

REVIEW OF BISMUTH TELLURIDE (Bi_2Te_3) NANOSTRUCTURE, CHARACTERIZATION AND PROPERTIES

Salit Khan¹, Dr. Meeta Chouhan²

^{1,2}Nanotechnology Department,
Gyan Ganga College of Technology, Jabalpur, India

Abstract— The research on nanotechnology has become challenging task for modern science and technology. Bismuth Telluride (Bi_2Te_3) is basically known for its unique properties for various ranges of several device applications. Now in nanotechnology, as devices are migrating to the level of nanometer scale, the significant amount of experiments are being progressed to keep it up with the rapidly growing research field of nanotechnology. In this paper, a recent review of Bismuth Telluride (Bi_2Te_3) nanostructure, its unique characterization at nanoscale and the properties is discussed through a theoretical and analytical process. The behavior of Bismuth Telluride at nanoscale is investigated and its application as a semiconductor, insulator, nanowire and other field of material technology is presented. Finally, it is concluded with many future aspects and applications.

Keywords— Bismuth Telluride (Bi_2Te_3), Nanotechnology, Nanoparticles, Thermoelectric Properties.

I. INTRODUCTION

In the age of nanotechnology, nanoparticles have been challenging researches since the large surface-to-volume ratio of nanomaterials produce an advanced enhancement of various physical properties [1]. Basically, nanoparticles are combined with organic or inorganic materials and their homogeneous miscibility has become another challenge in nanotechnology. For many nanoparticles, high surface-to-volume ratio produces large surface interaction among those aggregated nanoparticles. In this paper, a nanoparticle with reference to Bismuth Telluride (Bi_2Te_3) is analyzed. Bismuth telluride (Bi_2Te_3) basically is a gray powder which is a compound of elements bismuth (Bi) and tellurium (Te) [1][2]. It physically behaves like a semiconductor and, when it is alloyed with antimony (Sb) or selenium (Se) then it behaves like an efficient thermoelectric type material which can be used for refrigeration or portable power generation.

Bismuth Telluride (Bi_2Te_3) also exhibits itself as a topological insulator. The recent experimental analysis confirmed that Bismuth telluride is recognized as a topological insulator [3][4]. The properties of having metallic surface states with insulator bulk of Bismuth Telluride, classified itself as a topological insulator material. This type of behavior originates from a strong molecular spin-orbit coupling of its bulk material. The molecular band structure on its surface has a unique conic shape, its backscattering is generally suppressed and thus its thermoelectric behavior can be exhibited of thin layers of this material [4]. Since the space inversion symmetry will always be broken at the material surface, the metallic surface of Bismuth Telluride at nano structured state is topologically protected [3][4]. So Bismuth Telluride is a confirmed topological insulator by many experiments.

Basically, it has a quintuple layer molecular structure, where each quintuple molecular layer is single unit of Te-Bi bond of hexagonal layers. The Te-Bi bond is a covalent bond inside each of quintuple layer and the Te-Te bonds are relatively weak between its quintuple layers. So, thin films layers can be split easily [5]. In nanostructured thin layer samples of the Bismuth Telluride, definitely the surface area to volume ratio goes very high [4][5]. The Bismuth Telluride has unique properties, which is summarized in the table 1 below.

Table 1: Properties of Bi_2Te_3

Basic Bi_2Te_3 Properties		
1.	Molecular Weight	800.67 g/mol
2.	Crystal Structure	Hexagonal-Rhombohedral
3.	Lattice Constant	a = 4.38 Å, c = 30.45 Å
4.	Band Gap	0.21 eV
5.	Electron Mobility	1140 cm ² /Vs
6.	Hole Mobility	680 cm ² /Vs
7.	Thermal Conductivity	3 W/mK
8.	Density	7.73 g/cm ³
9.	Melting Point	585°C

Recently, many researches and analysis have improved the efficiency of Bismuth Telluride (Bi_2Te_3) materials by creating nano-structures where each dimensions reduced to make nanowires or thin films [6]. Modern research on n-type bismuth telluride was presented to have the improved Seebeck coefficient of $-287 \mu\text{V/K}$ at 54°C , Seebeck coefficient is a measure of voltage per unit temperature difference. The high Seebeck coefficient results in low electrical conductivity and low carrier concentration [6]. Modern researches presented that the electrical conductivity of Bismuth Telluride (Bi_2Te_3) is $1.1 \times 10^5 \text{ S.m/m}^2$ which is very high as well as its lattice thermal conductivity is 1.20 W/(m.K) which is very low and it is similar to the ordinary silicon glass [6].

