

Fabrication of Thermoelectric Sensor Using Group V-VI Elements

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Abstract: This paper details the development of novel thermal sensors that harness the unique thermoelectric properties of group V-VI compounds, specifically bismuth telluride and antimony telluride. These materials were chosen for their excellent ability to convert thermal gradients into electrical signals, leading to enhanced sensitivity and operational stability in the developed sensors. The thermal sensors with Sb_2Te_3 and Bi_2Te_3 thin film legs through aluminum ohmic contacts are fabricated by a thermal evaporation method in vacuum. The thin film thermal sensors annealed at 473 K for 1 hour. The output voltage generated by the thermal sensors increases with increasing the number of pairs of the p-n thermoelectric legs. The sensor having four pairs of p-n thermoelectric legs exhibited maximum output voltage of 41.24 mV at the temperature difference 70 °C between the hot and cold junctions. The thermal sensitivity and the output voltage are found to improve after annealing it. The thermal sensitivity of as-deposited and annealed sensor was established to be 0.32 mV/K and 0.60 mV/K respectively.

Keywords: Sb_2Te_3 , Bi_2Te_3 , Thermal evaporation, annealing, thermoelectric, thermal sensitivity

I. INTRODUCTION

Thermal sensors are critical components in various applications ranging from industrial process control to medical diagnostics, necessitating materials with high sensitivity and reliability across a broad temperature range. The judicious selection of sensing materials is paramount for optimal device performance, with particular emphasis on those exhibiting superior thermoelectric properties [1]. Group V-VI elements, particularly chalcogenides, are highly capable for such applications due to their exceptional thermoelectric characteristics, including high Seebeck coefficients and favorable electrical conductivities [2]. This combination of properties allows for efficient conversion of thermal gradients into electrical signals, making them ideal candidates for advanced thermal sensing technologies [3]. The challenge in developing high-performance thermoelectric materials lies in simultaneously optimizing the Seebeck coefficient, electrical conductivity, and thermal conductivity, as these parameters are intrinsically linked and often exhibit counteracting dependencies [4]. This inherent correlation presents a complex materials science problem, requiring innovative synthesis and characterization techniques to decouple these properties and enhance overall thermoelectric figure of merit [5]. Semiconductor materials, especially gallium nitride and other two-dimensional materials, have garnered significant attention due to their unique electronic properties and potential for gas adsorption and sensing applications [6]. Specifically, gallium selenide, a layered III-VI semiconductor, has emerged as a particularly interesting candidate due to its hexagonal structure and potential for detecting dissolved gases in transformer oils, thereby extending its utility beyond traditional thermal sensing into specialized environmental monitoring [7]. The intricate interplay between these properties necessitates sophisticated material design strategies, such as nanostructure engineering and defect manipulation, to independently tune electrical and thermal transport phenomena [8].

Variety of work has been performed on the utilization of thermoelectric thin films of Bi_2Te_3 and Sb_2Te_3 for thermopile sensor. Bi_2Te_3 and Sb_2Te_3 are narrow band gap semiconductors with better thermoelectric characteristics at room temperature and possess promising potential applications not only for thermal sensors but also for micro generators and micro coolers [9]. Such sensing devices have advantages in energy harvesting because they can convert thermal energy into electric energy without any moving parts and fuel. Thin film technology has a number of deposition methods such

as co-sputtering, metal organic chemical vapour deposition, flash evaporation, pulsed laser deposition, thermal evaporation, electrodeposition and co-evaporation [10]. Thermal evaporation is attractive because it has comparatively low production cost than any other method and rapid process. M. Y. Kim and T. S. Oh [11] fabricated thermopile thin film devices by successive electrodeposition of p-type Sb_2Te_3 and n-type Bi_2Te_3 films, consisting of thin-film leg 11.3 mm length, 50 μm in width and 2 μm in thickness, exhibited a sensitivity of 7.3 mV/K.

