IJREAT International Journal of Research in Engineering & Advanced Technology, Volume 5, Issue 3, June - July, 2017
ISSN: 2320 – 8791 (Impact Factor: 2.317)
www.ijreat.org

Thermoelectric Application Of Metal Telluride Nanostructures And Their Heterostructures

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Abstract

We needlessly squander heat energy through inefficient energy handling systems and usually this energy is low grade, whose recovery is generally futile. To this end, the thermoelectric field is a promising technology to directly transform some of this waste thermal energy back to electricity through the Seebeck effect. Among variety of thermoelectric materials, nanostructures and their heterostructures are the most auspicious for commercial applications due to their remarkably good thermoelectric performances. Although, the incorporation of metal telluride nanostructures and their heterostructures in thermoelectric devices has shown high performances, it is still questionable if such materials can be produced in scalable, reliable, and economical ways. Thus, this article is devoted to furnish the important breakthroughs in the metal telluride thermoelectrics during the last few decades.

Keywords: *thermoelectricity; metal tellurides; nanostructures*

1. Introduction

During the last few decades, there has been an urgent need for the clean and alternative renewable energy resources, because of environment destruction, global warming and energy crisis caused by our strong reliance on nonrenewable energy sources. Thermoelectric (TE) materials have engaged a substantial research not only due to their propitious efficacy in boosting energy conversion efficiency, in solid-state cooling and sensors [1–5], but also due to their potential advantages like, miniaturization, inexpensive, lightweight, noise and pollution free devices. Thermoelectric energy harvesting includes thermoelectric materials, devices and their applications in thermoelectric generators, refrigerators, automotive waste-heat recovery and in military systems. Thermoelectric effect is based on the fundamental interplay between the electronic and thermal properties of a material. The two predominant thermoelectric effects are the Seebeck effect and the Peltier effect. When a thermal gradient is applied across an electrically conductive material, charge carriers drift along the gradient from high to low temperature; this is the so-called Seebeck effect. On the contrary, when an electric current is made to flow through a junction between two conductors, heat is generated or removed at the junction; this is the Peltier effect. Thermoelectric generators can be of immense application to convert waste heat into electricity by employing the Seebeck effect [6,7]. Meanwhile, thermoelectric refrigerators employing the Peltier effect could potentially replace compressor-based refrigerators avoiding the use of hydrochloroflourocarbon refrigerant [6,7]. The efficiency of these devices crucially depends on the properties of the materials employed. The optimization of these devices generated a dimensionless parameter, ZT, called figure of merit, which is used to determine the performance of a thermoelectric material. The figure of merit is given by

$$ZT = \frac{S^2 \sigma}{\kappa} T \qquad (1)$$

where S is the Seebeck coefficient, σ is electrical conductivity, $\kappa = \kappa_L + \kappa_C$ is the thermal conductivity including the lattice thermal conductivity, κ_L, and the carrier thermal conductivity, κ_C, and T is absolute temperature [8]. The power factor ($S^2\sigma$) is a critical quantity to compare electrical properties of thermoelectric materials.

Recently, a number of research papers have been published to improve the figure of merit (ZT) of thermoelectric materials [9–15]. TE materials have been successfully employed in electric water pump, climate control seat and TE generator of BMW series cars [16]. They are also the primary material in the radioisotope TE generators which supply electrical power to the Cassini spacecraft [17]. TE devices have recently found their possible application in lithium-ion batteries [18] and dye-sensitized solar cells [19]. However, such type

of applications require TE materials with higher ZT, which in turn calls for higher Seebeck coefficient, higher electrical conductivity and lower thermal conductivity. Moreover, the lower efficiency of TE materials also forbids their wide applications. Till now, a number of materials have been identified that have superior ZT value and lower cost for potential industrial applications [20–24].

2. Thermoelectric materials

The leading material for thermoelectric applications in commercial devices is bismuth telluride (Bi_2Te_3) with ZT~1. It is a semiconductor with an indirect band gap of about 0.15 eV [25]. For producing p-type material it can be doped with Sb and with Se for n-type material. The atomic structure of Bi_2Te_3 consists of five layers of atoms $Te^{[1]} - Bi - Te^{[2]} - Bi - Te^{[1]}$, which is repeated. The layers are bound together by van der Waals interactions and owing to this factor Bi_2Te_3 crystals can be easily ripped along the layers. In context of the thermoelectrical properties, the Seebeck coefficient of doped Bi_2Te_3 is independent of orientation while Seebeck coefficient of undoped Bi_2Te_3 depends on the direction of the temperature gradient [26]. Recently, nanostructuring of Bi_2Te_3 has enhanced it's ZT value. Sootsman et al. reported a record ZT value of 2.4 for superlattice of Bi_2Te_3 and Sb_2Te_3 at room temperature, grown by low-temperature metal-organic chemical vapour deposition technique. The high ZT value was obtained in the direction perpendicular to Bi_2Te_3 layers.