The thermoelectric materials have a phenomenon which converts wasted heat energy into some useful electrical energy. To improve the Seebeck coefficient, thermal conductivity must be low whereas electrical conductivity must be high [6]. For recovering the waste heat from vehicles and industries pipes, the high performance thermoelectric materials are effective and applicable. Bismuth Telluride (Bi_2Te_3) exhibits itself as an excellent thermoelectric property when alloyed with antimony (Sb) or selenium (Se) [7][8]. To construct thermoelectric

modules Bismuth Telluride is used because it has high thermoelectric properties at figure of merit level [8].

II. FORMATION OF BISMUTH TELLURIDE NANOSTRUCTURES

Generally, there are mainly two approaches for Bismuth Telluride (Bi_2Te_3) or any nanostructure fabrication and formation. First is 'top-down' and second is 'bottom-up' approach [9].

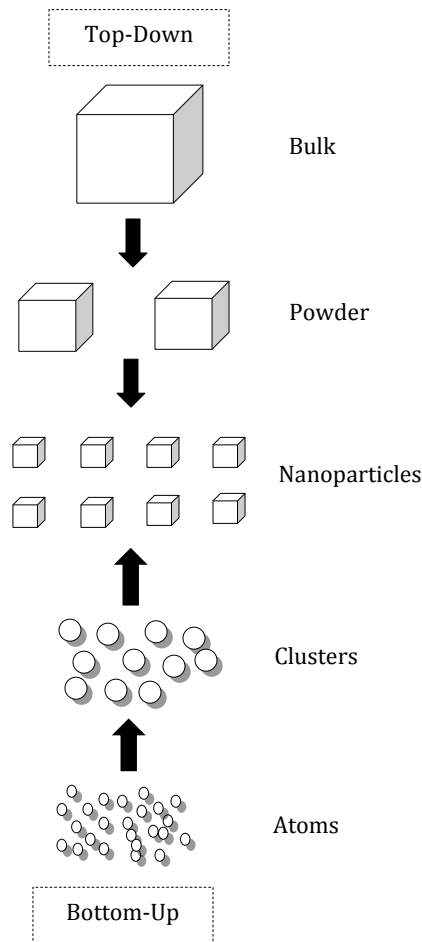


Figure 1: Formation of Nano-Structure

The formation of nanostructure is illustrated in Fig. 1. The top-down approach includes the successive splitting of the main bulk material to obtain the nanostructure of material. However, in bottom-up approach, the process to construct nanoparticles is started from building up from the atomic or molecular scale to until the nanoparticle is constructed [9]. Basically the top-down approach include splitting down to smaller particles of Bismuth Telluride (Bi_2Te_3), but the process arise the cases of imperfection of surface structures it produces massive crystallographic damage in the patterns of the produced nanostructure [9]. However, the top-down approach is harsh process, but surface contamination and internal stress are unavoidable in the produced Bismuth Telluride (Bi_2Te_3) nanomaterial. However, top-down approach aimed to bulk Bismuth Telluride nanomaterial productions. Now, top-down approach has been becoming outdated rapidly.

The bottom-up approach has been becoming popular in industrial applications over a decade. It produces significantly

better option of realizing nanostructures with very low record of defects in it and provides more homogeneous chemical compositions. Analysis on the characterization and synthesis of Bismuth Telluride (Bi_2Te_3) has already utilized both top-down and bottom-up approaches in the last three decades. In the synthesis process, the methods are generally categorized into two methods, first physical methods and second chemical methods.

