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Tellurium based thermoelectric materials: New directions and prospects

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ABSTRACT

Telluride alloys are widely used in thermoelectric devices which generate electricity from waste heat or act as Peltier coolers. Limited by toxicity these are best materials for room temperature range. It has been observed that figure of merit (ZT) of these rises with temperature but decreases attaining a peak. Thanks to modern synthesis and characterization techniques, an era of complex thermoelectric materials is approaching. This work explores the strategies used to improve the thermopower for the two most important tellurium based compounds namely Bismuth telluride (Bi_2Te_3) and Antimony telluride (Sb_2Te_3). With the variation in the composition of these compounds changes/ enhancement in the thermoelectric properties and possibility of compositions which may be optimized for development of applications above room temperature have been explored. It is concluded that although current experimental works reveals a few promising thermoelectric properties of these materials, intensive investigation should be initiated to achieve/ explore more improvable properties.

Keywords: Thermoelectronic phenomena, Thermoelectric energy conversion, Thermoelectric effects in thin films; Figure of merit (energy conversion).

INTRODUCTION

The electronic systems are becoming denser due to shrinkage in the size of components so heat dissipation in modern devices continues to be a challenge as it can be quite large for the small area of usages, hence thermal management has become necessary from the beginning of the design process.[1] Large area thermoelectric devices are in the marketplace since quite a long time now, but very recently lateral configuration (thin film) of thermoelectric materials have been recognized as a key class of energy materials, converting waste heat into electrical energy.[2] This has provided a possibility to scale down the thermoelectric devices to micro and nano dimensions with performance similar to that of bulk materials.[3] Moreover nano-scaled materials are predicted to exhibit outstanding thermoelectric performance over bulk materials due to their low dimensional quantum size effect.[4] This option has a superior possibility of using them right at the source of the heat generation. Hence it is important to explore and develop right type of materials which can be used to fabricate thermal interface devices having high thermal conductivity. There is a huge gap in need and availability of the variety of such materials and devices hence it is a promising area of research and development. Thermoelectric devices can convert waste heat into electricity or for heating and cooling without the use of other devices like mechanical pumps or fans. In present scenario widespread use of thermoelectric devices is less due to their relatively high cost and low efficiency. The energy shortage and global warming are big problems so lot of attention has been attracted by the issues of energy saving and reduction of carbon emission.[5] Hence, the application of thermoelectric materials is very promising for power generators and cooler.[6-9]

WHY TELLURIUM BASED MATERIALS

Tellurium based thermoelectric materials have been proven to be very effective in the room temperature range. Nano-scaled tellurium-based materials are expected to make a breakthrough in the present era technology. The bulk tellurium-based materials have already been extensively investigated and commercially exploited in thermoelectric devices. These devices exhibit a just acceptable performance moreover enhancement in their thermoelectric converting efficiency is a challenging task which is a challenge owing to the conflicting combination of material traits that are required. Most of these properties are those which determine the thermoelectric performance. Hence, fabricating high quality tellurium-based nanomaterials and further understanding their growth mechanisms and improving their thermoelectric performance is need of the day. This task is quite challengeable but key to realize real applications in power generation and refrigeration.[10-11]

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WHY THIN FILMS

In the last decades or so thin film deposition has evolved as a very useful technology penetrating all major industries. Thin films are thin layers of materials from nanometers to micrometers thick. Electronic semiconductor devices and optical coatings are the main applications of thin film construction. Thin film technology is used to produce thin film batteries, photo-, electro- chemical and dye sensitized solar cells, ceramic thin films, thin films used in aerospace industry and the machine tool industry. Possibility of fine tuning of hardness and inertness of thin films which protects the materials against corrosion, oxidation and wear extends the life of items by a significant magnitude.[12]

Hicks and Dresselhaus reported that low-dimensional materials have better efficiency than bulk because of low-dimensional effects on charge carriers and lattice waves.[13] The low-dimensional nanostructured thermoelectric materials have increased density of states of Fermi level and hence enhanced phonon scattering of the materials. Because to miniaturize the thermoelectric devices by sintering blocks is difficult so various techniques, depending on the variety of thin film required a large number of deposition techniques have been employed to obtain the thermoelectric thin films, such as flash evaporation, ion-beam sputtering, pulse laser deposition, sputtering, electrochemical deposition, metal organic chemical vapor deposition, molecular beam epitaxy, and electrochemical deposition.[14-15]