The leading method to enhance ZT in the 1960s was to control doping and form solid solutions such as $Bi_2Te_3 - Sb_2Te_3$, $PbTe - SnTe$. However, point defects in solid solutions decreases the lattice thermal conductivity by increasing heat carrying phonons scattering and also reduces charge carrier mobility, thus the ZT improvement by this method is limited [27]. From 1960-1990, there were no significant developments in thermoelectrics field and $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$ alloy family remained the key commercial material with ZT of about 1 [2]. During the last two decades, thermoelectric community started exploring the next generation thermoelectric materials on the basis of the following two criteria: one is exploiting families of bulk thermoelectric materials with complex crystal structures, and the other is employing low-dimensional thermoelectric materials systems obtained via nanostructural engineering. An appreciable enhancement in ZT has been witnessed in the PGEC materials, and nanostructured materials, such as superlattices, quantum dots, nanowires, and nanocomposites.

2.1 Nanostructured thermoelectric materials

Hicks et al. proposed that it may be possible to increase ZT of certain materials by preparing them in quantum-well superlattice structures, since quantum confinement in the interlayer direction can increase the DOS near the Fermi level [28]. Their calculation showed that layering can enhance the figure of merit of a highly anisotropic material such as Bi_2Te_3 with the proviso that superlattice multilayers are designed in a particular orientation. They also suggested that the interfaces between layers would effectively scatter phonons if the Bi_2Te_3 layer thickness will be less than the phonon mfp, which will ultimately result in the decrease of lattice thermal conductivity [28,29]. Venkatasubramanian et al. [30] reported a significant enhancement in ZT (~ 2.4) employing $Bi_2Te_3 - Sb_2Te_3$ p-type quantum well superlattices with a periodicity of 6 nm, while the highest ZT value for the bulk Bi_2Te_3 alloy is only $ZT = 1.1$. Later on, Harman et al [31] synthesized quantum-dot super lattices in the PbTe– PbSeTe system, wherein PbSe nanodots were embedded in a PbTe matrix, and reported $ZT = 1.6$, which is considerably higher than their bulk counterparts ($ZT = 0.34$). In addition, improved thermoelectric properties have also been reported for two-dimensional thin films and quantum well structures including Bi_2Te_3superlattice-based thin-film [32], $PbTe/Ag_2Te$ thin films [33], quantum well/barrier $PbTe/Pb_{1-x}Eu_xTe$ structures [34], $n - PbTe/pSnTe/n - PbTe$ quantum wells [35].

The motive behind these investigations was the conjecture that the quantum confinement of in-plane carrier transport could significantly enhance the power factor over that of homogeneous materials that can lead to ten-fold increase in ZT. In this context, Shakouri [36] proposed that such enhancement can happen because the sharp features in the DOS of quantum-confined structures allows a doping-level-tuneable increase in the asymmetry between hot and cold electron transport. This subsequently leads to a large number of carriers moving in the material, thereby imparting a large Seebeck coefficient and higher electrical conductivity [37].

It has been found theoretically and experimentally that the low-dimensional nanostructured thermoelectric materials have higher ZT (> 3), since the density of states (DOS) near Fermi level can be enhanced through quantum confinement leading to an increase in thermopower. Moreover, phonons in these materials can be effectively scattered by high density of interfaces over a large mean free path (mfp) range, ensuing a decrease in the lattice thermal conductivity [38]. The TE properties of the nanostructured materials depend on the size and morphology of the microstructural features,

thus microstructural engineering should be focused in the development of TE nanomaterials. Saleemi et al. synthesized bulk nanostructured (NS) undoped Bi_2Te_3 via a promising chemical synthetic route [39]. They employed spark plasma sintering for compaction and sintering of the Bi_2Te_3 nanopowders. The average grain size of the final compacts was found to be 90 ± 5 nm. An enhanced *ZT* for the bulk undoped Bi_2Te_3 is obtained with a peak value of ~1.1 at 340 K.