In the synthesis of Bismuth Telluride (Bi_2Te_3), the physical methods basically involve evaporation technique, sputtering technique, lithographic processes, spray pyrolysis, pulsed laser ablation, so no chemical reduction and finally inert gas phase condensation method and technique. In the chemical methods, it involves electrochemical deposition, electrolysis deposition, hydrothermal and solvo thermal techniques, chemical vapor deposition, laser chemical vapor deposition, laser pyrolysis and lyotropic liquid crystal templates. The lithographic process is the most common technique among the physical methods.

III. LITERATURE REVIEW

In this section, some realistic techniques and methods with reference to Bismuth Telluride (Bi_2Te_3) nanomaterials are analyzed and reviewed.

A. Bismuth Telluride (Bi_2Te_3) for Nanowire Applications

By using electrodeposition, Bismuth Telluride (Bi_2Te_3) nanowires and thin films are constructed, and the influence of hydrogen thermal treatment on thermoelectric properties of electrodeposited Bi_2Te_3 thin films and nanowires are examined [10]. Both the electrical resistivity and the Seebeck coefficient decreases with increasing Bi/Bi + Te single mole fraction of electrodeposited Bi_2Te_3 nanowires and thin films. The absolute value of Seebeck coefficient of the electrodeposited Bi_2Te_3 thin films and nanowires are much smaller than the bulk and powder Bi_2Te_3 [10]. Also the power factor of electrodeposited Te-rich Bi_2Te_3 thin films and nanowires are reported maximum as compared sputtered or evaporated $(\text{Bi,Sb})_2\text{Te}_3$ thin films and nanowires, however, it is lower than the values obtained for powder and bulk $(\text{Bi,Sb})_2(\text{Te,Se})_3$ alloys compounds. Due to the degradation in the electron concentration with hydrogen thermal treatment at very high temperature, the electrical resistivity and the Seebeck coefficient of the electrodeposited Te-rich Bi_2Te_3 thin films and nanowires increases significantly, which is applied to reduction in the Te-Bi anti-site dislocation density and defect density [10][12]. The hydrogen thermal treatment at very high temperature, the Bismuth Telluride (Bi_2Te_3) thin films and nanowires exhibits a Seebeck coefficient of equivalent to the value reported for bulk and powder Bi_2Te_3 single tiny crystals. With hydrogen thermal treatment at very high temperature, the power factor of the Bismuth Telluride (Bi_2Te_3) thin films and nanowires with a Bi/Bi + Te mole fraction are remarkably improved which is equivalent to bulk $(\text{Bi,Sb})_2(\text{Te,Se})_3$. Bismuth Telluride (Bi_2Te_3) nanowires with the diameter of around 200 nm have been successfully constructed by using electrodeposition.

B. Bismuth Telluride (Bi_2Te_3) as Thermoelectric Module and Material

Bismuth Telluride is recognized as the best thermoelectric module and materials with potential for a wide range of applications, such as refrigeration, gas sensors, and power generators [11]. It has a narrow band gap of 0.15 eV semiconductors and it exhibits a solid rhombohedral crystal structure. Today, the thermoelectric semiconductor material is basically used as coolants and it is an alloy of Bismuth Telluride (Bi_2Te_3) [11][13]. Thermoelectric materials are generally fabricated by either pressed powder metallurgy or directional crystallization from the melt material.