II. EXPERIMENTAL

The thin film thermal sensors were deposited on unheated well cleaned glass substrates by thermal evaporation in vacuum ($\approx 10^{-5}$ torr) using molybdenum boat as a source. Bismuth telluride powder (99.99+ % purity) and antimony telluride powder (99.96+ % purity) procured from Sigma Aldrich; USA is used as source material to deposit the n-type and p-type thin film legs respectively, while aluminum powder is used as source material to deposit ohmic contacts by using patterned shadow masks. At first n-type Bi_2Te_3 films were deposited and then p-type Sb_2Te_3 films and finally aluminum films provided shorting between n and p films on one end while there was an ohmic contact on both ends with suitable masking. All the films of nearly uniform thickness 0.3 μm were deposited under almost the same environment and conditions. The rate of deposition and thickness of the films were controlled by using quartz crystal thickness monitor model no. DTM-101 provided by HINDHIVAC. The deposition rate was maintained 5–7 $\text{\AA}/\text{sec}$ constant throughout the thin films preparations. The source to substrate distance was kept 14 cm for all the depositions. The alumel-chromel thermocouple placed in contact with the substrates revealed that the substrate temperature remains practically constant (at ≈ 305 K) during the deposition. Deposited films were kept under vacuum overnight after each deposition. In order to improve the performance of the thin film thermal sensors, annealing process is performed [35]. The selected three sensors TS_1 , TS_2 and TS_3 were annealed at 473 K for 1 hour under the vacuum of $\approx 10^{-5}$ torr and then used for characterization. The dimensions and the number of pairs of the p-n thermoelectric legs of the sensors are given below.

Thermal sensor (TS-1): The dimension of p- and n- type leg is 60 mm (length) $\times$ 10 mm (width) $\times$ 0.3 μm (thickness) and one pair of the p-n thermoelectric legs. Annealed at 473 K for 1 hour under the vacuum.

Thermal sensor (TS-2): The dimension of p- and n- type leg is 55 mm (length) $\times$ 4 mm (width) $\times$ 0.3 μm (thickness) and two pairs of the p-n thermoelectric legs. Annealed at 473 K for 1 hour under the vacuum.

Thermal sensor (TS-3): The dimension of p- and n- type leg is 25 mm (length) $\times$ 4 mm (width) $\times$ 0.3 μm (thickness) and four pairs of the p-n thermoelectric legs. Annealed at 473 K for 1 hour under the vacuum.

Thermal sensor (TS-4): The dimension of p- and n- type leg is 25 mm (length) $\times$ 4 mm (width) $\times$ 0.3 μm (thickness) and four pairs of the p-n thermoelectric legs. Used as deposited for characterization.

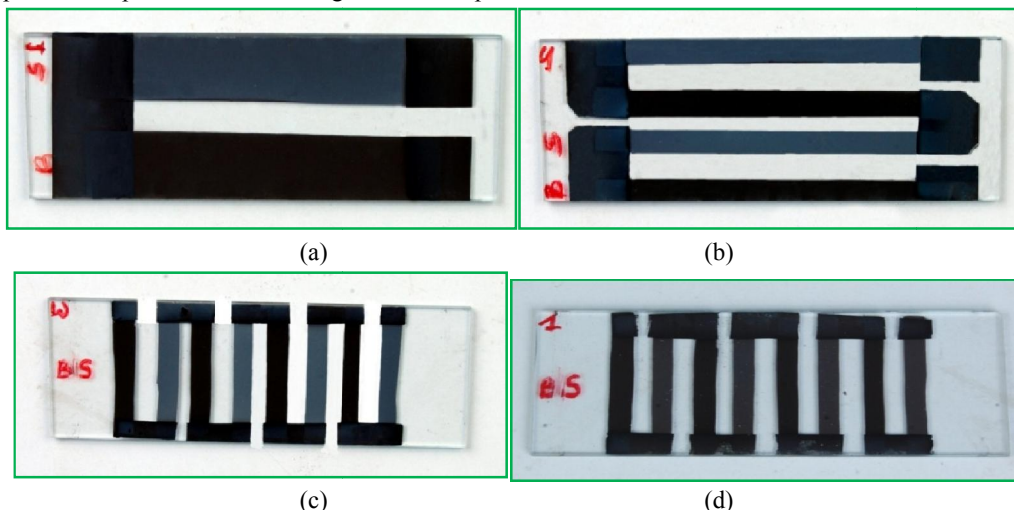


Fig. 1 Photographs of thin film thermal sensors (a) TS-1, (b) TS-2, (c) TS-3 and (d) TS-4

