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Unraveling energy consumption by using low-cost and reevaluated thermoelectric Thin Films

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Abstract: Energy is undoubtedly one of our most important demands whose consumption is constantly increasing and will continue to increase soon. One of the most important factors in attaining the required energy is to provide high efficiency at a low cost with the help of new technological improvements by evaluating wastes. Energy demand could be achieved for a relatively large thermoelectric power value by recycling the Peltier modules from waste ones and adjusting their properties with nanotechnology. For this aim, thermoelectric thin film modules were grown on silicon (Si), glass, and Kapton substrates with thermal evaporation method by using two different BiTeSb/BiTeSe alloy materials which are placed in industrial Peltiers as the p- and n-type semiconductor. The thin films structural and morphological characterizations were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) experiments reveal fine surface with uniformly distributed continuous structure. Seebeck coefficiency (|S|) of the substantial modules were investigated by forming certain temperature gradients on them making serial connections using a homemade measurement setup. $|S| = 143.86$ μV/K is obtained for the thermoelectric module on Si substrate and 44.96 μV/K and 24.98 μV/K are calculated for glass and Kapton, respectively.

Key words: Thermoelectric effect, BiTe, Seebeck effect

1. Introduction

Energy sources and carbon emission problems are coming to a state as important as green technology and its derivatives which continue to be reconceived with an increasing interest in the worldwide. In addition to green energy problems, the evaluation of wastes and the reevaluation of existing technologies and the development of more advanced technological products have gained importance today. To overcome these problems, the thermoelectric (TE) effect is presented as a choice of basic technology that can generate electrical energy using the temperature gradient in the environment. With the help of the thermoelectric effect, it is possible to obtain electrical energy from waste heat. The materials existing with the TE effect present many advantages over other generating energy technologies due to their environmentally friendly and renewable facts. Thermoelectric materials can directly convert thermal gradient into the electric potential gradient and vice versa, without any mechanical moving parts. Thermoelectric products can be evaluated as electrical generators or coolers/heaters in a variety of high-tech applications such as power generation systems, micro- and macrocoolers and heaters, and infrared detectors [1].

According to our best knowledge, commercially purchased industrial Peltiers including telluride (Te) based systems (n-type Bi_2Te_3 and p-type Sb_2Te_3) are thermoelectric materials commonly utilized in the

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thermoelectric community because of their elevated Seebeck coefficient, relatively low electrical resistance, and thermal conductivity properties. BiTe alloy is a semiconductor, which can be adapted to be n- or p-type by replacing the composition with minor deviations from its stoichiometry composition [2]. Due to the possible applications in low-dimensional thermoelectric devices, Bi_2Te_3 films ranging from submicron to several micron thicknesses are produced and several studies have been carried out on their applications [3–5]. To develop the Bi_2Te_3 films, detailed methods such as physical and chemical vapor deposition, sputtering, thermal evaporation, and electro-deposition methods have been realized [6–8]. Among these film deposition methods, thermal evaporation is explored extensively due to its many advantages such as including cost-effectiveness, rapid growth rates, and being relative in determining film thickness from nanoscale to a macroscale.

The facts of energy consumption, which is one of the problems in the world, could be achieved by evaluating the Peltier modules with a relatively large thermoelectric power value by justifying the properties with thin film production technology. Thin film deposition technology is used to shrink conventional bulk production devices to micron size. In general, commercial thermoelectric devices are produced from sintered bulk materials. However, these bulk materials have a low figure of merit (ZT) due to both their electrical conductivity and low Seebeck coefficients [2,9,13]. To increase thermoelectric properties, low-dimensional interactions are used to boost the density of states (DOS) in the vicinity of the Fermi level, enhancing phonon scattering on nanostructured materials and giving a lead to increase charge carrier mobility [10] and thin film nanotechnology allows for the probability of decorating the devices to micro- or nanodimensions and for easy coordination with the standard applications with different substrate options.

In this study, we reorganized the p- and n-type alloys in the commercially waste industrial Peltiers and deposited them in the thin film form to develop even more technologically advanced thermoelectric module products and examined the structural and thermoelectric properties of these modules to measure the waste of the heat recovery. We deposited the BiTeSe and BiTeSb thermoelectric thin films systematically by using thermal evaporation on Si, glass and Kapton substrates from the commercially industrial Peltier modules. By using a mask, p- and n-type series of thermoelectric modules were obtained. Simultaneously, the effects of different substrate on thermoelectric properties of BiTe alloys were also investigated for the possibility of coordination to the next-generation flexible electronic device applications.

