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Numerical and model predictions of the thermal conductivity of bismuth telluride nanoprism-assembled films

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ABSTRACT

This research aims at understanding the heat transfer phenomenon in the Bi_2Te_3 nanoprism-assembled films. For obtaining the associated effective thermal conductivity, the effective-medium-approximation (EMA) models existing in literature were examined and properly modified for prediction and Monte-Carlo numerical experiments based on unstructured grids were performed for confirmation. Cross-plane and in-plane thermal conductivities were both explored. For model predictions, the characteristic grain size of the nanoprisms is defined as either the phonon mean free path purely due to the grain boundary scattering (i.e. excluding the intrinsic scattering) or the averaged hydraulic diameter. A combination of a non-dilute 2D EMA model with the triple bond percolation theory turns out to be the best model for predicting the in-plane thermal conductivity. On the other hand, the evaluation of the cross-plane thermal conductivity by treating the nanoprisms as thermal conductors connected in parallel is satisfactory. The investigation shows that in addition to porosity, the scattering at the grain boundaries plays a dominant role in reducing the heat transfer in the direction perpendicular to the boundaries; the in-plane thermal conductivity is therefore much smaller than the cross-plane one.

1. Introduction

Due to the importance and urgency of the environmental protection issues and the energy crisis, people cannot care more about using the existing energy efficiently and exploring new green energies. Nowadays, more than 60% of energy consumed in the industry or daily life is wasted as heat, not to mention its contamination on the environment. There is thus a strong demand for recovering these wasted thermal energies. Among all, thermoelectric power generators (TEGs) are good for recovering energy from the waste heat because they can directly transform heat into electrical energy and have the advantages of light weight, no noise, and no mechanical vibration. The extremely low efficiency however limits their applications. The efficiency of TEGs is mainly determined by the thermoelectric properties of the materials, namely the figure of merit of the material $ZT = S^2\sigma T/k$, where appear the Seebeck coefficient S, the electric conductivity σ, the thermal conductivity k, and the absolute temperature T. Modern nanotechnology has helped improving the thermoelectric materials a lot in recent decades. Experimental as well as theoretical investigations have shown that the power factor $S^2\sigma$ can be enhanced and the thermal conductivity can be reduced by embedding low-dimensional structures [1–4] or introducing heterogeneous interfaces/grain boundaries [5–7] inside the materials. Among all, nanocomposite materials are easy to scale up at low price and possess a high homogeneous and/or heterogeneous interface density. They have become one of the most popular material types for thermoelectric applications [7,8]. Nanocomposites may be alloys fabricated by doping particular atoms in the crystal lattices [9], compact particle composites formed by hot pressing nanoparticles [10–12], polycrystals condensed from solutions with special formula and cooling rates [7] and so on.

Similar efforts have also been made to further enhance the thermoelectric properties of bismuth telluride which is known as the best thermoelectric material in room-temperature applications. Kashiwaqi et al. [13] fabricated a porous thin film of $Bi_{0.4}Te_3Sb_{1.6}$ by flash evaporation on an alumina substrate containing hexagonally arranged nanopores with an average diameter of 20 nm, separated by an average distance of 50 nm. Thanks to a significantly reduced thermal conductivity, an enhanced figure of merit of 1.8 at room temperature was obtained. Takashiri et al. [14] investigated the thermal conductivity of nanocrystalline bismuth–telluride-based alloys with nanoporous structures, which were

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obtained via a wet ball-milling process followed by a sintering process. The fabricated bulk alloys exhibit average grain sizes of 30 < d < 60 nm and porosities of 12% < ϕ < 18%. A thermal conductivity as small as 0.24 W/m K was observed; it was attributed to the grain size effect. Under the belief that electrical energy can be effectively transported in orderly structures and for the sake of controlling the microstructures, Chang et al. [15] presented an optimized one-step, large-area, noncatalytic and template-free growth approach to distinct Bi_2Te_3 nanostructures by pulsed laser deposition (PLD). The pollution of the residual templates or catalysts and the oxidation of the formed nanostructures were thus avoided. Physically self-assembled and well-aligned Bi_2Te_3 nanostructured films consisting of 0-D nanoparticles, 1-D nanorods, 2-D nanoflakes, and 3-D nanoprisms with specific preferential orientations normal to the insulated SiO_2/Si substrates were successfully fabricated. An in-plane power factor as large as 1.43 μW/cm K^2 for the 3-D nanostructures was obtained. The improvement in the power factor mainly originates from the reduction of the electric resistance.

Although power factors have been often measured, not many thermal conductivities of thin films are available. Chang et al. [16] measured the cross-plane thermal conductivity of thin films by a well-developed 3ω technique. An intrinsic thermal conductivity of 0.93 W/m K was found for a 3-D self-assembled $Bi_{0.5}Sb_{1.5}Te_3$ thin film; it is 0.98 W/m K for the Bi_2Te_3 thin film. The in-plane thermal conductivity however is unobtainable due to the measurement difficulty. Analytical predictions are also not possible due to the complicacy of the nanostructures. Therefore, in this work we aim at finding a model suitable for predicting the in-plane thermal conductivities of these emerging materials. More precisely we look to the effective medium approximation (EMA) models. An EMA model treats a composite material as a new homogeneous material and calculates the effective transport properties based on the macro properties of its ingredients. The pioneer work of Landauer [17] so estimated the electric conductivity for two bond percolation systems. Kirkpatrick [18] generalized the model to two dimensional (2D) square nets and three dimensional (3D) cubic nets of electric conductances. Liang and Ji [19] extended this model to three bond percolation systems and used an averaged bond number to study the layer thickness effect on the thermal conductivity of disordered composite thin films. Starting from the analytical solution of the thermal diffusion equation for a spherical particle embedded in some host material, Hasselman and Johnson [20] derived a formula for the effective thermal conductivity of particle-embedded-in-host composites. This model works pretty well on microcomposites while compared to experimental data. The dilute-particle-concentration assumption however limits its application. Poon and Limtragool [21] and Chuang and Huang [5] extended this EMA model for arbitrary particle concentrations. By introducing geometry-dependent view factors and porosity functions, Liu and Huang [22] proposed a ballistic–diffusive EMA model for porous medium with various pore shapes. Instead of in series [23], they joined ballistic and diffusive thermal resistances in parallel and obtained good predictions for regularly aligned pore wires.