III. RESULT AND DISCUSSION

Characterization

The X-ray diffraction patterns of selected Bi_2Te_3 and Sb_2Te_3 annealed samples were recorded by X-ray diffractometer (Bruker, model D-8 Advance) with $\text{CuK}\alpha$ radiation (1.5406 Å). The surface morphology of these films was investigated by field emission scanning electron microscope (FESEM) using model Hitachi S-4800-II (Japan).

Structural Characterization

The XRD patterns of the thermally evaporated Bi_2Te_3 and Sb_2Te_3 thin films annealed at 473 K for 1 hour in vacuum are shown in Fig. 2 (a) and (b) respectively. It shows that, all the films are polycrystalline exhibiting rhombohedral structure. The XRD pattern of the Bi_2Te_3 samples, Fig. 2 (a) has the characteristics features corresponding to (015), (1010), (0111), (110), (0015), (116) and (1013) planes and are in very good agreement with rhombohedral structure JCPDS card No. 15-0863 ($a = 4.3852$ Å and $c = 30.483$ Å). The peaks (1010) and (0015) are strong, as compared with the other peaks.

The presence of sharp peaks in the XRD pattern of the Sb_2Te_3 , Fig. 2 (b) shows the polycrystalline nature of the film. For the Sb_2Te_3 films, all peaks corresponding to (015), (1010), (0111), (110), (113), (0015) and (300) planes could be indexed to rhombohedral phase, are in good agreement with the JCPDS X-ray file data (card number 15-0874, $a = 4.262$ Å and $c = 30.450$ Å). The sharp and intense XRD peaks direct the Sb_2Te_3 films have high degree of crystallinity. The peaks (1010) and (113) are strong, as compared with the other peaks. The strongest intense line indicates the (1010) plane is about 2θ of 37.59° . These samples also shows very lower intensity peaks for (015), (0111), (110), (0015) and (300) planes.

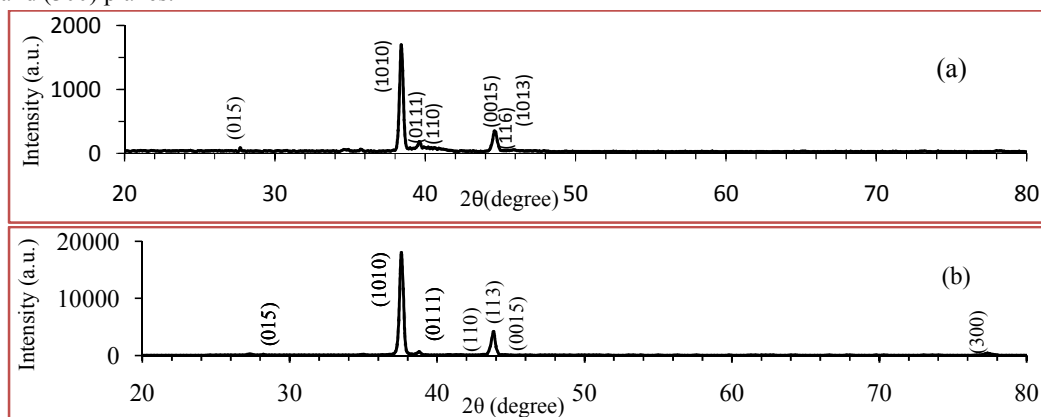


Fig. 2 X-ray diffraction patterns of Bi_2Te_3 and Sb_2Te_3 thin films annealed at 423 K for 1 hr in vacuum

Measurement of output voltage

The output voltage of the thin film thermal sensors is measured by imposing a temperature difference (ΔT) between hot and cold junctions of the sensors. The schematic diagram of the measurement for the output voltage is shown in Fig. 3. One end of the substrate is contacted with a heater, while another end with a heat sink. By applying a current to the heater, the temperature difference is imposed ranging from 5°C to 75°C between hot and cold junctions of the sensors. The imposed temperature gradient is parallel to the length of thermoelectric legs. The temperatures of hot and cold junctions are measured near the center of the substrate by using alumel-chromel thermocouples. The output voltage of all the thin film thermal sensors is measured at the aluminum contacts deposited on the thermoelectric legs. The output voltage of the thermal sensors is compared with number of pairs of the p-n thermoelectric legs. The sensitivity of annealed and as-deposited sensors is also compared.