2. Materials and methods

BiTe was deposited on p-type Si (100), glass and Kapton substrates by using a conventional thermal evaporation method. The molybdenum crucible is utilized as a heater resistive element for rapid heating and to achieve a uniform pattern of the vapor flow. The low purity BiTe-based pieces which were obtained from commercially industrial p- and n-type Peltier alloys manage as the source alloy in the thermal evaporation process. BiTe film within the approximate deposition rate was 4 Å/s. The thin films were evaporated at room temperature with pressure below 3.5×10^{-5} Torr. The thickness of films was established approximately 30 nm by the X-ray reflectometer (XRR). Then, the thermoelectric thin film modules were heat-treated at a temperature ranging from 523 K to 600 K for 120 min under a vacuum atmosphere. The effect of substrate features on the structure and thermoelectric properties of BiTe thin films was examined.

Two basic techniques for measuring the Seebeck coefficients were used in this study. One of the basic parameters used to define the thermoelectric effect is integral and differential methods. In the differential method, a Seebeck coefficient is found for each temperature value using low temperature gradients (ΔT), and deviations from the origin of this voltage magnitude (ΔV) that is generally observed. In order to avoid these deviations, an initial calcinations value is determined for each temperature value and thus results that are more accurate are sought. However, in the integral method, temperature gradient (ΔT) can be much larger. Thus, it is unnecessary to obtain a calibration value for each temperature value. Also, the integral method largely overcomes the problems having the attendance of poor electrostatic strengths produced in the system due to the large Seebeck voltage or difference in the electrical potential leading to the large temperature gradients. The deficiency of this method is that it provides more accurate results for more accessible temperatures. The integral method is preferred for metal samples whose one side is kept at a constant temperature (usually 300 K) and the other side is in the selected temperature. The Seebeck coefficient at a chosen temperature value can be acquired from the slope of the Seebeck voltage, i.e. any point of the curve 'S = (dV(T))/dT' [11]. The large thermal difference is a natural characteristic of integral method. As shown in Figure 1, the differential method is also used in the experimental part of the work and refrigerant for the cold side (273 K) (Peltier module I, TC) and for the hot side (Peltier module II, TH) modules are used to provide a high temperature gradient. It is shown that the Seebeck coefficient obtained from the voltage values used for different temperatures of the integral method was used in this study.

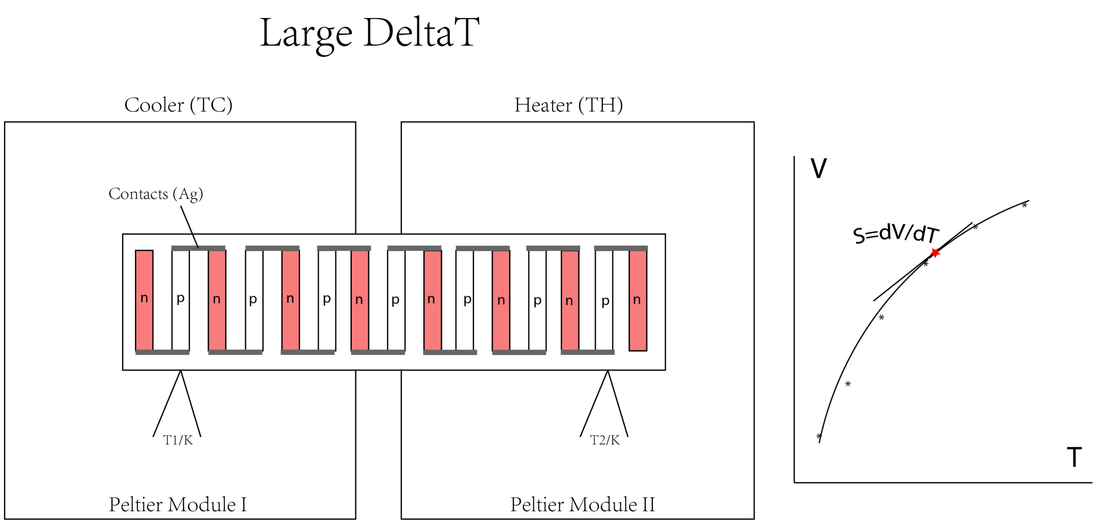

Figure 1. Schematic presentation of integral method in this study and graphical presentation of integral method voltage (V) and temperature (T) [11].

