Research Article 1(2)191-194 Advanced Materials Proceedings

Thermoelectric performance of Bi_2Te_3, Sb_2Te_3 thin film

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Received: 23 March 2016, Revised: 06 August 2016 and Accepted: 30 August 2016

DOI: 10.5185/amp.2016/214
www.vbripress.com/amp

Abstract

Thermoelectric thin films of Bi_2Te_3 and Sb_2Te_3 were deposited by using sputtering technique. Structural characterizations of as deposited films were done by using X-ray diffraction (XRD), Energy Dispersive X-ray Analysis and electrical properties have been evaluated at room temperature by Seebeck coefficient and electrical resistivity measurement. These sputtered films were established to be polycrystalline and of desired single phase in nature with stoichiometric composition. The Seebeck coefficient and electrical resistivity of *p*-type Sb_2Te_3 thin film and *n*-type Bi_2Te_3 thin films were found to be about 111 μV/K, $8.25\times10^{-5}\,\Omega$-m and −98.52μV/K, $5.87\times10^{-6}\,\Omega$-m, respectively whereas to that of *n*-type Bi_2Te_3-Sb_2Te_3 multilayer having 5BL combination is −145μV/K, $9.31\times10^{-5}\,\Omega$-m and 10BLcombination is −170 μV/K, $9.86\times10^{-5}\,\Omega$-m. The power factor value has increased reasonably well in case of multilayer as compared to that of individual single layer, maximum power factor value 2.95×10^{-3} W/m K^2 has been achieved for 10BL combination. These results indicate that good quality antimony telluride, bismuth telluride and their multilayer thin films can be grown easily by using sputtering technique. It also suggests that these types of nano-structuring (multilayer structure) in these categories of materials can be promissory engineering concept for the fabrication of micro-Peltier modules. Copyright © 2016 VBRI Press.

Keywords: Thermoelectric, thin film, sputtering, multilayer, seebeck, Bi_2Te_3.

Introduction

Thermoelectric materials have attracted significant attention for their ability to directly convert thermal energy to electrical energy with lot of merits, such as low environmental load, silent operation with long life. Therefore, thermoelectricity can play a vital role in modern era by converting the waste thermal heat into useful electrical power. These devices have become more popular as many objects produces large amount of waste heat with which we encounter in our everyday lives and usually we dissipate this in the environment. Thermoelectric modules could potentially convert part of this low-grade waste heat to useable power. The efficiency of TE materials depends on the thermoelectric figure of merit ZT, which is a function of the Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature. It is a challenging task to increase ZT, since the parameters of ZT are generally interdependent [**1,2**]. For extracting better thermoelectric performance from any material system, their Seebeck coefficient and electrical conductivity must be enhanced simultaneously along with the reduction in thermal conductivity [**3**]. Recently, thin film materials show high potential in thermoelectric properties because certain nanostructured materials have better scattering structures for reducing thermal conductivity, such as, quantum confinement, superlattices, etc. [**4**]

The figure of merit Z of thermoelectric materials can be defined by the following equations,

$$\mathbf{Z} = \mathbf{P}/\kappa$$

$$\mathbf{P} = \alpha^2/\rho$$

where P is power factor, κ is thermal conductivity, α is thermoelectric power, ρ is electrical resistivity. For achieving higher Z, large thermoelectric power, low electrical resistivity and low thermal conductivity are required. ZT, multiplying Z with absolute temperature T, is called non-dimensional figure of merit and ZT > 1 is one of the benchmark for practical use of thermoelectric materials.

Bi_2Te_3 and Sb_2Te_3 are known thermoelectric material with superior thermoelectric properties at around room temperature which is desirable for various practical applications. They belong to a category of narrow band-gap semiconductors with the homologous layered crystal structure. Bi_2Te_3 and Sb_2Te_3 are semi-metal alloys, and have good electrical conductivity and low thermal conductivity [**5-9**]. Bi_2Te_3 is reported as N type whereas Sb_2Te_3 as P type semiconductors. But the presence of excess tellurium may change the type. Both of them have high thermoelectric power compared to that of other semiconductors. They have high electrical conductivity and low thermal conductivity than pure semiconductors. However, recently it is reported that thermoelectric conversion devices using superlattice structure in multilayer thin films showed anomalous large thermoelectric power [**7-9**].