Later on, a variety of Bi_2Te_3-based compounds possessing different morphologies have been successfully synthesized by various research groups. These morphologies include nanowires [40], nanotubes [41], nanoplates and self-assembled nanoflowers [42], and nanobelts [43] via hydrothermal method [21] with ethylenediamine tetraacetic acid (EDTA) as an additive. However, ZT values of these structures after fortification with SPS are only about 0.7 [80, 83] but dense nanostructures can impart greatly enhanced phonon scattering, and therefore the thermal conductivity can be dramatically decreased to lower values.

Microstructural tailoring can be carried out to produce anisotropic polycrystalline, hierarchical nanostructure and nanocomposites via various techniques of synthesis and sintering process like hot-press or SPS. Recently, Jiang et al. synthesized nanostructured p-type $Bi_{0.5}Sb_{1.5}Te_3$ alloys with preferred orientation via the densification of nanostructured powders followed by a two-step hot forging process [45].

The nanopowders sintered for 20 minutes at 330 ℃, produced samples with a density of 96% and the particle size was in nanometer range (50-300 nm, while that sintered at 450 ℃ for 5 minutes produced samples with randomly oriented flake-like grains with a density of 99% and size of several microns. The nanosized grains became elongated micro-sized flakes being well arranged perpendicular to the direction of the applied pressure.

Nanostructured thermoelectric materials can also be fabricated by introducing nanometer-sized polycrystallines and interfaces into the bulk materials; this inclusion can decrease the thermal conductivity by enhancing the phonon scattering. Since the phonon mfp generally ranges from several to a few hundred nanometres, while the carrier mfp is typically only a few nanometers, there is a high probability of preferential phonon scattering [46]. A variety of nanostructure composites have been fabricated by incorporating nanometer-sized polycrystallines (grain size $\sim 5\,\text{nm} - 10\,\mu\text{m}$) via hot pressing or spark plasma sintering (SPS) of fine powders formed by grinding and milling or wet chemistry processing [38]. The nanocomposites produced by this method possess multitude of advantages over conventional fabrication techniques that generate very large-grain or single crystal material, such as reduced thermal conductivity owing to phonon scattering at grain boundaries, improved mechanical properties and isotropy [37]. Bi_2Te_3 nanocomposites are outstanding thermoelectric materials at room temperature and are widely employed for commercial Peltier elements. Poudel et al. fabricated a polycrystalline p-type $Bi_{0.5}Sb_{1.5}Te_3$ bulk nanocomposite by hot pressing nanopowders that were ball-milled from crystalline ingots under inert conditions [47]. They reported a peak *ZT* of 1.2 at room temperature and *ZT* of 1.4 at 373 K, and thermal conductivity reduction from 1.3 $W\,m^{-1}K^{-1}$ in the bulk ingots to 1.0 $W\,m^{-1}K^{-1}$ in the nanocomposite form. However, the electrical conductivity of the nanocomposite was found to be reduced slightly due to which the maximum *ZT* of the nanocomposite was only 30% higher than the bulk ingots. The transmission electron microscopy (TEM) images revealed complex polygonal grain structures, with diameters ranging from few nanometers to few microns. Furthermore, the microstructure characterization showed Sb-rich nanodots ranging from 2 to 10 nm in diameter having diffused boundaries and pure Te precipitates with diameter between 5 to 30 nm. Poudel et al. proposed that these nanostructures could efficiently scatter larger wavelength phonons at the grain boundaries which might have imparted enhanced thermoelectric properties to Bi_2Te_3-based nanocomposites [47]. Further researches unravelled that various other p-type Bi_2Te_3-based nanocomposites can also achieve a high *ZT*, around 1.3 between 75 and 373 K [48] and 1.4 at 373 K [49], whereas n-type Bi_2Te_3-based nanocomposite can approach a *ZT* of 1.04 at 398 K [50].

A relatively surpassing *ZT* of around 2.2 was attained with complex nanostructured PbTe-based alloy $AgPb_mSbTe_{2+m}$ (abbreviated as LAST) fabricated by the melt-grown method [51]. LAST alloys comprises of Ag–Sb rich nanoscale inclusions in the nanostructured matrix; these nanoscale inclusions played a critical role in reducing the thermal conductivity to about 2.3 $W\,m^{-1}K^{-1}$ at room temperature. A variety of other PbTe-based nanostructured thermoelectric materials have been developed including $AgPb_mSn_nSbTe_{2+m+n}$ (LASTT), $NaPb_mSbTe_{2+m}$ (SALT-m), KPb_mSbTe_{m+2}(PLAT-m) and $PbTe - PbS$, that achieved *ZT* values higher than 1 [52–68]. Androulakis et al. [55] demonstrated that certain compositions in $Ag(Pb_{1-y}Sn_y)_mSbTe_{2+m}$ series display high performance p-type thermoelectric properties owing to their very low thermal conductivity; for instance ZT~ 1.45 at 630 K. They also showed that these materials are actually bulk nanocomposites and illustrated that properties such as carrier concentration, TE power, and thermal conductivity can be carefully tuned by varying the m and y values, as well as the Ag and Sb concentrations.