Figures 2a–2c show the nanofabricated thermoelectric thin film modules. Figure 2a reveals the thermoelectric thin film module, which has been subjected to heat treatment in the order of 10^{-6} mbar, placed on the heat treatment sample holder. On a 2.5 $\times$4 cm^2 Si, glass, and Kapton substrates BiTeSb as p-type material is growth by evaporation with vertically aligned 0.2 $\times$1 mm^2 a rectangular form. Then, another mask is performed with the same size parallel to the previous one where BiTeSe is used as n-type material for the modules within 10 legs. To measure the thermal gradient difference, thin film modules were placed on the top of two Peltier modules (TEC1-12707) and Ag paste was used to connect the p- and n-type series electrically. The potential difference was obtained using a nanovoltmeter (Keithley 2182A). A thermal imager (Fluke Ti25) was accessed to obtain the temperature difference between contacts which varied by the heating and cooling of the two Peltier elements under the sample module as seen by thermal camera images of Figure 2c. In order to realize temperature characterization, hot and cold tips were determined by thermal camera. As given in Figure

2c, the temperature differences created by the temperature gradient obtained from the film surface are clearly observed.

Elementary composition and surface morphology properties of the thin films were investigated by a scanning electron microscope (SEM) and energy dispersive X-ray (EDS) Jeol-6510. X-ray diffraction analysis was measured in a GIX-ray diffractometer (GIXRD) RIGAKU SmartLab by using Cu-K_α radiation and the XRD patterns were examined the angular 2θ ranging between 20°and 110°.

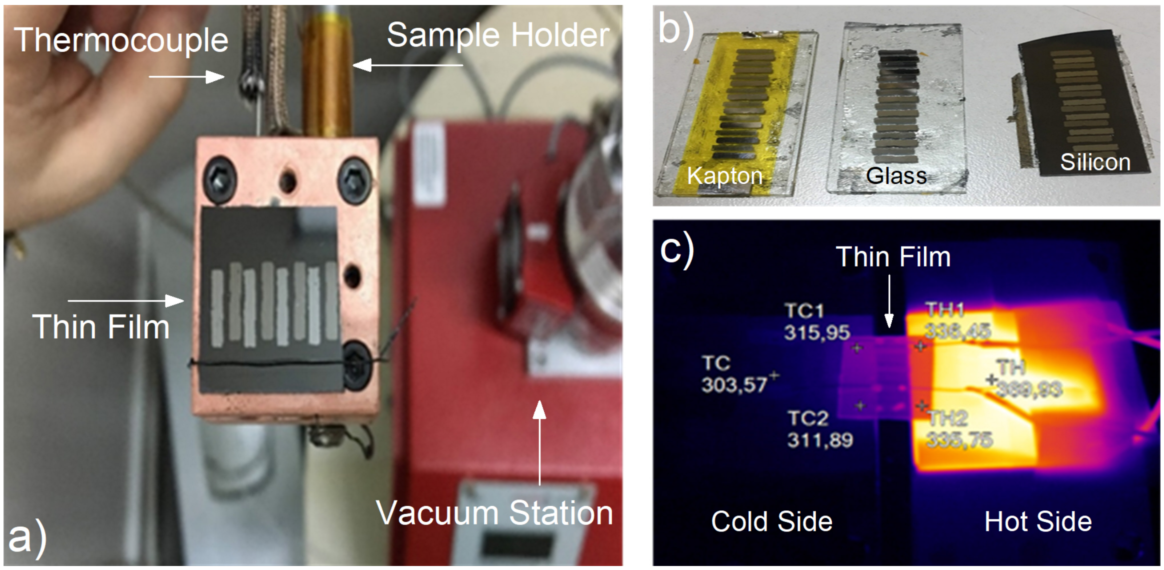

Figure 2. a) Heat treatment process stage (sample holder-thermocouple-vacuum station-mounted thin film), b) BiTe modules on Kapton–glass–silicon substrates, c) thermal camera image of thin film (cold and hot side temperature values) in the integral method.

3. Results

Generally, p- and n-type modules are underlined to the utility from two different carrier types to increase the thermoelectric properties of the module. These are often connected thermally in parallel and electrically in series, demonstrating the efficiency and enhancing diversity for applications. In this study, thin films of Antimony (Sb) were chosen as an p-type material, and Selenium (Se) was chosen as a n-type material [12, 13].

