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Thermoelectric Performance Theory Research on Bi_2Te_3 Nanowires under the Quantum Size Effect

Xiao-Jing ZHANG, Qi-Chen XU, Wei-Tai XU, Xi WU*,[a] and Jian-Xiang WANG*,[b]
College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nanoscience and Technology, Soochow University, Suzhou 215006, China
[a]wuxi@suda.edu.cn

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Abstract. Based on the existing theoretical study of Bi_2Te_3 nanowires, this paper establishes the relationships among the band structure, relaxation time and *ZT* values by solving the Boltzmann equation. Then, comprehensive analysis is made to figure out how these factors have influence on *ZT* values of Bi_2Te_3 thermoelectric materials, including the size of rectangular nanowires, doping concentration and temperature. The results show that level discretization occurs because of the quantum size effect, when the relationships between the relaxation time and *ZT* values have been built. Therefore, *ZT* values of Bi_2Te_3 nanowires have step oscillation changes with the change of the side length, doping concentration and temperature. Among four types of Bi_2Te_3 rectangular nanowires researched in this paper, the thermoelectric performance of the p-type nanowires with [110] direction is best for the *ZT* value reaching 65.3, when the side length a_x = 6.5nm, a_z = 5.3nm, doping concentration n = 4.41018cm^{-3} and temperature T = 300K.

1 Introduction

Thermoelectric materials are a kind of functional materials, which can realize the direct transformation between the heat and electricity through the usage of the solid internal carrier movement. Thermoelectric materials are able to be manufactured into tiny semiconductor refrigeration devices with light weight and small volume. So, it has a good application prospect, especially in the fields of computer technology, space technology, superconducting technology, microelectronic technology, etc.

The Bi_2Te_3 materials have relatively good thermal performance and highly anisotropic band structure in normal temperature. Hence, it has become a hot topic in the study of low dimensional thermoelectric materials, and its theoretical research is also in constant development and improvement [1]. In 1993, L. D. Hicks, M. S. Dresselhaus, et al concluded that the *ZT* value of the square Bi_2Te_3 nanowires increases monotonously with the decrease of the side length by solving the Boltzmann equation. The *ZT* value is up to 14, when the side length is 5Å [2]. In 1999, X. Sun, Y. M. Lin, et al analyzed the effect of band structure of the square Bi nanowires on *ZT* values. The study found that n-type nanowires have best thermoelectric properties in the trigonal direction. The *ZT* value can reach 6, when the side length is 5nm [3]. In 2000, Y. M. Lin, et al calculated the *ZT* values of the cylindrical Bi nanowires on this basis. Similar results were concluded that n-type nanowires have best thermoelectric performance in trigonal direction. The *ZT* value reaches the maximum 6.36, when the diameter is 5nm [4]. In 2008, I. Bejenar, et al analyzed how the residual impurities affected the *ZT* values of squre Bi_2Te_3 nanowires. The results showed that the optimal concentration of electron holes is 5×10^{18}cm^{-3} for the [110] direction of p-type nanowires. At the same time, the *ZT* value can reach 2.8, when the side length is 7 nm and the temperature is 480 K [5]. In 2009, I. Bejenari researched *ZT* values of the square Bi_2Te_3 nanowires with an external electric field. The *ZT* value of p-type nanowires is 3.1 for the [110] direction in normal temperature with the side length of 7nm, ionized donor concentration of 5×10^{18}cm^{-3} and the electric grid voltage of 60V. The value fell to 1.65, when the electric grid voltage is 0 [6]. In 2010, S. Farhangfars first considered the effect of the relaxation time on *ZT* values of square Bi_2Te_3 nanowires. It found that *ZT* values didn't

increase with the drop of the side length, but presented the trend of decrease after initial increase. And its peak appeared with the side length of 6.5nm [7]. In 2013, A. Sellitto, et al proposed a model to calculate the properties of thermoelectric materials based on the nonlocal equation. The results showed that the maximum *ZT* value is 1 for the cylindrical p-type Bi_2Te_3 nanowires, when the radius is just between the mean free path of phonons and that of electrons [8].

So far, the model optimization and improvement are often limited in a certain aspect, lack overall consideration for the effect of various factors on *ZT* values. On the basis of previous studies, the relationships are built among the band structure, the relaxation time and *ZT* values, by solving the Boltzmann equation. To seek the feasibility of enhancing the performance of Bi_2Te_3 thermoelectric materials, this paper aims to comprehensively analyze how the three factors influence *ZT* values of Bi_2Te_3 thermoelectric materials, including the rectangular nanowires size, doping concentration and temperature.