Another providential category of nanostructures are the nanotubes possessing high *ZT* values owing to their structural features such as low dimensionality and hollow tubular morphology [116, 117]. The V-VI nanotubes have been successfully prepared by the pulsed electrodeposition and the solution-phase method [5]. The pulsed electrodeposition method comprises of the fabrication of a porous anodic alumina (PAA) template with a meshlike Au layer, however, hitherto only Bi, Sb, Bi_2Te_3 and their derived ternary alloy nanotubes can be fabricated through this procedure [71–73]. Furthermore, the diameter, thickness, and crystallinity of the produced nanotubes cannot be precisely controlled with this method which can be a hurdle in achieving superior thermoelectric materials. In contrast, the solution-phase method has also been employed to prepare V–VI-based nanotubular structures, such as Bi, Bi_2Se_3 and Bi_2Te_3 nanotubes being synthesized through hydrothermal and galvanic replacement-reaction processes [74–77]. Nevertheless, these solution-phase methods have their own shortcomings, such as low production yields, crudely controlled size, and polycrystalline products. Zhang et al. [78] successfully synthesized highly crystalline Bi_2Te_3 nanotubes employing Te nanowires as the templates via ethylene glycol mediated solution phase method. The produced nanotubes were uniform and single crystalline with diameter and wall thickness of around 70 and 10–15 nm, respectively.

2.2 Heterostructures of Metal Telluride

It has been confirmed that the *ZT* of one-dimensional heterostructures of metal tellurides surpasses the *ZT* of other types of nanostructures, for instance conventional nanowires and nanoparticles [28,70,79,80]. Thus, during the last few years, fabrication of one-dimensional metal telluride heterostructures has became a research motif of paramount importance, owing to their practical applications as thermoelectric materials [81–83]. In comparison to conventional nanowires, the heterostructure interface between every two adjacent segments in a multisegmented nanowire or between the core and shell in a core/shell nanowire can decrease the lattice thermal conductivity by confining the phonon scattering along the wire axis [5,28,70,79,80]. Consequently, the current juncture calls for adroit and uncomplicated ways for synthesizing high-quality heterostructured nanowires in order to fabricate high performance thermoelectric devices.

A variety of V-VI based heterostrcutured nanowires have been produced via different chemical routes, including electrodeposition and solution-phase epitaxial growth. In particular, Bi/Sb, $Bi/Bi_{0.5}Sb_{0.5}$, Bi_2Te_3/Sb and $Bi_2Te_3/(Bi_{0.3}Sb_{0.7})_2Te_3$ multisegmented nanowires have been fabricated employing pulsed electrodeposition in porous membrane templates [5,84–87]. It was found that the thermoelectric performance intensely depends upon the length of each segment, which can be well governed by varying the deposition time, deposition potential, and/or ion concentration in the electrolyte [5]. Bi_2Te_3 has been regarded among V-VI alloys as the leading thermoelectric material at room temperature [88].

Nevertheless, the Bi_2Te_3-based multisegmented nanowires that were reported previously were polycrystalline, which may reduce the electrical conductivity and diminish the *ZT* value. Thus, there was a dire need to develop and fabricate Bi_2Te_3-based multisegmented nanowires with a single-crystal structure. To this end, Wang et al. [89], synthesized Bi_2Te_3/Te multiple heterostructure single-crystalline nanowire arrays via a facile thermal annealing process of the supersaturated $Bi-Te$ alloy nanowire arrays. It was found that the precipitation confined by porous anodic alumina (PAA) membranes resulted in the spontaneous formation of the block-by-block structure. Furthermore, an intriguing result was unveiled promulgating that the length of each segment is dependent on the x value in the supersaturated Bi_xTe_{1-x} nanowires; these segment length can be subtly controlled by varying the x composition.