Figure 3 represents the X-ray diffraction (XRD) patterns of BiTeSb and BiTeSe thin films on various substrates at room temperature. In Figure 3a, a polycrystalline structure of the BiTe thin films which is given for silicon substrates is revealed. Because of the low purity of the evaporated alloys and deposition at room temperature, there is not enough energy to grow the samples in crystal form. Therefore, the diffraction peak intensities are a little bit smaller than those in the literature. The most observed diffraction peak at $2\theta = 43.5^{o}$agrees well with the literature for BiTe when preferential orientation is considered in the analysis of X-ray diffraction [14]. It was achieved preferentially oriented with their (115) planes parallel with using X-ray diffraction. Due to the small concentration of Sb and Se elements, no difference is obtained from the XRD peaks. The X-ray reflectometry (XRR) measurement is also given in the inset of Figure 3a. The calculated thickness value for all types of thin film is around 30 nm. In Figures 3b and 3c, the XRD peaks of BiTe thin films on glass and Kapton substrates are exhibited. Because of the amorphous substrates, there is no indexable peak obtained for BiTe thin films.

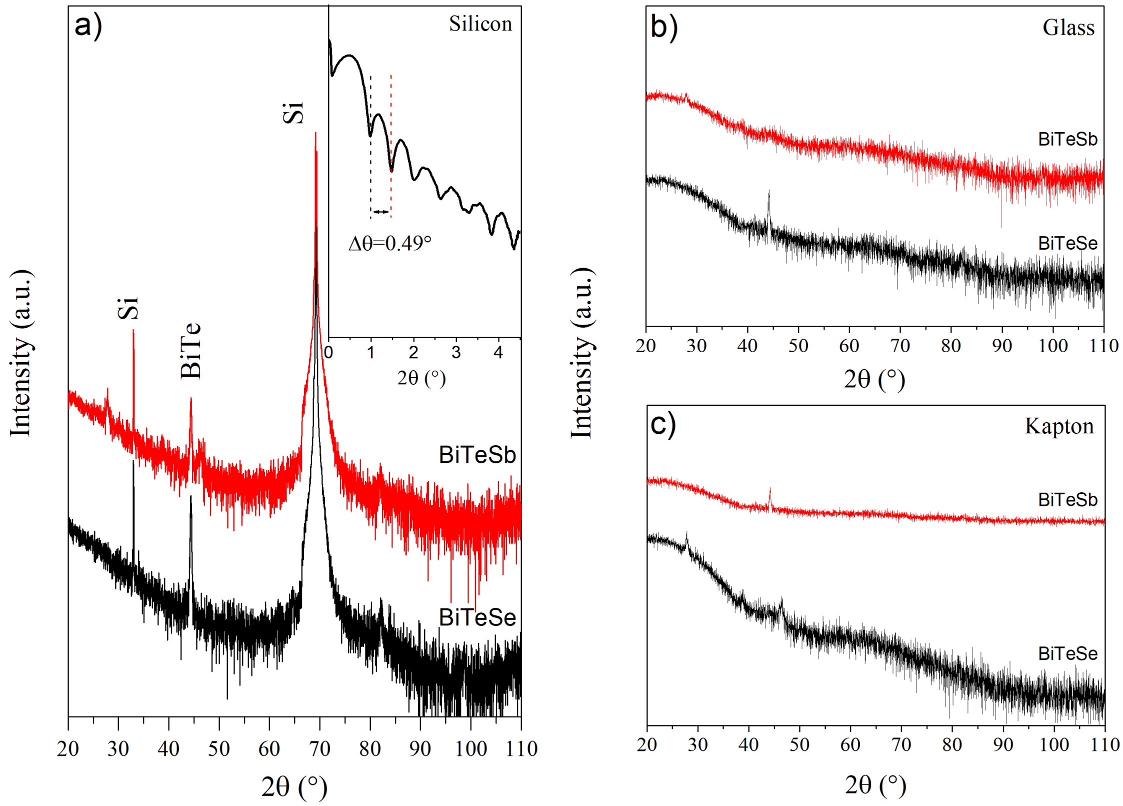

Figure 3. XRD patterns of BiTe thin films on a) silicon, b) glass, c) Kapton substrates, inset of a) XRR measurement of thin film.

The SEM images in Figures 4a and 4b illustrate that the surface morphologies of evaporated BiTe thin films are deposited at room temperature. The granular structures are obtained for two different types of as-deposited thin films. They also show a fine surface with the uniformly distributed continuous structure. Total performance of thermoelectric thin films critically lies in both crystal structure and film surface morphology. Presenting grain boundaries to enhance phonon scattering is often performed to increase electrical transport. For this aim, heat treatment process is performed for the film modules at various temperature values.

