materials Engineering, Ben-Gurion University, Beer-Sheva, Israel
E-mail: ohadbenyehuda@yahoo.com

Abstract

In this research p- type thin films based on $Bi_{0.5}Sb_{1.5}Te_3$ compound were developed for radiation sensors. The films were grown by two physical vapor deposition methods, namely an electron gun and flash evaporation techniques. The parameters of the different processes were examined and compared in order to maximize the c axis preferred orientation of the film as well as its thermoelectric figure of merit. The crystal structure and Seebeck coefficient of these films were investigated at room temperature. The electrical conductivity and Hall coefficient were measured from 80 to 300 K. The results indicate a high c axis preferred orientation for the films developed by the electron gun technique accompanied by a power factor in the vicinity of 30 µW cm^{-1} K^{-2} at room temperature.

Introduction

Thin film thermoelectric sensors are applied in various areas of science and engineering for the detection, measurement, observation and control of optical signals over the infrared wavelength range [1, 2]. The device is consisted of four parts (Fig. 1): (1) an infrared absorbing layer, (2) a thermoelectric transducer including p- and n-type thin layers, interconnected with metallic layers, (3) a cantilever substrate, preferable one with a very low electrical and thermal conductivity, (4) a massive base which has a high thermal conductivity and a high heat capacitance.

The absorbing layer is evaporated and placed on the cantilever substrate. It is sensitive to infrared radiation and converts this energy into a heat. The p- and n- type layers of the transducer are deposited between the absorbing layer and the massive base. The hot thermo-junctions are placed near the boundary of the absorbing layer while the cold thermo-junctions are placed at the joint of the substrate layer with the massive base. The massive base is used as a heat sink and possesses the ambient temperature T_0.

When an infrared signal hits the sensor it is absorbed and causes a temperature gradient along the thermoelectric transducer, by that, a Seebeck voltage is generated. It is very important to use an extremely thin cantilever substrate with a low thermal conductivity in order to minimize the substrate's thermal bypass. The specific detectivity of thermoelectric sensors D^*, is highly dependent on the thermoelectric figure of merit Z, as expressed in Eq. 1 [3],

$$D^* = \frac{\sqrt{Z \cdot T}}{(\sqrt{1 + Z \cdot T} + 1)} \cdot D_{ideal} \qquad (1)$$

Where T is the absolute temperature and D^*_{ideal} is the ideal sensor's detectivity which depends on T only [4].

It can be seen from Eq.1 that materials with high Z values are required for obtaining high D^*. Bi_2Te_3 based materials are well known p- and n- type semiconductors for thermoelectric applications near room temperature [5]. They display the highest values of the figure of merit ($Z = \alpha^2 \sigma / \kappa$) or power factor ($P = \alpha^2 \sigma$), where α is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. These compounds are characterized by a remarkable anisotropy linked to their crystal structure. This structure belongs to a space group R**3**m and the atomic layers stack in quintets. Inside each quintet strong covalent bonds prevail, while the quintets are bound by weak Van

der Waals bonds. This crystal anisotropy lies at the basis of the anisotropy of the thermoelectric figure of merit. While the Seebeck coefficient is isotropic, the electrical and thermal conductivities perpendicular and parallel to the *c* axis display anisotropic ratios. Thus the figure of merit perpendicular to the *c* axis is much higher than the one parallel to it. Therefore, the first objective in developing a high quality thermoelectric device based on Bi_2Te_3 compound is to maintain its *c* axis preferred orientation as much as possible.

In this research, *p*- type $Bi_{0.5}Sb_{1.5}Te_3$ thin films were fabricate by physical vapor deposition methods using both an electron gun and flash evaporation techniques. The crystal and transport properties of the different films were investigated in order to determine their quality and adjustment for sensors.
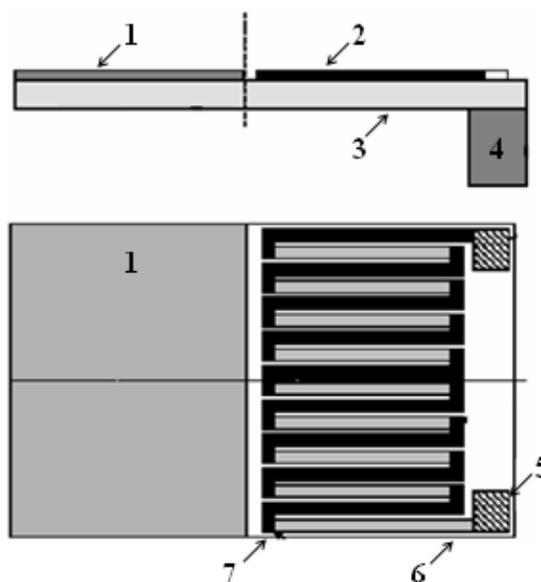
Figure 1: Schematic view of thin film thermoelectric sensor:
1 – Absorbing layer, 2 – Thermoelectric transducer, 3 – Cantilever substrate, 4 – Massive base, 5 - Contacts, 6 – The cold thermo-junction, 7 – The hot thermo-junction.