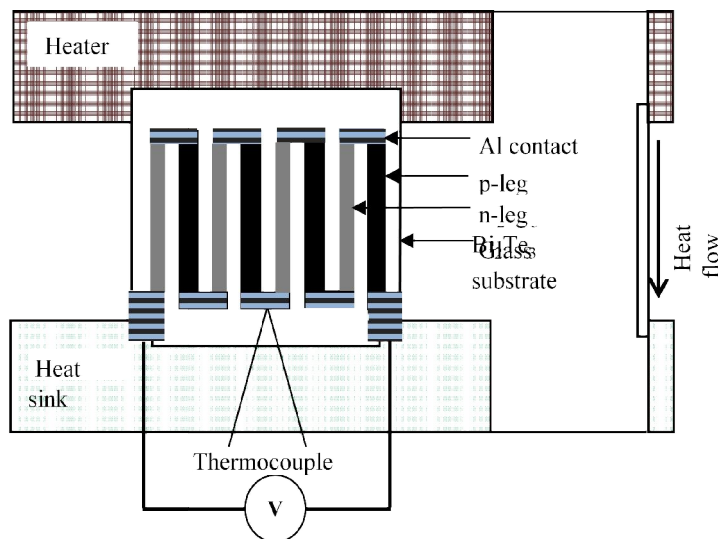


Fig. 3 Schematic diagram of the measurement for the output voltage of the thin film thermal sensors

Characterization of thin film thermal sensor

The performance of n-type Bi_2Te_3 and p-type Sb_2Te_3 thin film thermal sensors deposited by thermal evaporation and annealed at 473 K for 1 hour is investigated near room temperature. The output voltage is measured by making the temperature difference (ΔT) between the hot and cold junctions of the thermal sensors. Fig. 4 shows the output voltage of thermal sensors TS-1, TS-2 and TS-3 measured as a function of the temperature difference.

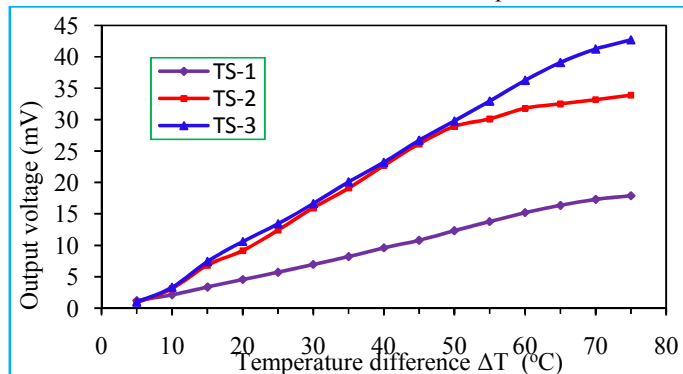


Fig. 4 Output voltage of thermal sensors as a function of the temperature difference (ΔT)

Fig. 4 illustrates that the output voltage of all the thin film thermal sensors is nearly proportional to the temperature differences over the range 5 °C to 50 °C. The linearity changes to some extent above the temperature differences 50 °C, major change is observed in the case of sensor TS-2.

Fig. 5 reveals the dependence of output voltage at temperature difference (ΔT) = 70 °C generated by the thermal sensors depend upon the number of pairs of the p-n thermoelectric legs (type of thermal sensor). It illustrates that the output voltage of the sensor increases with increase in the number of p-n pairs. The sensor TS-3 composed of four pairs of the p-type Sb_2Te_3 and n-type Bi_2Te_3 thin film legs exhibited output voltage 41.24 mV at temperature difference 70 °C between the hot and cold junctions of the thermal sensor.