2 Models

Dimensionless thermoelectric optimum value *ZT* is usually used to measure thermoelectric performance of materials:

$$ZT=\frac{S^2\sigma}{\kappa}T \tag{1}$$

Where *T* is the average temperature on cold end and hot end of the thermoelectric material, *S* is Seebeck coefficient (or thermoelectric force). σ is conductivity. κ is thermal conductivity, consisting of the carrier thermal conductivity κ_e and the lattice thermal conductivity κ_L. *S*, σ and κ_e can be defined as the transmission factors, representing influence of the carrier transmission on *ZT* values. They can be obtained by solving the following discrete equations [7]:

$$\sigma \equiv L^{(0)} \tag{2}$$

$$S \equiv \pm\frac{1}{eT}\frac{L^{(1)}}{L^{(0)}} \tag{3}$$

$$\kappa_e \equiv \frac{1}{e^2T}\left[L^{(2)}-\frac{(L^{(1)})^2}{L^{(0)}}\right] \tag{4}$$

Where e is an electron charge, $L^{(\alpha)}$ is a transfer matrix element, α is the lattice site, respectively taking 0, 1, 2. For the rectangular nanowires, the lattice thermal conductivity of nanowires κ_L can be expressed as [8]:

$$\kappa_L = \kappa_{L,bulk}\left(1+\beta_p\frac{l_p}{\sqrt{A}}\right)^{-1} \tag{5}$$

Where $\kappa_{L,bulk}$ is the lattice thermal conductivity of the block Bi_2Te_3, β_P is numerical calculating coefficient. l_p is the mean free path of a phonon, l_p of Bi_2Te_3 nanowires is about 1 nm [2]. A is the cross-sectional area of nanowires.

The volume of the nanowires is $V=a_xa_ya_z$, with the width a_x, length a_y and thickness a_z. Considering the multi-energy valley band structure of Bi_2Te_3, $L^{(\alpha)}$ can be defined as [7]:

$$L^{(\alpha)}=\sum_\beta L_\beta^{(\alpha)}=\sum_\beta\left(\frac{s}{a_xa_z}\frac{4\pi\mu}{(k_BT)^{\alpha+0.5}}\sqrt{\frac{m_y^\beta}{2}}\frac{e}{\hbar}\sum_{i,j}\frac{1}{\langle\tau_{i,j}^\beta\rangle}\sum_{n,l}F_{n,l}^{(\alpha,\beta)}\right) \tag{6}$$

Where β is the number of the energy valley ($\beta\in N$), taking from 1 to 6. *s* is span degeneracy, μ is carrier mobility, k_B is the Boltzmann constant, m_y^β is effective mass of β energy valley in the direction of y axis, $\hbar$ is reduced Planck's constant. *n* and *l* are quantum numbers of the sub energy band, their values can refer to the literature [5]. $\langle\tau_{i,j}^\beta\rangle$ is the statistical average of β energy valley's relaxation time in the state of (*i*, *j*), taking (*i*, *j*) from [0, *n*] and [0, *l*], $i、j\in N$. $F_{n,l}^{(\alpha,\beta)}$ is the Fermi integral of β energy valley in sub band (*n*, *l*), which can be indicated as [7]:

$$F_{n,l}^{(\alpha,\beta)}=\int_0^\infty\cosh^{-2}\left[\frac{\varepsilon+\eta_{n,l}^\beta}{2}\right]\tau_{n,l}^\beta(\varepsilon)\left(\varepsilon+\eta_{n,l}^\beta\right)^\alpha\sqrt{\varepsilon-\varepsilon_{n,l}^\beta}\,d\varepsilon \tag{7}$$

Where ε is reduced energy, $\tau_{n,l}^{\beta}(\varepsilon)$ is the relational expression of the relaxation time when ε and β energy valleys are in band (n, l). $\eta_{n,l}^{\beta}$ is the reduced chemical potential of β energy valley in sub band (n, l). $\varepsilon_{n,l}^{\beta}$ is the reduced energy of β valley in sub band (n, l), $\varepsilon_{n,l}^{\beta} = (\hbar^2\pi^2/2)\cdot\left[n^2/(a_x{}^2 m_x^{\beta}) + l^2/(a_z{}^2 m_z^{\beta})\right]$.