Heat-treated thermoelectric modules time dependent voltage measurements and Seebeck coefficient calculation on different substrates are shown in Figure 5.

In Figures 5a–5c, an increasing voltage trend is obtained for the p-n thermoelectric module on Si substrate because of the dominated p-type structure. The resulting voltages of the films prepared in different substrates depending on the time obtained in the determined periods were found. The internal voltage gradually increased with the temperature difference. Each step observed in the voltages given in the graphs corresponds to the increased temperature change. In other words, the upper temperature was reached in time where the voltage is plan form, and thus, it was tried to be created in semiadiabatic and equilibrium conditions. According to calculation, $|S| = 143.86$ μV/K is obtained for the thermoelectric module on Si substrate and 44.96 μV/K and 24.98 μV/K are calculated for glass and Kapton, respectively.

It is seen that the Seebeck coefficient of the thin film enlarged on Si substrate is better than those obtained on glass and Kapton. The main reason for this is that the Si substrate is crystalline. As is known, single crystals have higher electrical conductivity than amorphous materials. Thermal conductivity values of these materials

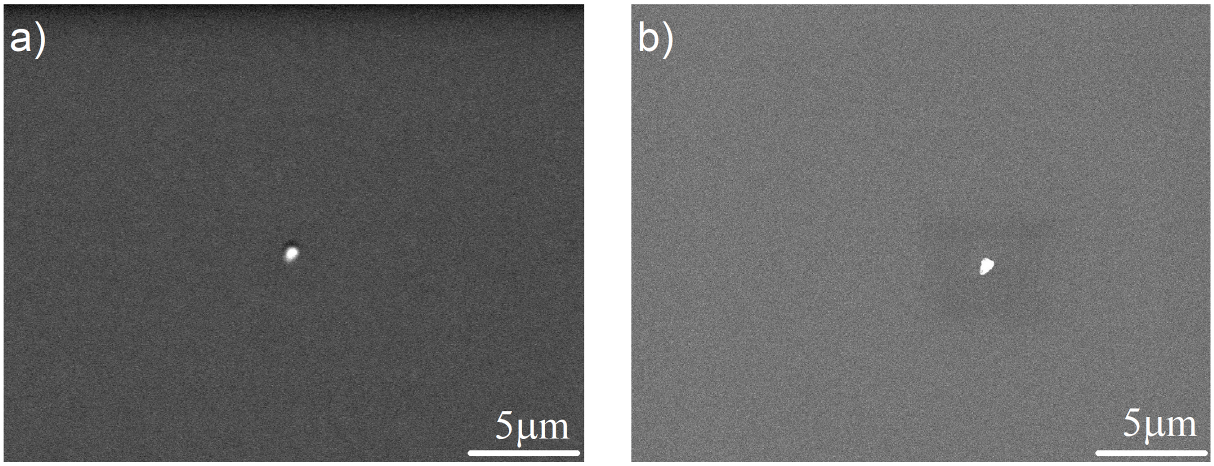

Figure 4. SEM images of a) BiTeSe, b) BiTeSb thin films.

