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Thermoelectric properties variation in antimony telluride nanofilm using molecular dynamics

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Abstract

In recent years, thermoelectric materials that have the advantage of directly converting heat into electricity, have become a hot research topic. In this study, we designed a series of Sb$_2$Te$_3$ nanofilms using molecular dynamics simulation to explore the effects of structural defects on the phonon transport properties of thermoelectric materials. We predicted that temperature variations and structural defects can greatly increase the transfer of energy invalid and decrease thermal conductivity. Designing thermoelectric materials as composite interfaces, multilayer films, and defect structures is an effective way to achieve this goal.

1. Introduction

With rising awareness of environmental protection and a sharp decline in the stock of petrochemical energy, clean and green energy has become a hot topic of development today. In recent years, thermoelectric (TE) materials that have the advantage of directly converting heat into electricity have become a hot research topic. Their research applications include semiconductors, the automotive industry, aviation technology, and other industries [1–3]. The V$_2$VI$_3$ family, such as antimony telluride (Sb$_2$Te$_3$), bismuth telluride (Bi$_2$Te$_3$), and bismuth selenide (Bi$_2$Se$_3$), is the most promising TE materials for room temperature operation [4, 5]. The conversion efficiency of TE materials is evaluated using the dimensionless figure-of-merit $zT$, which is expressed as $zT = S^2\sigma T/k$. Here, $S$, $\sigma$, $T$, and $k$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. However, general materials usually have good electrical and thermal conductivity, whereas good thermoelectric materials should have good electrical conductivity but poor thermal conductivity. Therefore, this study enhances the $zT$ value of TE materials.

Fortunately, the rapid development of nanotechnology and computer equipment allows us to eliminate the experimental process that previously required much labor, time, and money and can predict and obtain the characteristic of materials and provide important information, which greatly accelerates the development of new-TE materials [6–8]. This study on TE materials is divided into two areas, one is to find new materials with good thermoelectric properties, and the other is to change the structure of existing materials. Nanostructured materials can increase the density of electronic states, and the mean free path of electrons can be shorter than that of phonons; therefore, the scattering rate of phonons can be much higher than that of electrons, which cannot change the lattice thermal conductivity, and may even greatly reduce the thermal conductivity [9–12]. The main contribution of k at the nanoscale is the lattice thermal conductivity of phonon vibrational energy transfer [13, 14]. Compared with the bulk structure, the $zT$ value of the nanostructure is significantly higher because of the lattice thermal conductivity of the thermoelectric material through efficient phonon scattering at the nanostructure boundary [15–17]. Thermal properties are important in nanoscale materials, and the TE properties of nanostructures are significantly enhanced, but the relevant parameters are difficult to determine experimentally.

In this study, we designed a series of Sb$_2$Te$_3$ nanofilms using non-equilibrium molecular dynamics simulations to explore the effects of structural defects on the phonon transport properties of thermoelectric materials. The effects of temperature, hole defect, and substrate were investigated to optimize the TE devices. The remainder of this study is organized as follows. Section II presents the parameter settings of the model,
potential, and method of calculation. Section III discusses the results obtained for Sb₂Te₃ nanofilms affected by the effects of structural defects. Section IV details the conclusion.

2. Materials and methods

For complex materials, the state of atomic motion and material properties can be accurately reproduced with high precision through molecular dynamics (MD) simulation, and it is important to select the correct potential functional form. Interatomic or intermolecular interactions are the sum of interactions between all different pairs of atoms or molecules, i.e. two-body interactions [18, 19]. Compared to many-body potentials that involve multiple parameters and whose complex forms are not readily available under a wider range of simulation conditions, the two-body potential form is easy to implement and ensures better accessibility while enabling good predictions of phonon properties, such as thermal conductivity.

In this study, we refer to Chowdhury et al [20], who used density functional theory to develop two-body interatomic potential parameters. The two-body interatomic potentials \( \varphi(r_{ij}) \) show a distance potential between two atoms \( i \) and \( j \), comprising a long-range Coulombic term for electrostatic interactions and a short-range Morse term for interatomic pair potentials. The equation can be expressed as follows:

\[
\varphi(r_{ij}) = \varphi_0 \left[ \left(1 - \exp \left[ -\alpha (r_{ij} - r_0) \right] \right)^2 - 1 \right] + \frac{q_i q_j}{r_{ij}}
\]

where \( \varphi_0 \) is the depth of the Morse potential well, \( \alpha \) is the measure of bond elasticity, \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( r_0 \) is the equilibrium bond distance, and \( q_i \) and \( q_j \) are the effective charges of atoms \( i \) and \( j \), respectively. The effective charge values used in the potential parameters are \(-0.22\), \(0.30\), and \(-0.16\) for Te₁, Sb, and Te₂ atoms, respectively. The Sb₂Te₃ quintuple layer substrate and the potential energy parameters that were used are shown in figure 1 and table 1, respectively.