The electron and hole carrier concentration of the Bi_2Te_3 nanowires with a single valley are [5]:

$$n_{1D} = N_c^{1D}\sum_{n,l} F_{-1/2}(\eta_{n,l}^{\beta}) \tag{8}$$

$$p_{1D} = N_v^{1D}\sum_{n,l} F_{-1/2}(\eta_{n,l}^{\beta}) \tag{9}$$

Where N_c^{1D} is effective state density of electrons, N_v^{1D} is that of electron holes. $F_{-1/2}(\eta_{n,l}^{\beta})$ represents the Fermi integral with an independent variable $\eta_{n,l}^{\beta}$, which is defined as:

$$F_{-1/2}(\eta_{n,l}^{\beta}) = \frac{1}{\Gamma(1/2)}\int_0^{\infty}\frac{\varepsilon^{-1/2}}{\exp\left(\varepsilon-\eta_{n,l}^{\beta}\right)+1}d\varepsilon \tag{10}$$

But for different carriers, $\eta_{n,l}^{\beta}$ has different expressions:

$$\eta_{n,l}^{\beta} = \left(E_F - E_{n,l}^{e,\beta}\right)/\left(k_B T\right) \tag{11}$$

$$\eta_{n,l}^{\beta} = \left(E_{n,l}^{h,\beta} - E_F\right)/\left(k_B T\right) \tag{12}$$

Where E_F is Fermi level, $E_{n,l}^{e,\beta}$ represents the sub-band edge for an electron of Bi_2Te_3 nanowires. $E_{n,l}^{h,\beta}$ denotes the valence band top of sub band for electron holes. Here, $E_{n,l}^{e,\beta}$ and $E_{n,l}^{h,\beta}$ can be respectively defined as:

$$E_{n,l}^{e,\beta} = E_g + \frac{\hbar^2}{2}\left[\frac{(n\pi/a_x - k_{0x})^2}{m_x^{\beta}} + \frac{(l\pi/a_z - k_{0z})^2}{m_z^{\beta}}\right] \tag{13}$$

$$E_{n,l}^{h,\beta} = -\frac{\hbar^2\pi^2}{2}\left(\frac{n^2}{m_x^{\beta}a_x^2} + \frac{l^2}{m_z^{\beta}a_z^2}\right) \tag{14}$$

Where m_x^{β} is the effective mass component of Bi_2Te_3 β energy valley along the x axis, m_z^{β} is that along the y axis. E_g is the energy gap of Bi_2Te_3. k_{0x} and k_{0z} are vectors from the top of valence band to the bottom of the conductivity in momentum space, taking 0.091 and 0.152.

The transition rate from the state (i, j) to the state (i', j') is indicted as:

$$\tau_{i,j\to i',j',\beta}^{-1}(\varepsilon) = \frac{\pi}{2}\frac{\rho}{\hbar}V_0^2\Lambda_{i',j'}^{i,j}g_{i',j'}^{\beta}(\varepsilon) \tag{15}$$

Where ρ is the volume density of scatterers, $\rho = N/V$. i' and j' are quantum numbers, and they have the same value range with i and j. $g_{i',j'}^{\beta}(\varepsilon)$ is energy density of state,

$$g_{i',j'}^{\beta}(\varepsilon) = \frac{s}{2\pi\hbar}\frac{V}{a_x a_z}\sqrt{\frac{m_y^{\beta}}{2}}\sum_{n,l}\frac{\Theta(\varepsilon-\varepsilon_{n,l}^{\beta})}{\sqrt{\varepsilon-\varepsilon_{n,l}^{\beta}}} \tag{16}$$

Where Θ is the unit step equation. The statistical average of relaxation time $\left\langle\tau_{i,j\to i',j'}^{\beta}\right\rangle$ is:

$$\left\langle\tau_{i,j\to i',j'}^{\beta}\right\rangle = \frac{\int\tau_{i,j\to i',j',\beta}(\varepsilon)\varepsilon g_{i',j'}^{\beta}(\varepsilon)\partial_{\varepsilon}f\,\mathrm{d}\varepsilon}{\int\varepsilon g_{i',j'}^{\beta}(\varepsilon)\partial_{\varepsilon}f\,\mathrm{d}\varepsilon} \tag{17}$$

Where $\partial_{\varepsilon}f$ is first partial derivative of ε for Fermi distribution equation. $\left\langle\tau_{i,j}^{\beta}\right\rangle$ and $\tau_{n,l}^{\beta}(\varepsilon)$ can be respectively obtained from Matthiessen law:

$$\left\langle\tau_{i,j}^{\beta}\right\rangle^{-1} = \sum_{i',j'}\left\langle\tau_{i,j\to i',j'}^{\beta}\right\rangle^{-1} \tag{18}$$

$$\tau_{i,j,\beta}^{-1}(\varepsilon) = \sum_{i',j'}\tau_{i,j\to i',j',\beta}^{-1}(\varepsilon) \tag{19}$$

After parameters $\eta_{n,l}^{\beta}$, $\left\langle\tau_{i,j}^{\beta}\right\rangle$ and $\tau_{n,l}^{\beta}(\varepsilon)$ determined, ZT values of Bi_2Te_3 nanowires are obtained.