In this Article, the role of interface in case of multilayer has been investigated along with synthesis and characterization of thin film of Bi_2Te_3, Sb_2Te_3 and their multilayer combination. It has been shown that interface plays a vital role and act as a scattering center for phonons which result in enhancement of thermoelectric parameters for 10 BL as compared to that of 5BL and individual Bi_2Te_3, Sb_2Te_3 layers.

Experimental

Thin films of Bi_2Te_3 (BT), Sb_2Te_3 (ST) and Bi_2Te_3-Sb_2Te_3 -5 bilayer (BT-ST-5BL) and 10 Bilayer (BT-ST-10BL) were prepared under vacuum condition using DC sputtering method (Minilab Deposition System, Model ES60A, Moorefield UK) having 2-inch readymade targets of Bi_2Te_3, Sb_2Te_3 (Vin Karola, USA) with 99.9% purity. Deposition was done over glass substrates, prior to deposition the substrate was cleaned ultrasonically in order to avoid any contamination. The working pressure during the sputtering process was kept constant at ~6 m bar. The deposition was done at 150°C substrate temperature for 2 hrs in total for any combination for keeping overall thickness nearly constant. Target was sputtered cleaned for 5 min just before deposition for removing any contamination from target surface.

X-ray diffraction (XRD) technique (ULTIMA IV, Rigaku-Japan) was used to characterize film crystallinity. A surface profilemeter (Nanomap, AEP Technology USA) was used to measure the thickness of the samples. Electrical and thermoelectric properties were measured in the direction parallel to the layers using seebeck coefficient measurement setup (ZEM-3, ULVAC-RIKO Japan) in low-pressure He gas atmosphere. The electrical resistivity of the sample was measured by a four-point direct current (dc) current-switching technique, and the Seebeck coefficient was measured by a static dc method based on the slope of the voltage versus temperature-difference curves.

Results and discussion

In order to study the effect of interfaces the overall thickness of 5BL and 10 BL were made same, by keeping 5BL individual layer thickness twice as compared to that of 10 layers. The thickness of the films was measured by a stylus profilometer, for keeping constant thickness the individual layer deposition time was increased by two fold. The overall thickness of 5BL and 10 BL were found out to be ~3.2μm as shown in **Table 1**.

Comparative XRD patterns of above structure have been shown to mark the peak of BT and ST in BT-ST-5BL and BT-ST-10BL films. In Case of BT film, three major diffraction peaks are located at 28.2°, 37.9° and 41.3°.

Table 1. Thickness of Bi_2Te_3 (BT), Sb_2Te (ST), BT-ST-5BL, BT-ST-10BL.

Films structure	Thickness
Bi_2Te_3 (BT),	3.11 μm
Sb_2Te_3 (ST)	3.01 μm
Bi_2Te_3-Sb_2Te_3 -5 BL	3.18 μm
Bi_2Te_3-Sb_2Te_3 -10BL	3.22 μm

Fig. 1. Shows multilayer arrangement in BT-ST-5BL, BT-ST-10BL multilayer structure.

They were indexed as the reflection from (015), (1010) and (110) planes of Bi_2Te_3. This indicates a rhombohedral crystal structure (JCPDS -820358) belonging to the R3−m space group for Bi_2Te_3. In case of ST film major diffraction peaks were located at 29°, 39.09° and 42.7° and were indexed as (015), (1010) and (110) planes of Sb_2Te_3. This also reveals a rhombohedral crystal structure (JCPDS -710393) with R3− m space group. All the observed peaks in BT and ST XRD spectra matches quite well with the reported literature confirming single phase nature of the deposited film [**8,9**]. The observed broadening of the peak in all the XRD spectra might be due to the decrease in particle size/ lower thickness of the film.