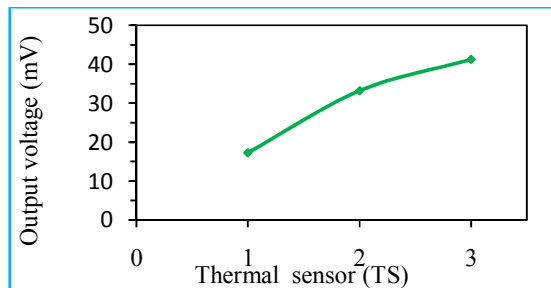


Fig. 5 Output voltage of sensors as a function of type thermal sensor (Number of p-n pairs)

The slope of the output voltage against temperature difference curve gives thermal sensitivity of the sensor. The output voltage and sensitivity of the annealed sensor TS-3 and as-deposited sensor TS-4 composed of four pairs of the p-type Sb_2Te_3 and n-type Bi_2Te_3 thin film thermoelectric legs deposited under the same environment and conditions is compared and shown in Fig. 6.

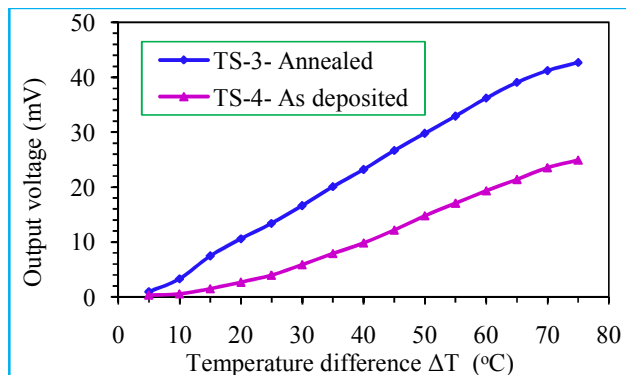


Fig. 6 Output voltage of annealed and as-deposited sensors as a function of the temperature difference (ΔT)

As shown in Fig. 6, the output voltage of annealed and as-deposited sensors is proportional to the temperature difference over this range of temperatures. It is clear that output voltage of the thin film thermal sensor improves upon annealing treatment at 473 K for 1 hour. The annealed thermal sensor (TS-3) exhibited sensitivity, i.e. the slope of output voltage - temperature difference curve, of 0.60 mV/K, whereas as-deposited thermal sensor (TS-4) exhibited sensitivity of 0.32 mV/K. This was much larger than 0.19 mV/K measured for a thermoelectric sensor prepared with single pair of silicon-on- insulator structure by L. M. Goncalves et al [13]. Again Fig. 7.9 reveals that sensitivity of annealed and as-deposited sensors decreases at higher temperature difference (ΔT above 70 °C).

The sensitivity of thermo-pile sensor depend upon annealing temperature, number of the p-type Sb_2Te_3 and n-type Bi_2Te_3 thin film legs, thickness of thin film legs and other many factors [10,12,14]. The fabricated thermal sensor device can directly produce a small electrical power from thermal energy. This same type of device can be used to implement a thermoelectric generator as an alternative power source for small electric devices and systems by employing high performance thermoelectric materials and miniaturization. The endorsement of thermoelectric technology largely depended on the research and development of more optimum thermoelectric materials.

IV. CONCLUSIONS

The thermal sensors with p-type Sb_2Te_3 and n-type Bi_2Te_3 thin film legs through aluminum ohmic contacts are successfully fabricated by a thermal evaporation method in vacuum. The output voltage of the thin film thermal sensors annealed at 473 K for 1 hour is practically proportional to the temperature difference (ΔT) between hot and cold junctions of the sensors. The output voltage generated by the thermal sensors increases with increasing the number of pairs of the p-n thermoelectric legs. The sensor having four pairs of p-n thermoelectric legs exhibited maximum output voltage of 41.24 mV at the temperature difference 70 °C between the hot and cold junctions. The thermal sensitivity

and the output voltage of the thin film thermal sensor are found to improve after annealing it at 473 K for 1 hour. The thermal sensitivity of as-deposited and annealed sensor was established to be 0.32 mV/K and 0.60 mV/K respectively.

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