RESULTS AND DISCUSSION

Pradyumnan and Swathikrishnan prepared Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3- Sb_2Te_3 thin films using thermal evaporation technique.[16] It was concluded that Sb_2Te_3 thin films showed excellent thermoelectric behavior in the room temperature region while Bi_2Te_3 films showed good thermoelectric behavior in the room temperature as well as relatively low temperature range. It was also concluded that thermoelectric performance will increase if Bi_2Te_3- Sb_2Te_3 bilayer film used instead of single layer film. Takashiri *et al* reported highly-oriented nanocrystalline bismuth antimony telluride thin films having improved thermoelectric properties.[17] Films were deposited by flash evaporation method, followed by annealing in hydrogen which exhibited almost perfect orientation with the c-axis normal to the substrate, composed of nano-sized grains with an average grain size of 150 nm. Bismuth telluride thin films have been synthesized by Ma *et al* employing electrochemical deposition onto stainless steel substrates in acidic solutions.[18] The carrier concentration of these films was better than for optimized bulk bismuth telluride. This resulted in the unusually low Hall mobility and Seebeck coefficient values were found for the electrodeposited films. Ethylene glycol was investigated as an electrolyte for the electrodeposition of thermoelectric bismuth telluride films by Nguyen *et al*.[19] This study employed cyclic voltammetry, rotating ring disk electrode and electrochemical quartz crystal microbalance (EQCM) methods for charaterisation of the films. It was found that diffusion coefficients and the rate constants for reduction were similar for Bi and Te. The Seebeck coefficient measurements indicated that both p- and n-type films could be developed by this method. Zheng *et al* reported N-type bismuth telluride (Bi_2Te_3) thermoelectric thin films which were deposited on BK_7 glass substrates by ion beam sputtering method.[20] It was found that Seebeck coefficients increased from – 28 $\mu V\ k^{-1}$ to – 146 $\mu V\ k^{-1}$ and the electrical conductivities increase from 1.87×10^3 S cm^{-1} to 3.94×10^3 S cm^{-1} when the deposition temperature rose to 250 °C and 300 °C, respectively. An optimal power factor of 6.45×10^{-3} $Wm^{-1}\ K^{-2}$ was gained when the deposition temperature was 300 °C. The thermoelectric properties of bismuth telluride thin films had been found to be strongly enhanced by increasing the deposition temperature. Fan *et al* fabricated Bismuth antimony telluride thin films by a tri-target co-sputtering deposition technique on soda-lime glass.[21] The influence of Bi doping on the structure, surface morphology and thermoelectric properties of the thin films were studied. The results indicated that the thin films changed from p-type semiconductor to n-type semiconductor with the increase in Bi content. Recently, Zeng *et al* prepared N-type Bismuth telluride thin films of different thicknesses deposited on cleaned glass substrate at room temperature by co-sputtering technique.[22] This study revealed that both the electrical conductivity and the Seebeck coefficient increased with increasing of film thickness and grain size. The dimensional sizes of the resultant bismuth telluride alloyed (BTA) nanorods obtained in this work were around 500 nm in length and 20 nm in diameter. N-type bismuth telluride (Bi_2Te_3) thermoelectric thin films were deposited by co-sputtering simple substance Te and Bi targets by Cai *et al*.[23] The deposited films were annealed under various temperatures. The structural and thermoelectric properties of the films were greatly improved by annealing. In this study the Seebeck coefficient, electrical conductivity and power factor increased with the rise in temperature. This study showed a way which could be a guideline for preparing the high-performance thin film materials for thermoelectric applications. Zhou *et al* reported preparation of nanocrystalline n-type bismuth telluride (Bi_2Te_3) thin films doped with lead (Pb) deposited by radiofrequency magnetron sputtering.[24] The experimental data demonstrate that Pb doping can effectively control the carrier concentration of the n-type Bi_2Te_3 film. Takashiri *et al* studied the effects of homogeneous irradiation of electron beam (EB) on the crystal growth and thermoelectric properties of nanocrystalline bismuth selenium telluride thin films.[25] They found that with increasing EB irradiation dose both the electrical conductivity and the Seebeck coefficient were improved. This resulted into improvement of the power factor (enhanced from 0.14 to 0.96 $\mu W/cm/K^2$). Lee *et al* studied the theoretical and experimental characteristics of thermal transport of 100 nm and 500 nm-thick antimony telluride (Sb_2Te_3) thin films prepared by radio frequency magnetron sputtering.[26] Zhao *et al* studied the nano scale thermoelectric behavior of $(Bi,Sb)_2\ Te_3$ (BST) films using 3ω- technique for thermal conductivity imaging and quantitative thermal characterization.[47] This developed Scanning thermoelectric microscopy (STeM) using commercial atomic force microscope. The nanoscale thermoelectric images obtained exhibited remarkable inhomogeneous distribution of local Seeback coefficient in the films. Agarwal *et al* studied the effect of nanocrystallite size on thermal and electrical properties of thin films of Bi_2Te_3.[28] Different crystalline sizes were obtained by