In case of multilayer i.e. BT-ST-5BL and BT-ST-10BL XRD patterns, the characteristic peak of both BT and ST phase is present confirming the presence of both Bi_2Te_3 and Sb_2Te_3. Since the overall thickness of both the multilayer pattern is same i.e. ~3.2 μm, hence the XRD patterns originated from Bi_2Te_3 and Sb_2Te_3 combination look identical in 5BL and 10BL arrangement as overall content of Bi_2Te_3 and Sb_2Te_3 is same as a whole. SEM and EDAX has been performed on above sample, results not shown here.

SEM shows the multilayer arrangements as proposed and EDAX shows the presence of Bi, Te and Sb in required proportion along with element present in the substrate.

Thermoelectric properties, the most important and decisive factors for selecting good thermoelectric materials for BT, ST, BT-ST-5BL and BT-ST-10BL thin films at room temperature are summarized in **Table 2**.

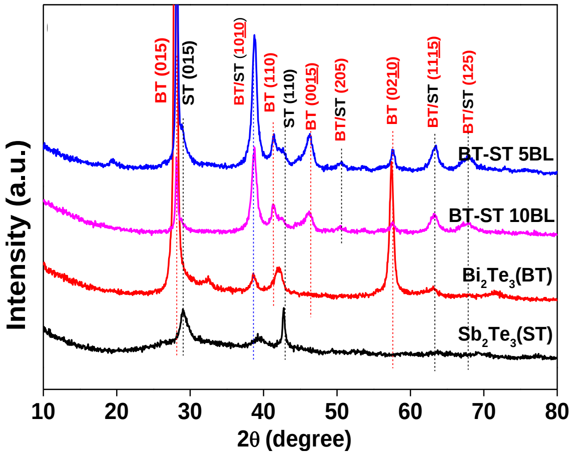

Fig. 2. Comparative room Temperature X-Ray Diffraction pattern of Bi_2Te_3 (BT), Sb_2Te (ST), BT-ST-5BL, BT-ST-10BL

Table 2 shows important results by which one can choose good quality thin films i.e. high Seebeck coefficient and acceptable power factor. The respective figures of merit at 300 K were also shown in the table. (thermal conductivity of 1.5 $Wm^{-1}K^{-1}$ was assumed for calculations).

Table. 2. Seebeck coefficient, Electric Resistivity, Power factor Figure of merit (ZT) of BT, ST, BT-ST-5BL, BT-ST-10BL.

Thin film arrangement	**Seebeck Coefficient [μV/K]**	**Electric Resistivity [μΩ-m]**	**Power factor [10^{-3}x W/m.K^2]**	**Figure of merit (ZT)**
Bi_2Te_3 (BT),	-98.52	5.87	1.65	0.33
Sb_2Te_3 (ST)	111.06	8.25	1.50	0.30
Bi_2Te_3-Sb_2Te_3 -5 BL	-145.29	9.31	2.27	0.45
Bi_2Te_3-Sb_2Te_3 -10BL	-170.46	9.86	2.95	0.59

It can be realized from the table the seebeck coefficient value in case of BT is with negative sign suggesting that BT is having n-type charge conduction whereas in case of ST, the positive value of seebeck coefficient suggest it has p-type charge conduction, which is in accordance with the literature [**9**]. When the multilayer structure was formed, the negative value of overall seebeck coefficient suggests that n-type charge carrier dominates in this arrangement. It can be seen from the table that, when the film composition is same throughout the thickness level we observe the low value of seebeck coefficient in both the case i.e. BT or ST. The Seebeck coefficient of the multilayer arrangement was improved substantially.

In **Fig. 3** it is clear that the room temperature resistivity of ST is higher than BT, but when it has been stacked into multilayer of 5 or 10 periods, the overall resistivity has been enhanced further (from 5.87 μΩ-m to 9.86 μΩ-m) which is obvious because of multilayer structure arrangement.