There are few other techniques that can be found in literature for synthesizing Bi_2Te_3 nanowire heterostructures, although they require templates [87,89], complex surfactants [90], or catalysts [91] for the synthesis. More recently, Zhang et al. [92] explored the synthesis of 1D thermoelectric nanowire heterostructures fabricated via solution-phase chemical methods, specifically focusing on telluride-based compounds. They demonstrated a catalyst-free synthesis of $Te-Bi_2Te_3$ "barbell" nanowire heterostructures exhibiting strait diameter and length distribution. They were also able to almost control the density of the hexagonal Bi_2Te_3 plates fixed on the Te nanowires by changing the reaction conditions. Furthermore, they also synthesized other telluride-based compositionally transmuted nanowire heterostructures such as $PbTe-Bi_2Te_3$. The bulk pellets fabricated from $Te-Bi_2Te_3$ heterostructures exhibited a significant enhancement in the Seebeck coefficient and highly decreased thermal conductivity, which result in large figure of merit.

The synthesis steps in the fabrication of $Te-Bi_2Te_3$ nanowire heterostructures include growth of Te nanowires and then growth of two Bi_2Te_3 plates at the ends of Te nanowire by adding Bi precursor. The further characterization of intermediate product, Te nanowires, and the final product $Te-Bi_2Te_3$ "barbell" nanowire heterostructures, with X-ray powder diffraction (XRD) revealed pure hexagonal phase of Te (JCPDS No. 36-1452) and partial formation of Bi_2Te_3 (JCPDS No. 15-0863) after adding the Bi precursor.

3. Conclusion and Outlook

During the last two decades, research on thermoelectric materials has gained an unprecedented momentum, ultimately, boosting the figure of merit (*ZT*) of the materials from ~1 to 2.2– 2.4 by nanostructure engineering. It is now established that the thermoelectric properties of metal tellurides can be improved through microstructural tailoring of their nanostructures, which leads to the decreased thermal conductivity by the selective scattering of phonons at the grain boundaries and amplified Seebeck coefficient by altering the density of states (DOS). It has been demonstrated that telluride nanowires and nanowire heterostructures can be easily synthesized in solution, which is an alternate method to fabricate bulk thermoelectric nanocomposites [92] . The reinforced pellets from nanowires and nanowire heterostructures exhibits exceptionally low thermal conductivities that results in superior thermoelectric properties. Furthermore, nanowires and nanowire heterostructures can be future paradigms for investigations such as energy filtering and modulation doping. Undoubtedly, these nanostructured materials and their heterostructures have opened new avenues for further research in thermoelectric materials.

Hitherto, attaining *ZT* vaues of 3 or more appears to be a strenuous task, which will require further cutback of thermal conductivity while simultaneously escalating electronic conduction. However, reduction in thermal conductivity below the amorphous limit will call for the alteration in the group velocity or decreasing the number of phonon modes that propagate. This can be achieved by coherent or correlated scattering effects, but thus far it has been proved to be insurmountable task for the phonons, and thermal conductivity reduction via such techniques has never been illustrated by researchers. This notion thus put forth an open challenge to the theorists and experimentalists to conceive neoteric scattering mechanisms and concepts that will further reduce the thermal conductivity.

Since, the microstructure morphology of TE materials governs the transport properties, controlled microstructural tailoring of grain size and shape is advantageous to obtain higher ZT values. Thus there is a dire need to comprehend phase diagrams and related defect theory and assess the effect of defects on the transport properties of TE materials. More investigations should be focused on synthesizing nanostructured particles at a large scale and cheap price, which will ultimately result in commercial applications of TE materials.

Moreover, the thermoelectric properties seems to be crucially influenced by the nanostructure, synthesis approach and device assembly. Thus, researchers should focus on thermoelectric nanomaterials with narrow bandgaps, heavy elements doping, point defects loading and nanostructuring [38]. For realistic thermoelectric applications, the synthesis techniques for thermoelectric materials should be scalable, have superior quality and cheap. The nanostructured materials must be in compact form so as to aid machining and the nanoscale characteristics should possess high thermal stability at longer time scales.

The high-performance shape-engineerable thermoelectric painting has also been a novel innovation in thermoelectric technology, wherein the painting is demonstrated to be geometrically compatible to surfaces of any shape [93]. The inorganic paint was based on Bi_2Te_3 and the molecular Sb_2Te_3 chalcogenidometalate as a sintering agent for thermoelectric particles. The ZT values was found to be 0.67 for n-type and 1.21 for p-type painted materials which are well in comparison with their bulk counterpart.

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