Experimental
$Bi_{0.5}Sb_{1.5}Te_3$ thin films are prepared by using both electron gun (EGT) and flash evaporation (FET) techniques. For the FET,

an initial fine $Bi_{0.5}Sb_{1.5}Te_3$ powder with grain size in the range of 177÷300 μm is supplied to a joule heated crucible from a container through a chute. The supplied powder is flashed evaporated and deposited on a glass plate fixed in a substrate holder. The substrate is heated by thermal radiation of the crucible. During the FET process two substrate's temperatures were investigated, 270°C and 220°C for sample A and B respectively. For the EGT, the same initial powder is used as the source for the thin films preparation. The powder is bombarded by electrons and the vapors are deposited on a glass plate. During the EGT process the investigated substrate's temperatures are 250°C and -86°C for sample C and D respectively. For both of the techniques, the vacuum pressure is 10^{-5} Torr, and the growth rate is 0.6 nm/sec, when the films thickness is 1 μm. After their preparation, the different films are annealed at 350°C for 1 hour.

The crystal structure of the different thin films was examined by X-ray diffraction using a Brucker D8 Advantage Diffractometer. TEM micrographs and Electron Diffraction patterns were conducted on samples prepared by EGT using substrate temperatures of 250^oC and -86^oC (similar to samples C and D). These samples were grown by two layer technique when the glass substrate was covered by NaCl layer (in order to separate the thermoelectric layer from the glass substrate). The samples didn't have any annealing treatment and their thickness is 0.1 μm.

For the transport properties measurements, gold film contacts on a chromium sub layer were prepared by thermal evaporation technique. The current-voltage characteristics were found to be linear for all samples over the whole temperature range. The electrical conductivity and the Hall Effect were investigated over the 80 to 300 K temperature range, inside a cryostat. The Seebeck coefficient was measured at 300 K.

Results and Discussion

Structural Properties

The strong *c* axis preferred orientation of the films prepared by EGT was determined from the XRD pattern, as shown in Fig. 2. All the (00*l*) peaks are very dominant in this pattern, while the other peaks, especially (015) and (110), are significantly lower. On the contrary, both of the films prepared by FET do not show any preferable orientation and their pattern resembles that of a randomly oriented powder. Therefore, the films prepared by EGT should exhibit higher figure of merit values than the films prepared by FET.
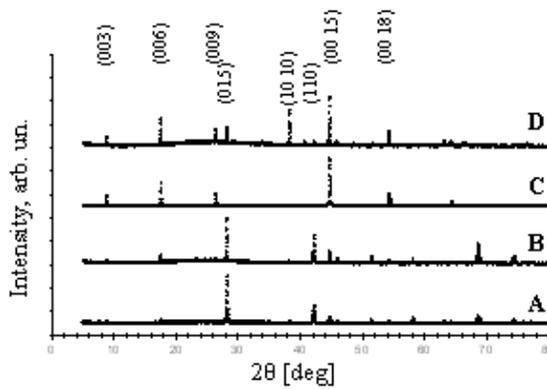
Figure 2: XRD pattern of the thin films prepared by: **A** – FET at 270°C, **B** - FET at 220°C, **C** – EGT at 250°C, **D** - EGT at -86°C.

TEM micrographs and Electron Diffraction patterns of samples prepared by EGT (without annealing) are presented in Fig. 3. Both of the electron diffractions present ring patterns, indicating some disordered in the structure which is less enhanced in the case of the higher substrate temperature (Fig. 3a). Based on the TEM micrographs (Figs. 3c and 3d), it is found that the average grain size was ~50nm and ~5nm for growing temperatures of 250°C and -86°C, respectively. The extremely small grains of the lower temperature substrate may indicate a reduced lattice thermal conductivity for this sample.
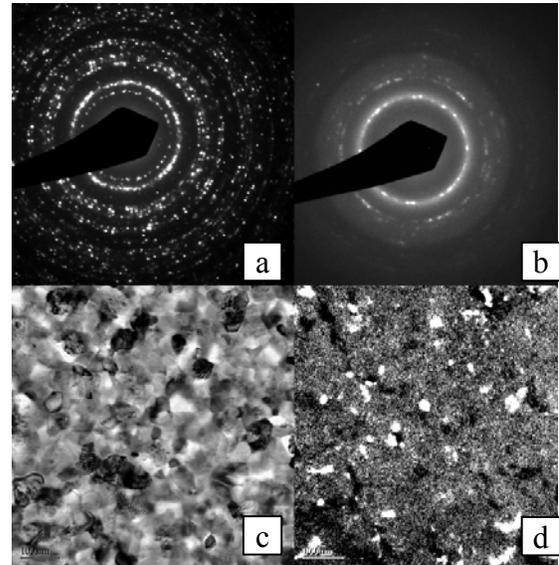
Figure 3: Electron Diffraction pattern and TEM micrograph of samples prepared by EGT using substrate temperatures of 250°C (a and c respectively) and -86°C (b and d respectively).