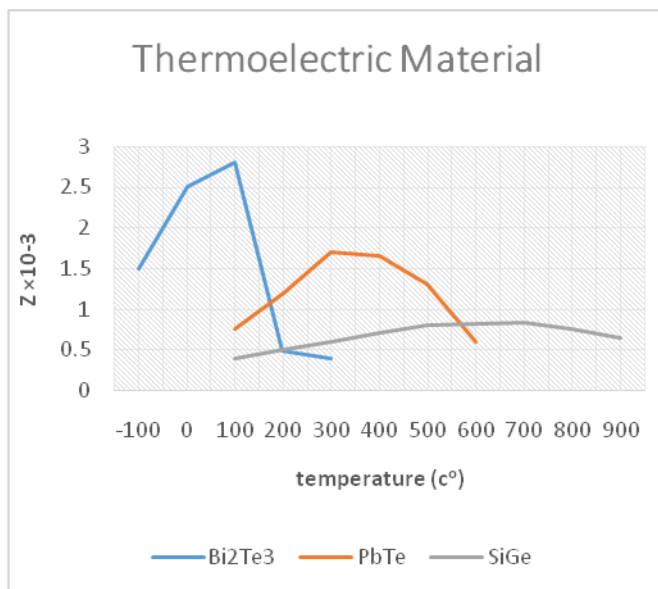


Figure 2: Performance of Thermoelectric Materials at Various Temperatures

There are several manufacturing methods and each method has its own unique advantage, however directionally grown materials are very common. Besides, Bismuth Telluride (Bi_2Te_3), there are some other thermoelectric materials including Silicon Germanium (SiGe), Lead Telluride (PbTe), and Bismuth-Antimony (Bi-Sb) alloys which can be applied in specific conditions [13]. Figure 2 illustrates the Figure-of-Merit or comparative performance of various materials like Bi_2Te_3 , SiGe, PbTe over a temperature range. It can be observed from this graph of figure 2 that the performance of Bismuth Telluride (Bi_2Te_3) at peak within the range of temperature which is best thermoelectric material for industrial cooling applications [13].

C. Bismuth Telluride Nanoparticles for Using Flexible Polymer-Nanoparticle Hybrid Thermoelectric Devices

Polymer-based thermoelectric material shaves readily-tuned properties with simple control of its reaction. It offers the assurance of providing low-cost, flexible and lightweight modules for eco-friendly conversion of the waste heat into the electrical energy without requiring moving components [14]. This quality can be used in the applications ranging from the improved efficiency to increased mileage in mechanical machines and automobile engines. However, extensive industrial implementation of these polymer-based materials is limited because they have low performance related to their heavy inorganic and mechanically rigid, material-based counterparts. So, there is a requirement to design the polymer-

based nanoparticle composite materials for increasing the energy conversion within the thin film thermoelectric devices [14]. Particularly, by using Bismuth Telluride (Bi_2Te_3) nanoparticles which is embedded in the conducting polymer-based matrix of poly (ethylene dioxythiophene) and doped with poly (styrene sulfonate) which provides desired results and performance. Bi_2Te_3 nanoparticles are synthesized in the aqueous solution at a very low temperature in the presence of poly (ethylene dioxythiophene). Basically, this process allows the conducting polymer for coating the surface of nanoparticle that improves the performance of the device. The purified polymer-coated nanoparticles are cast into the thin films and the thermoelectric qualities of the composite materials are analyzed [14][15]. The performance of the polymer-based nanoparticles composite thin films enhances with increased Bismuth Telluride (Bi_2Te_3) loading while retaining the same mechanical integrity combined with polymer-based thermoelectric materials.

D. Electrochemical Deposition and Optimization by Bismuth Telluride (Bi_2Te_3)

Bismuth Telluride (Bi_2Te_3) thick films are useful in thermoelectric devices which cover wide areas and operate at low-to-moderate temperature differences. The high coefficient of performance and high efficiency are achieved by applying thick films in few cooling applications [16][17]. Bismuth Telluride (Bi_2Te_3) thick films fabrication are achieved by using Potentionstatic and Galvanostatic depositions. Stoichiometric Bismuth Telluride (Bi_2Te_3) thick films are constructed by Galvanostatic deposition [18]. The effects of current density and constitutions of electrolyte into Galvanostatic deposition are analyzed and the current density affects the film density, here films deposited on lower current density are denser than that deposited on higher current density. The effects of constitutions of electrolyte solution, distance between electrodes and stirring in Potential static deposition are analyzed and better performance are found [19]. When distance between electrodes are reduced, then the electric field become higher, so the higher current density is applied and deposited film is kept less compact.