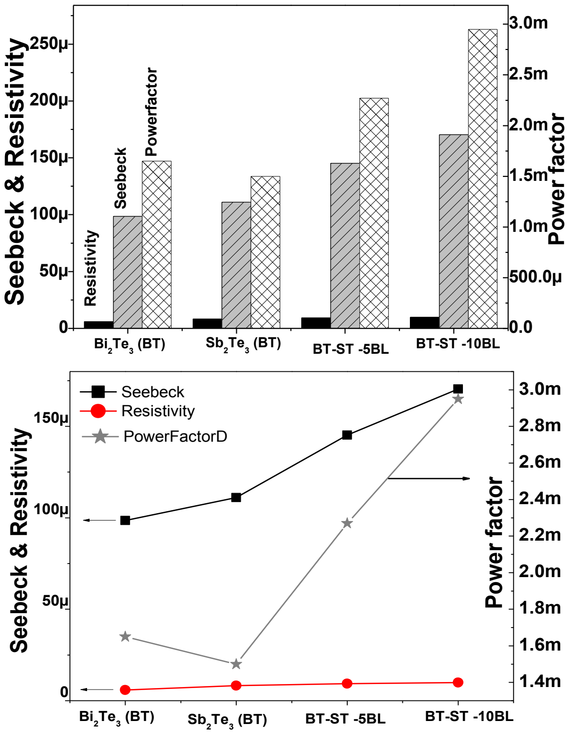

Fig. 3. Comparative Seebeck coefficient, Electric Resistivity, Power factor of BT, ST, BT-ST-5BL, BT-ST-10BL

The main attraction is the variation of modulus value of Seebeck coefficient in multilayer arrangement. This enhancement is not due to the thickness variation as we intentionally kept the overall thickness of 5BL and 10BL constant. This may be due to diffusion of charge carrier between the layers.

The variation of calculated power factor as shown in figure and table is also very surprising. The power factor value has increased reasonably well in case of multilayer as compared to that of individual single layer. The power factor of 10BL has shown better performance than 5BL. Since the material content of 5BL and 10BL is same, hence it can be understood that interface plays a critical role in modifying thermoelectric properties.

It has already been discussed in the literature that the superlattice multilayer structure are anisotropic and different mechanisms play role in improving *ZT* along different directions, both parallel (in-plane) and perpendicular (cross-plane) to the film plane. The mechanism that dominates in-plane direction for improving PF is quantum size effect that improves its electronic performance by taking advantage of sharp features in the electron density of states and reduction of phonon thermal conductivity through interface scattering [**1, 7, 8**].

In our case also, the lattice mismatch and electronic potential differences at the interfaces, resulting phonon and electron interface scattering band structure modifications will reduce phonon heat conduction while maintaining or enhancing the electron transport.

Conclusion

Single layer and multi-layer thermoelectric thin films of Bi_2Te_3 and Sb_2Te_3 were synthesized by sputtering technique. The quality of deposited films, e.g. structure, composition and morphology, were examined by x-ray diffraction (XRD), energy dispersive x-ray analysis. The thermoelectric properties of the thin films have been evaluated at room temperature via Seebeck coefficient, and electrical resistivity measurement. XRD peaks of Bi_2Te_3, Sb_2Te_3 and their multilayer films revealed the existence of stoichiometric crystalline phases. The power factor value has increased reasonably well in case of multilayer as compared to that of individual single layer. 10BL shows better PF than 5BL hence interface plays critical role in modifying thermoelectric properties. These results indicate that good quality antimony telluride, bismuth telluride and their multilayer combination of thin films were grown by Sputtering technique and enhancement of seebeck coefficient and power factor by increasing interface will be a good engineering aspect which designing and fabrication of micro-Peltier modules.

Acknowledgements

This work was financially supported by CSIR-IMMT under project no OLP-46 and ESC-401. Central characterization Cell of CSIR-IMMT is acknowledged for characterization facilities.

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