Three Source Electron-Beam Co-deposited Thermoelectric BiSbTe Thin Films.

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Abstract

We present our ongoing research on three source electron-beam co-deposition of thin $Bi_xSb_yTe_z$-films. We show first promising results of the thin films while taking advantage of the high speed, cleanliness, reproducibility and low operating costs of e-beam co-evaporation.

A variation of the film thickness of the $Bi_xSb_yTe_z$ thin films was performed in the range of d = 240 nm to 620 nm as well as two different stoichiometries to compare the resulting layer properties. Additionally, one annealing step was applied to analyse its impact on said properties. For all samples Seebeck coefficient and electrical conductivity have been measured, and thermoelectric power factor has been derived before and after annealing.

Keywords

electron beam deposition, co-evaporation, BiSbTe, bismuth, antimony, tellurium, thin films, thermoelectric materials, Seebeck effect

1. Introduction

Thermoelectric materials are used in a wide field of applications, for example IR-sensing, thermometry, or electrical power generation using thermoelectric generators [1, 2, 3, 4]. A temperature gradient in a thermoelectric material leads to the forming of internal diffusion currents and generates a thermoelectric voltage (Seebeck effect).

The performance of a thermoelectric material with Seebeck coefficient α and specific electrical conductivity σ is described by the power factor:

$$PF = \alpha^2 \cdot \sigma \quad (\text{in W/m/K}^2)$$

where α is given in units V/K and σ is given in units of 1/Ω/m. For thermoelectric microdevices it is necessary to develop fast, clean, and reproducible thin film deposition techniques. The deposition of $Bi_xSb_yTe_z$-thin films has been shown in the past by several methods like flash evaporation [5, 6, 7], sputtering [8, 9, 10], electrodeposition [11, 12] or pulsed laser deposition [13]. However, as a fast, clean and reproducible method with low operating costs [14] electron beam (e-beam) co-evaporation should be taken into account. Compared to other common methods for the deposition of thin films on silicon wafers at production level, it also reduces the preparation time and cost. The produced thin films are then investigated in terms of σ, α and the resulting PF.

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2. Experimental details

All investigated films were deposited on 10 cm diameter borofloat glass discs. The samples were co-deposited out of seperate crucibles filled with 5n purity bismuth, 5n purity antimony, and 5n purity tellurium. The distance between the three separately controlled electron beam evaporator systems and the substrate amounts to 50 cm.

The $Bi_xSb_yTe_z$ thin films were deposited with a variation in stoichiometry and thickness in the range of d=240 nm to 620 nm. The film deposition was performed in high vacuum at a working pressure of 5×10^{-6} mbar or lower with a rotating substrate holder. For the whole e-beam co-evaporation process a total deposition rate of 7 Å s^{-1} to 8 Å s^{-1} was targeted and monitored by quartz crystal oscillators. For the e-beam co-evaporation the evaporation rates from the three separate targets were measured separately. After the deposition process, the glass wafers are coated with a protective layer of photoresist for further processing, and in this step they are subjected to a short annealing step at 80 °C for 20 min. After separation the resist is removed with acetone and afterwards cleaned with isopropyl alcohol and deionized water. Then the layers were characterized to determine their Seebeck coefficient and the sheet resistance was measured with a four point probe. The composition of the films was measured via wavelength-dispersive X-ray spectroscopy (microprobe analyzer Jeol JXA8800). Film thicknesses were measured with quartz crystal oscillators during the deposition and afterwards checked using a Dektak profilometer (Veeco DekTak 8), to evaluate the electrical conductivity of the films by using the before measured sheet resistance. As in several practical fabrication processes thermal annealing steps are necessary, for the films annealing steps of 14 h at 200 °C in nitrogen atmosphere were performed with a repetition of the above mentioned measurements, respectively.

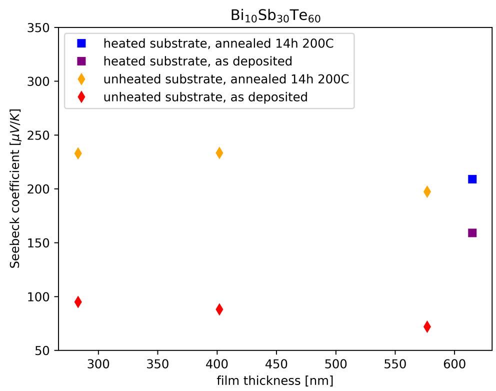

Figure 1: Seebeck coefficients of $Bi_{10}Sb_{30}Te_{60}$ thin films for different thicknesses. After annealing at 200 °C for 14 h there is an increase in value for all measured films.