IV. PERFORMANCE MEASURE

The performance evaluation of Bismuth Telluride (Bi_2Te_3), the parameter 'figure of merit' (zT) is mostly used [6]. It characterizes the performance of the alloy, material and its nano-structure, in the thermo electronic applications. It is expressed as the temperature T times z as shown in the equation (1):

$$z = \frac{\sigma \cdot S^2}{k} \dots \dots (1)$$

where, σ = electric conductivity,
 S = Seebeck Coefficient,
 k = Thermal conductivity.

The perfect thermal electronic Bismuth Telluride (Bi_2Te_3) nano-structures have very high Seebeck value and electric conductivity [6]. This property allows it to convert waste heat flow into the electrical energy or inversely, electrical energy into cooling power.

Here, the Seebeck coefficient in Bi₂Te₃ is basically of the voltage per unit temperature difference. Also, the Seebeck coefficient can be calculated by the electrical conduction of two-carrier [20]. The total Seebeck coefficient as shown in equation (2) which can be calculated as

$$S = \frac{S_p \sigma_p + S_n \sigma_n}{\sigma_p + \sigma_n} \dots \dots (2)$$

where, S_p = Seebeck coefficients for p-type carriers,
 S_n = Seebeck coefficients for n-type carriers,
 σ_p = Electrical conductivities for the p-type carriers,
 σ_n = Electrical conductivities for the n-type carriers.

V. CONCLUSION AND FUTURE RESEARCH

In this review, the exploratory, experimental, theoretical and comprehensive analyses of Bismuth Telluride (Bi₂Te₃) nano-structures are presented. Basic properties of (Bi₂Te₃) are summarized and its unique characterizations are investigated based on the analytical methods and experiments. The formation and fabrication approaches of Bi₂Te₃ are reviewed as well. The thermoelectric modules and properties, applications in industries, hybridization into other alloys, and electrochemical deposition and optimization are analyzed with reference to the Bismuth Telluride (Bi₂Te₃). There will be several further future analysis of Bismuth Telluride (Bi₂Te₃) nano-structures when it is combined with other nano-materials and alloys. The properties and characterization of Bi₂Te₃ will be applied to many industrial applications.

REFERENCES

[1] H. Julian Goldsmid, "Bismuth Telluride and Its Alloys as Materials for Thermoelectric Generation", *Materials* 2014, MDPI, 2014, Vol - 7(4), pp. 2577-2592.

[2] Zonggen Ding, Shu-Chuan Huang, D. Marcus, R. B. Kaner, "Modification of bismuth telluride for improving thermoelectric properties", *IEEE Eighteenth International Conference on Thermoelectrics*, 1999, pp. 721 – 724.

[3] H. Julian Goldsmid, "Porous Thermoelectric Materials", *Materials*, MDPI, 2009, Vol. 2(3), pp. 903-910.

[4] Zheng Zhang, Yushan Chen, "Research on a Novel Thermoelectric Generator Module Made of Bismuth Telluride", *Advances in Mechanical and Electronic Engineering*, Springer, 2012, Vol. 176. pp. 443-448.

[5] I.K. Ng, K.Y. Kok, C.Z. Che Abd Rahman, T.F. Choo, N.U. Saidin, "Bismuth Telluride Based Nanowires for Thermoelectric Power Generation", *Materials Today: Proceedings*, Elsevier, 2016, Vol. 3, Issue 2, pp. 533-537.

[6] H. Julian Goldsmid, Jeff Sharp, "Extrapolation of Transport Properties and Figure of Merit of a Thermoelectric Material", *Energies*, MDPI, 2015, Vol. 8(7), pp. 6451-6467.

[7] Jyun-Min Lin, Ying-Chung Chen, Chi-Pi Lin, "Annealing Effect on the Thermoelectric Properties of Bi₂Te₃ Thin Films Prepared by Thermal Evaporation Method", *Journal of Nanomaterials*, Hindawi, Vol. 2013 (2013), pp. 6.

[8] Abdellah Boulouz, Alain Giani, Brice Sorli, Lahcen Koutti, Abdellah Massaqa, Frederique Pascal-Delannoy, "Fabrication of Thermoelectric Sensor and Cooling Devices Based on Elaborated Bismuth-Telluride Alloy Thin Films", *Journal of Materials*, Hindawi, Vol. 2014 (2014), pp. 8.