Electrical Properties

The Seebeck coefficient results are summarized in Table 1. The specific values in the vicinity of 135 μV/K indicate that the layers are more practical for above room temperature application [6] (for room temperature applications, Seebeck coefficient should be in the vicinity of 180 μV/K).

Table 1. Seebeck coefficient measurements at room temperature for the different films.

Sample	α, μV/K
A	140
B	135
C	125
D	145

The Hall coefficients of samples C and D were measured perpendicular to the growth axis at 88 and 300 K. The results show constant values as function of temperature, indicating a constant free carrier concentration at the valance band. The practical values of 0.11 ± 0.01 cm^3/C and 0.095 ± 0.01 cm^3/C, for sample C and D respectively, indicate the same free carrier

concentration regardless of the substrate temperature.

The electrical conductivities of samples B, C and D were measured perpendicular to the film growth from 80 to 300 K, as shown in Fig. 4. From the linear dependence of $\ln(\sigma)$ as function of $\ln(T)$ above 120 K, the scattering parameter x from $\sigma \sim T^x$ was deduced [7].
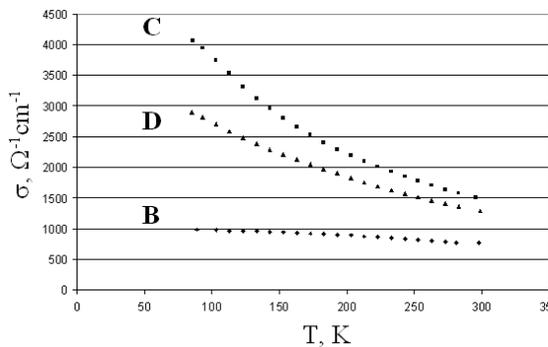
Figure 4: Electrical conductivity of the thin films vs. temperature.
Notations are the same as those in Fig. 2.

The higher conductivity values for the layers prepared by EGT indicating a better Z values. The scattering parameters are about 0.8 and 0.35, for the layers prepared by EGT and FET respectively. The theoretical value for lattice vibration scattering is 1.5, therefore other scattering mechanisms are dominant inside the films such as, surface and dislocation scattering [2, 8]. These scattering mechanisms are prone to reduce the Z values, thus a further optimization in the growth parameter is required.

Finally, based on Seebeck coefficient and electrical conductivity measurements, the power factor of the different layers was calculated at room temperature. This calculation yields values of 15, 26 and 28 μW cm^{-1} K^{-2} for samples B, C and D respectively. Combining the power factor value and the potentially reduced lattice thermal conductivity of sample D (due to its small grain size), indicates its potential higher Z values. However, stability effects of the grains size upon annealing should be further investigated in the future.

Conclusions

Thermoelectric $Bi_{0.5}Sb_{1.5}Te_3$ thin films were prepared by FET and EGT for different substrate temperature. The films prepared by EGT exhibit high c axis preferred orientation accompanied with good power factor values in the vicinity of 30 μW cm^{-1} K^{-2} at room temperature. On the contrary, the films prepared by FET do not show any preferable orientation while their electrical conductivity and scattering parameter are very low. Based on the Seebeck coefficient values, it seems that the p- type films are more appropriate for above room temperature applications. Therefore, the EGT process with the specific parameters described before can be considered for radiation sensors, which are performing at above room temperature surrounding.

References
1. A.G. Kozlov, *Sensors and Actuators* **84**, 259 (2000).
2. Z. Dashevsky, E. Rabih, V. Kasiyan, H. Halfin and M.P. Dariel, *Proceedings of the 25th International Conference on Thermoelectrics*, 180 (2006).
3. R. Fettig, *Proceedings of the 15th International Conference on Thermoelectrics*, 315 (1996).
4. R.A Smith, E.F. Jones and R.P. Chasmar, *The Detection and Measurement of Infra-Red Radiation* (Oxford University, England, 1957).
5. G.S. Nolas, J. Sharp and H.J. Goldsmid, *Thermoelectrics Basic Principles and New Materials Developments* (Springer, Berlin, 2001).
6. O. Ben-Yehuda, R. Shuker, Y. Gelbstein, Z. Dashevsky and M.P. Dariel, *J. Appl. Phys.* **101**, 113707 (2007).
7. B. Gol'tsman, V.A. Kudinov and I.A. Smirnov, *Thermoelectric Semiconductors Materials Based on Bi_2Te_3* (Nauka, Moscow, 1972) (In Russian).
8. G.C. Jain and W.B. Berry, *Transport Properties of Solid and Solid State Energy Conversion* (McGrew-Hill, New-Delhi, 1972).