3. Results & discussion

$Bi_{10}Sb_{30}Te_{60}$

For different film thicknesses the Seebeck coefficient of $Bi_{10}Sb_{30}Te_{60}$-thin films is shown in Figure 1. We deposited three layers of that composition on unheated glass substrates and one layer on a glass substrate that was heated to about 185 °C. The as deposited films without heating show Seebeck coefficients close to 100 μV/K while for an increase in film thickness, the Seebeck coefficient slightly decreases. After annealing for 14 h at 200 °C, the Seebeck coefficient increases by more than 100 % for each film deposited on unheated glass substrates with the highest value at 233 μV/K for 402 nm thickness. While the Seebeck coefficient for the thin films with 283 nm and 402 nm are nearly identical, it slightly decreased for the 577 nm-film with 197 μV/K. The $Bi_{10}Sb_{30}Te_{60}$-thin film deposited onto a heated substrate has a higher Seebeck coefficient of 159 μV/K as deposited compared to the films deposited on the non heated substrates. After annealing the Seebeck coefficient has increased to 209 μV/K, but is still even lower then of the before mentioned annealed even thinner films deposited without active substrate heating. What catches the eye is that the Seebeck coefficient for all $Bi_{10}Sb_{30}Te_{60}$-thin films are on a comparable range after annealing, but decreases slightly for higher film thickness. For the electrical conductivity of the $Bi_{10}Sb_{30}Te_{60}$-thin films, shown in Figure 2, there is a rather big difference between the deposition on the heated and non heated substrates. While the as deposited thin films on unheated substrates have electrical conductivities of about 6.9×10^3 Ω/m to 8.4×10^3 Ω/m, the as deposited film on the heated substrate has an electrical conductivity of 37.2×10^3 Ω/m. After annealing, the films on unheated substrates show a slight increase in electrical conductivity, while the annealing of the film deposited on the heated substrate led to a significant reduction to about 16.9×10^3 Ω/m.

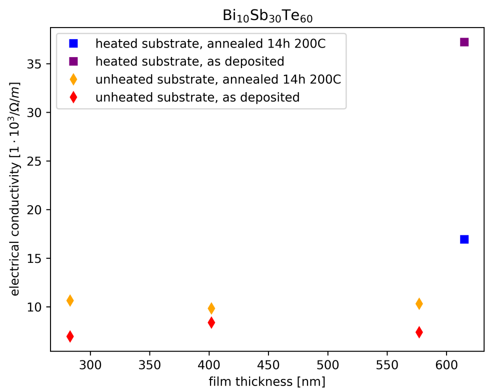

Figure 2: Electrical conductivity of $Bi_{10}Sb_{30}Te_{60}$ thin films for different thicknesses. The annealing at 200 °C for 14 h caused only small a increase for the depositions on unheated substrates and strong decrease for the film deposited on the heated substrate.

The power factor of the $Bi_{10}Sb_{30}Te_{60}$-thin films is shown in Figure 3. For the thin films deposited on unheated substrates a significant increase in the thermoelectric power factor is achieved through the annealing for 14 h at 200 °C, with a decrease towards higher film thickness. The power factor of the film deposited on the heated substrate is also significantly higher with 0.94 mW/m/K, while through annealing it decreases to 0.74 mW/m/K, but is still higher then the films deposited on unheated substrates.

$Bi_{11}Sb_{35}Te_{54}$

The results for the Seebeck coefficient of the second stoichiometry studied can be seen in Figure 4. All films

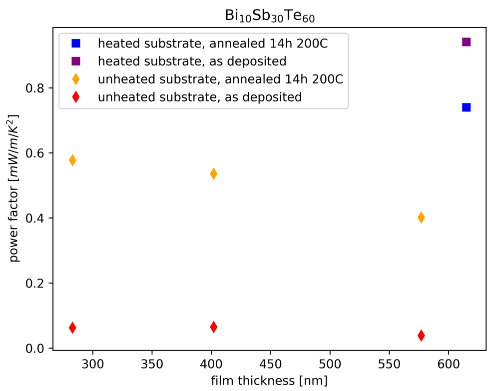

Figure 3: Power factor of $Bi_{10}Sb_{30}Te_{60}$ thin films for different thicknesses. After annealing at 200 °C for 14 h the power factor of all films deposited on unheated substrates have a strong increase. For the film deposited on the heated substrate the power factor decreased with annealing but is still higher compared to the before mentioned films.