Figure 2 shows the simulation model’s parameter settings for the thermal loading characteristics. In the thermal simulation, we refer to Jund et al [21], who reported the principle of thermal conductivity determination by setting the hot source range in \( \delta/4 \) (pink) and the cold sink range in \( 3\delta/4 \) (blue), where \( \delta \) is the substrate length. A stable heat (\( \Delta \varepsilon \)) was generated in the hot source range and removed in the cold sink range for each simulation time step (\( 1 \times 10^{-15} \) s). We can obtain a constant heat flux (\( q \)) on a time-averaged basis using the velocity-rescaling algorithm. The equation can be expressed as follows:

\[
q = \frac{\Delta \varepsilon}{2A \Delta t}
\]

where \( A \) is the cross-sectional area and \( \Delta t \) is the time step. After 200,000 operational time steps, the system reached a steady state to establish thermal equilibrium at a specific temperature. The temperature gradient (\( dT / dy \)) of each section can be obtained and the thermal conductivity can be calculated using Fourier’s law. The equations can be expressed as follows:
The loading direction of the simulation model was divided into 20 equal regions, and periodic boundary conditions were applied in the X, Y, and Z directions, effectively overcoming the limitation of a small simulation domain to keep the system stable during the simulation \[22, 23\]. In the tensile simulation, we stretched along the Y-direction of the bilateral at a speed of 10 ms\(^{-1}\). To avoid the need for quantum corrections, the minimum temperature of the simulated environment during this period must be higher than the Debye temperature. The Debye temperature of Sb\(_2\)Te\(_3\) is approximately 165 K \[24\]. The initial simulated temperature was set at room temperature (300 K), ranging from 200 to 500 K with an interval of 50 K.

### 3. Results and discussion

First, the literature reported that infinite length converging thermal conductivity can be predicted by simulating nanowire thermal conductivity as a function of nanowire length using MD \[25, 26\]. We constructed various lengths of 60 to 240 Å of Sb\(_2\)Te\(_3\) nanowires with a cross-sectional area of 60 \(\times\) 60 Å to verify the credibility of the simulation prediction results under thermal loading at 300 K, and the results are shown in figure 3. The 60 Å length of Sb\(_2\)Te\(_3\) nanowires had a rugged temperature gradient curve and a lower thermal conductivity of 0.385 W mK\(^{-1}\) (figure 3(a)). The temperature gradient curve smooths out as the length of the Sb\(_2\)Te\(_3\) nanowires increases, enhancing the thermal conductivity to 0.667 W mK\(^{-1}\) with a 240-Å length. The thermal conductivity of the Sb\(_2\)Te\(_3\) nanowires increased in a proportional relationship with the length (figure 3(b)). Then, we plot the relationship between reciprocal thermal conductivity (1/k) and reciprocal length (1/L) (figure 3(c)). The reciprocal thermal conductivity (1/k) of the nanowires increases linearly as a function of the reciprocal length (1/L), and extrapolation is used to obtain an infinite length converging thermal conductivity (\(k_0\)). The equation

\[
k = -\frac{q}{dT/dy}
\]
can be approximated as follows [27]:

\[ \frac{1}{k} = \frac{1}{k_0} \left( 1 + \frac{\lambda}{L} \right) \]  

(4)

where \( \lambda \) is the mean free path of the phonon (MFP). The thermal conductivity-converged length and mean free path of the phonon \( \lambda \) of the Sb\(_2\)Te\(_3\) nanowires are 0.789 W mK\(^{-1}\) and 6.28 nm at 300 K, respectively. The results are similar to previous reports [20, 28].