In this work, we intend to examine, properly modify, and then apply the existing EMA models mentioned above to the porous thin films. To confirm and compare the accuracies of these models, Monte-Carlo simulations based on unstructured grids [5] are performed; the Bi_2Te_3 thin film consisting of 3D nanoprisms is targeted for its exhibiting the highest power factor among all the well-aligned Bi_2Te_3 nanostructured films of Chang et al. [15].

The rest of this paper is arranged as follows. The nanostructure of the Bi_2Te_3 nanoprism-assembled film and its numerical model are introduced in Section 2. Followed in Section 3 is a brief review of the existing EMA models; also presented is how these models are modified and applied to the porous films. Simulation results are then compared with the model predictions in Section 4. Finally the conclusion is given in Section 5.

2. Bi_2Te_3 nanoprism-assembled film

The Bi_2Te_3 nanoprism-assembled film was fabricated by the pulsed laser deposition at 550 °C [15]. The cross section SEM images are given in Fig. 1. The measured in-plane power factor is 1.43 μW/cm K^2, larger than the common power factors of unstructured thin films (usually less than 1 μW/cm K^2). These SEM images show that the nanostructures are basically triangular columns aligned along the thickness direction. Although each nanoprism in Fig. 1(b) is seemingly laminated-flakes-like, the HRTEM images and the corresponding fast Fourier-transform (FFT) electron diffraction (ED) patterns reveal a completely same orientation and crystallinity within a single column. We thus conclude that the nanoprism-assembled column is a single crystal. The triangular cross sections have an average width of 440 nm. Besides, the film thickness (L) is 800 nm–1000 nm, much larger than the bulk mean free path (about 74 nm at room temperature) of Bi_2Te_3. Therefore, the nanostructure can be viewed as two dimensional and the end effect may be ignored when heat transfer is studied. In between nanoprisms, air is fulfilled.

To build a numerical sample imitating the real sample, 64 nanoprisms and 28 void regions are first identified from the SEM images; so are their shapes as close as possible. They are then put together like a jigsaw puzzle; the so-constructed numerical sample is shown in Fig. 2. The dimension of the numerical sample is $3875\ \mathrm{nm}(x) \times 2925\ \mathrm{nm}(y) \times 800\ \mathrm{nm}(z)$. The porosity is 0.146 and the interface density is $6.14 \times 10^{-3}\ \mathrm{nm}^{-1}$. In simulation, a heat flux will be generated either along the x direction (in-plane) or the z direction (cross-plane) by injecting phonons at prescribed boundary temperatures [24]. To avoid/reduce the contamination of this temperature-controlled boundary condition, two blocks of bulk Bi_2Te_3 of $2000\ \mathrm{nm}(x) \times 2925\ \mathrm{nm}(y) \times 800\ \mathrm{nm}(z)$ are added beside the nanoprism-assembled region as shown in Fig. 3(a) for the in-plane simulation and two blocks of $3875\ \mathrm{nm}(x) \times 2925\ \mathrm{nm}(y) \times 200\ \mathrm{nm}(z)$ are added as shown in Fig. 3(b) for the cross-plane simulation. Phonons are thus injected into and travel through the bulk regions before they enter the nanoprism-assembled region in a natural way. Also shown in Fig. 3(a) and (b) are the unstructured grid systems with triangular and tetrahedron cells for the in-plane (2D) and cross-plane (3D) simulations respectively. Furthermore, grain boundaries are assumed totally diffuse by default. The Monte-Carlo simulators developed by Huang and Chuang [24] as well as Chuang and Huang [5] are employed. For details, the readers are referred to these works. In particular, the experimentally measured phonon spectrum [25] was employed to calculate the averaged phonon properties under the grey medium approximation; they were averaged over the in-plane directions (Γ–Y) and the out-of-plane direction (Γ–Z) first and over the frequency next. The bulk phonon mean free path (Λ_h) was on the other hand

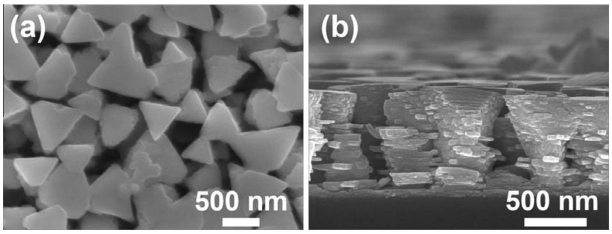

Fig. 1. The top (a) and side (b) cross-section SEM images of the Bi_2Te_3 nanoprism-assembled film.