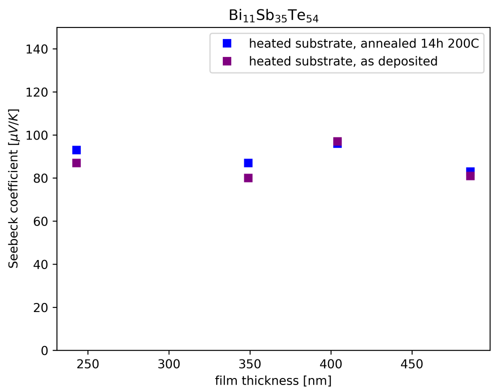

Figure 4: Seebeck coefficient of $Bi_{11}Sb_{35}Te_{54}$ thin films for different thicknesses. The values are similar for all investigated films, even after annealing at 200 °C for 14 h, but are lower compared to the $Bi_{10}Sb_{30}Te_{60}$-thin films.

were deposited on heated the substrates at 185 °C and show a comparable Seebeck coefficient, despite the variation of thickness. Furthermore after annealing for 14 h at 200 °C the Seebeck coefficient just slightly changes, which can be expected due to the small change in temperature. Compared to the previous shown stoichiometry the Seebeck coefficient of this films is significantly lower, which shows that stoichiometry is probably more important than layer thickness for good thermoelectric performance of $Bi_xSb_yTe_z$-thin films. The electrical conductivity of the thin films is shown in Figure 5 which again does not seem to show any dependence on the layer thickness, but the annealing shows more of an impact then for the Seebeck coefficient,

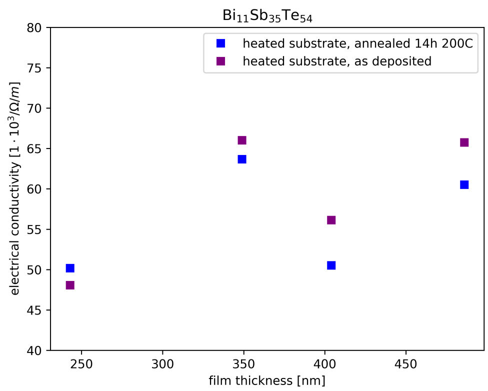

Figure 5: Electrical conductivity of $Bi_{11}Sb_{35}Te_{54}$ thin films for different thicknesses. Before and after annealing the values are significantly higher then that of the $Bi_{10}Sb_{30}Te_{60}$-thin films .

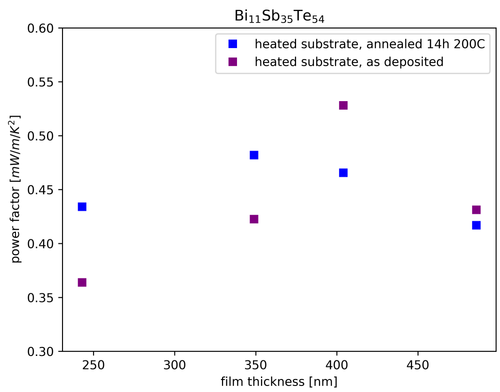

Figure 6: Power factor of $Bi_{11}Sb_{35}Te_{54}$ thin films for different thicknesses. The values are comparable to the $Bi_{10}Sb_{30}Te_{60}$-thin films deposited on unheated substrates even after annealing.

which is decreasing for the majority of the films, but not as much as for the $Bi_{10}Sb_{30}Te_{60}$-thin film showed earlier. In general, the electrical conductivity in these thin films is higher than that of the previous shown films of other stoichiometry. The power factor of the $Bi_{11}Sb_{35}Te_{54}$-thin films, as presented in Figure 6, is in general slightly lower compared to those of the the $Bi_{10}Sb_{30}Te_{60}$-thin films, especially when compared to the film deposited on the heated substrate. This leads to the conclusion, that in terms of thermoelectric power factor, the $Bi_{10}Sb_{30}Te_{60}$ stoichiometrie is the better composition.

4. Conclusion & Outlook

We presented our ongoing research on three source electron-beam co-deposition of thin $Bi_xSb_yTe_z$-films. We showed first promising results of the thin films.
A variation of the film thickness of the $Bi_xSb_yTe_z$ thin films was performed in the range of d = 240 nm to 620 nm to compare the resulting layer properties. Additionally, one annealing step was applied to analyse their impact on said properties. For all samples Seebeck coefficient and electrical conductivity have been measured, and thermoelectric power factor has been derived before and after annealing.
Promising thermoelectric properties were obtained for these preliminary samples. The promising results of $Bi_{10}Sb_{30}Te_{60}$-thin films will be verified by additional samples and further investigation by structure analysis to find the reason for the decrease in electrical conductivity.

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