varying deposition temperature and gas pressure using vaccum evaporation and inert gas evaporation techniques. It was conclude that strain may influence the electron transport and thermoelectric properties of Bi_2Te_3 films along with nanocrystallite size. Tasi *et al* investigated the micro structural, morphological and nanomechanical properties of Bi_2Te_3 thin films using XRD, scanning electron microscopy (SEM), atomic force microscopy (AFM) and nanoindentation techniques.[29] They deposited Bi_2Te_3 thin films on c-plane sapphire substrates using pulsed laser deposition under the various helium gas pressures. It was concluded that the Bi_2Te_3 thin films were textured with the c-axis preferentially oriented normal to the films surface. Both the grain size and surface roughness of the Bi_2Te_3 thin films exhibited an increasing trend with increasing the helium gas pressure. Park *et al* studied the effect of grain size and strain on the temperature dependent thermal transport of Bi_2Te_3 thin films controlled using post-annealing at 200ºC to 350ºC, and 3-omega method.[30] It has been concluded that grain size rather than the strain had the most prominent effect on the reduction of the total thermal conductivity of the films. Song *et al* electrodeposited the thin films of Bi_2Te_3 at room temperature using nitric baths in the presence of cetyltrimethylammonium bromide (CTAB).[31] Good quality stoichiometric Bi_2Te_3 films were obtained and it was found that the surface morphology and mechanical properties were improved by the addition of CTAB to the electrolyte. The electrical and thermoelectric properties remained unaltered and it remained inert to post-deposition annealing in a reducing environment. Rahman *et al* studied the effect of Bi_2Te_3 concentration on the thermoelectric properties of PEDOT: PSS- Glycerol thin films at room temperature.[32] They fabricated thermoelectric devices by depositing the n-type and p-type Bi_2Te_3 doped PEDOT: PSS- Glycerol on a glass via a spin coating method and conclude that the electrical conducting of both type films increase with increasing of BT doping. Park *et al* worked on the thermal conductivity of layered Bi_2Te_3 films by solving the boltzman transport equation using full phonon dispersion.[33] After comparing their results with experimental data it was concluded that their model incorporates the typical interaction impeding transmission through Van Der walls interfaces of adjacent Bi_2Te_3 quintuple layers. Zhang *et al* discussed the influence of excess antimony on the Seebeck coefficient of antimony telluride.[34] It was concluded that by altering Sb content various Seebeck coefficients would be acquired in Sb-rich Bi_2Te_3 films.

CONCLUSIONS

Although a lot of research work has been done on tellurium based materials but practical uses of it will be highly restricted by the less availability of tellurium itself in future. From the discussion above and review of recent work it is apparent that there are many strategies and efforts which are continuing the hope of next generation materials which will transform the present day thermoelectric materials technology and energy harvesting. This motivates to optimize the use of these materials and explore new materials having better thermoelectric properties. Certainly ongoing research indicates that there is much scope for work in this field. Theoretical band structure calculations and modeling have also been initiated and will essentially be very useful in the identification of the prospective materials and their compositions. Some of the work has been done which indicates very promising and a bright future of thermoelectrics.

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