To investigate the effects of structural defects on TE properties, we designed a perfect structure, a hole defect, and a sandwich structure of Sb\(_2\)Te\(_3\) nanofilms under thermal loading at different temperatures, with a nanofilm size of approximately 120 \( \times \) 120 \( \times \) 120 Å. The perfect structure of Sb\(_2\)Te\(_3\) nanofilms under thermal loading at different temperatures results are shown in figures 4. The temperature difference and thermal conductivity calculated using equation (3) were 25.44 K and 0.797 W mK\(^{-1}\) at 300 K, respectively; these values are similar to those reported previously [29]. The simulation temperatures ranged from 200 to 500 K with an interval of 50 K, with the temperature difference increasing from 14.29 to 47.61 K. The temperature gradient curve at higher simulation temperatures became steeper under thermal loading and the thermal conductivity decreased linearly from 0.899 to 0.713 W mK\(^{-1}\). The lower simulation temperature keeps the nanostructures between atoms ordered, and phonons can effectively transfer energy by reducing lattice scattering, resulting in higher thermal conductivity. The hole defect structure of Sb\(_2\)Te\(_3\) nanofilms under thermal loading at 300-K results are shown in figure 5. The temperature difference in the hole defect structure, the diameter range of 0–30 Å with an interval of 5 Å, and thermal conductivity at 300 K are from 25.44 to 51.15 K and 0.797 to 0.315 W mK\(^{-1}\), respectively. When phonons collide with the hole boundary, scattering occurs, and the larger the hole defect, the lower the thermal conductivity. In the sandwich structure of Sb\(_2\)Te\(_3\) nanofilms (Te--Sb\(_2\)Te\(_3\)--Te), the thickness of Te is 5 Å, and under thermal loading at different temperatures, the simulation temperature was set to the same perfect structure case, the results are shown in figure 6. The temperature difference in the sandwich structure and thermal conductivity at different temperatures ranges from 23.82 to 64.90 K and 0.528 to 0.426 W mK\(^{-1}\), respectively. The lower simulation temperature effectively causes phonons to transfer energy, but there are phonon scattering opportunities at the interface between Te and Sb\(_2\)Te\(_3\), resulting in reduced thermal conductivity. The thermal conductivity of the sandwich structure is still lower than the perfect structure value because the sandwich structure (Te--Sb\(_2\)Te\(_3\)--Te) differs from the perfect structure (Sb\(_2\)Te\(_3\)).
To obtain a high $zT$ based on the dimensionless figure-of-merit $zT$, we need a lower thermal conductivity $k$. Published reports [22, 23, 30–35] show that surface roughness, pore and point defects, grain size, strain, and interfacial effects contribute to phonon scattering, which affects energy transfer and reduces lattice thermal conductivity by

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**Figure 4.** Sb$_2$Te$_3$ nanofilms with perfect structure under thermal loading at different temperatures: (a) temperature gradient curves, (b) thermal conductivity, and (c) snapshot diagrams of atomic motion.

**Figure 5.** Sb$_2$Te$_3$ nanofilms with a hole defect under thermal loading at 300K: (a) temperature gradient curves, (b) thermal conductivity, and (c) snapshot diagrams of atomic motion.

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To obtain a high $zT$ based on the dimensionless figure-of-merit $zT$, we need a lower thermal conductivity $k$. Published reports [22, 23, 30–35] show that surface roughness, pore and point defects, grain size, strain, and interfacial effects contribute to phonon scattering, which affects energy transfer and reduces lattice thermal conductivity by
inducing atomic configurational disorder. A similar phenomenon has been observed in various pure carbon nanomaterials and discussed influences on the thermal conductivities of the vibration density of states (VDOS) \[36, 37\]. The low-frequency phonons are generally major energy carriers in thermal transport, and the higher averaged group velocity is also in the low-frequency range. That is, the main contribution of thermal conductivity is from the low-frequency phonons vibrational to transport energy, and the high-frequency phonons contribute little to total thermal conductivity. Meanwhile, Kothari et al.\[38\] reported that when phonons carry heat and transport through the defect structure, the main contribution is from the phonon scattering of long wavelengths, while the phonon scattering of short wavelengths is ignored, which affects energy transfer and reduces lattice thermal conductivity by inducing atomic configurational disorder. Therefore, we predicted that temperature variations and structural defects can efficiently increase the transfer of energy invalid and decrease thermal conductivity.

4. Conclusions

In this study, we used MD simulation to design a series of Sb$_2$Te$_3$ nanofilms under thermal loading and calculate the thermal conductivities of the various effects. The temperature variation and structural defects can efficiently increase the transfer of energy invalid and decrease the thermal conductivity. Designing thermoelectric materials as composite interfaces, multilayer films, and defect structures is an effective way to achieve this goal.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.
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