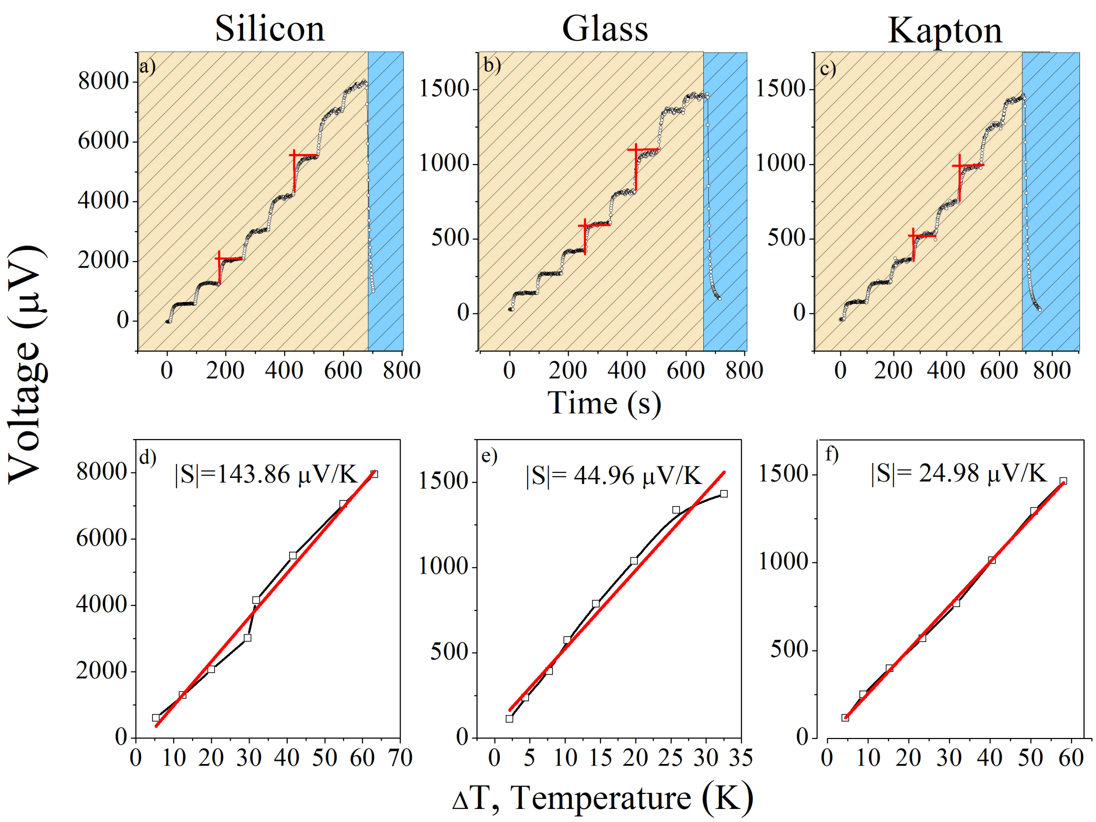

Figure 5. Time dependence of voltage generated BiTe thin films on a) silicon, b) glass, c) Kapton and applied temperature gradient dependence of voltage generated a) silicon, b) glass, and c) Kapton substrates.

have higher conductivity than amorphous materials because of their lower resistance. It is known that the thermal conductivity coefficient must be low in order to have high thermoelectric properties. The main reason for this is that the more heat is stored in the material, the higher the Seebeck coefficient can be obtained. The proof of this statement is thought to be due to the constant magnitude of the thermoelectric effect. Thus, thermoelectric properties are observed to be lower as the thermal conductivity coefficient of amorphous materials is lower than that of crystal materials. This result confirms similar studies in the literature which is also given in Table.

Table . Seebeck coefficients of BiTe thin films.

Thin film	|Seebeck coefficient|(μV/K)	Reference
BiTeSb-BiTeSe on silicon	143.86	This work
BiTeSb-BiTeSe on glass	44.96	This work
BiTeSb-BiTeSe on Kapton	24.98	This work
$Bi_2Te_3/SiO_2/Si$	150	[5]
Al_2O_3/ZnO-BiSbTe on Si	–62.4	[15]
BT-BST on Si	390	[15]
AZO on glass	–134	[16]
Mg_2Si - Mg_2Sn on glass	110	[17]
p-type Bi_2Te_3/Sb_2Te_3	130	[18]
n-type δ-doped $Bi_2Te_{3-x}Se_x$	–276	[19]

Thermal and electrical properties of the materials are improved by using only nanotechnological production method when passing from bulk form to thin film ones. These material systems, which exhibit superior properties in the bulk form, showed even more superior properties when produced and developed by nanotechnological method. This is mainly due to the reduction of the particle size and increase of the boundaries of the particles during the nanotechnological production, resulting in a decrease in thermal conductivity and an increase in the electrical conductivity. Thus, the Seebeck coefficient is prognosticatively increased. Also, in our studies on different substrates, we had the opportunity to examine these features in detail. Modules made on Si and glass substrates will provide use in areas with a flat geometry, while modules on Kapton tape will allow the use of the geometry in irregular places to be formed and the waste heat generated therefore.

4. Discussion

In this work, the thermal evaporation of BiTe thin film modules on various substrates was successfully obtained from the industrially commercial Peltier elements. Structural and thermoelectrical characterization of these thin films was performed. After all properties were examined separately, they were subjected to annealing process in order to improve thermoelectric properties of thin films combined in the form of modules. The substrate effect of the thin film thermoelectric properties was characterized by using a homemade measurement setup. The obtained Seebeck values are comparable with the literature which is deposited from the pure elemental alloys. According to the results, the waste thermoelectric alloys deposited in thin film form can be developed as the even more technologically advanced thermoelectric module product and these can be used to measure the waste of the heat recovery systems.

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