[9] Kyung Tae Kim, Yeong Seong Eom, Injoon Son, "Fabrication Process and Thermoelectric Properties of CNT/Bi₂(Se,Te)₃ Composites", *Journal of Nanomaterials*, Hindawi, Vol. 2015 (2015), pp. 6.

[10] C. Frantz, N. Stein, L. Gravier, S. Granville, C. Boulanger, "Electrodeposition and Characterization of Bismuth Telluride

Nanowires", *Journal of Electronic Materials*, Springer, Sep 2010, Vol. 39, Issue 9, pp 2043-2048.

[11] G. Kunjomana, E. Mathai, "Direct Observation of Frank-Read Sources in Stoichiometric Bismuth Telluride Crystals", *Journal of Materials Science*, Springer, November 1991, Vol. 26, Issue 22, pp. 6171-6175.

[12] N. Gothard, G. Wilks, T. M. Tritt, J. E. Spowart, "Effect of Processing Route on the Microstructure and Thermoelectric Properties of Bismuth Telluride-Based Alloys", *Journal of Electronic Materials*, Springer, Sep 2010, Vol. 39, Issue 9, pp. 1909-1913.

[13] P. Jones, T. E. Huber, J. Melngailis, J. Barry, M. H. Ervin, T. S. Zheleva, A. Nikolaeva, L. Konopko, M. Graf, "Electrical Contact Resistance of Bismuth Telluride Nanowires", *IEEE 25th International Conference on Thermoelectrics (ICT '06)*, 2006, pp. 693 – 696.

[14] Chunjin Hang, Shaopeng Sun, Panpan Lin, Chunqing Wang, "Molecular Dynamics Study of Thermal Conductivity in Bismuth Telluride Thin Films", *IEEE 14th International Conference on Electronic Packaging Technology (ICEPT)*, 2013, pp. 413 – 416.

[15] W. P. Lin, P. J. Wang, C. C. Lee, "Bonding/barrier layers on bismuth telluride (Bi₂Te₃) for high temperature applications", *IEEE 60th Electronic Components and Technology Conference (ECTC)*, pp. 447 – 450.

[16] Jianhua Zhou, Chuangui Jin, Jae Hun Seol, Xiaoguang Li, Lio Shi, "Measurement of thermoelectric properties of individual bismuth telluride nanowires", *IEEE 24th International Conference on Thermoelectrics, ICT 2005*, pp. 17 – 20.

[17] Jinhee Ham, Wooyoung Shim, Do Hyun Kim, Seunghyun Lee, Jongwook Roh, Sung Woo Sohn, Kyu Hwan Oh, P. W. Voorhees, Wooyoung Lee, "Direct growth of Bismuth Telluride nanowires by On-Film Formation of Nanowires for high-efficiency thermoelectric devices", *IEEE 3rd International Nanoelectronics Conference (INEC)*, 2010, pp. 105 – 106.

[18] Kyung Tae Kim, Hye Young Koo, Gil-Geun Lee, Gook Hyun Ha, "Synthesis of alumina nanoparticle-embedded-bismuth telluride matrix thermoelectric composite powders", *Materials Letters*, Elsevier, Vol. 82, Sep 2012, pp. 141-144.

[19] Wen Hsuan Chao, Yi Ray Chen, Shih Chun Tseng, Ping Hsing Yang, Ren Jye Wu, Jenn Yeu Hwang, "Enhanced thermoelectric properties of metal film on bismuth telluride-based materials", *Thin Solid Films*, Elsevier, Vol. 570, Part B, Nov 2014, pp. 172-177.

[20] Masayuki Takashiri, Saburo Tanaka, Koji Miyazaki, "Improved thermoelectric performance of highly-oriented nanocrystalline bismuth antimony telluride thin films", *Thin Solid Films*, Elsevier, Vol. 519, Issue 2, Nov 2010, pp. 619-624.