3 Results and Analysis

3.1 The effects of length change on *ZT* values for Bi_2Te_3 square nanowires

Figure 1 shows the relationships between the length change and *ZT* values of four types of Bi_2Te_3 square nanowires in normal temperature (300 K). The results find that *ZT* values decrease sharply after sharp increase with the decrease of the length a_x, when the carrier concentration is $5\times10^{18}cm^{-3}$. For n-type doping, both the *ZT* value of [110] direction and that of [015] direction reach the maximum, respectively 25.3 and 36.4, when a_x=5.5nm. However, *ZT* values of [015] direction nanowires may have phase step oscillation with the change of ax from 5.2 to 6.2 nm. As for p-type doping, both of the two *ZT* values reach the maximum, respectively 41.5 and 29.6, when a_x = 7 nm. Therefore, it is found that the thermoelectric performance of nanowires with p-type doping is superior to that with n-type doping in [110] direction, while that with n-type doping is superior to that with p-type in [015] direction.

Figure 2 lists the schematic diagrams of the relationship between the transmission factor of p-type nanowires in [110] direction and the side length. It is illustrated from the figure that σ increases monotonically as well as κ_L, with the increase of the side length, when a_x changes between 5.5 and 7.5 nm. *S* also decreases monotonically. However, κ_e shows the tendency of oscillation increase, which is approximately consistent with the oscillation curves of *ZT* values for p-type nanowires in [110] direction in figure 1.

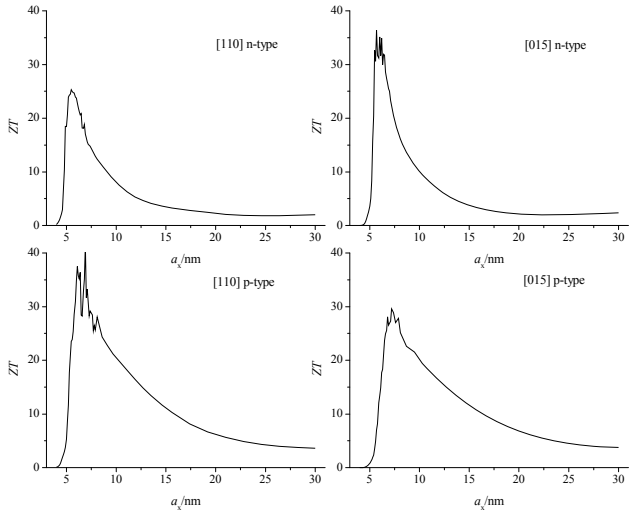

Figure 1 Schematic diagrams of the relationship between *ZT* values of Bi_2Te_3 square nanowires and the side length in normal temperature (300K)

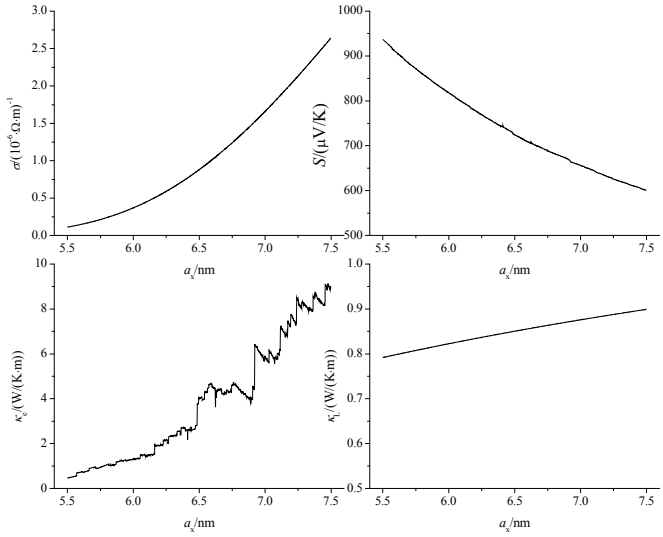

Figure 2 Schematic diagrams of the relationship between the transmission factors of p-type nanowires and the side length in [110] direction

3.2 Effects of the length changing of Bi_2Te_3 nanowires on *ZT* values

Based on the analysis of calculating results above for Bi2Te3 square nanowires, the relationship between the ZT values and the length of Bi2Te3 nanowires will be further researched. Figure 3 shows the schematic diagrams of the relationship between ZT values with the length for four types of Bi2Te3 rectangular nanowires in normal temperature (300K). As shown in the figure, the minimum ZT values of all types occur at the smallest length, which agrees well with the analysis results above. Due to the band structure differences of various types of nanowires, the changes of ZT values differ a lot, with the changing of ax and az. In these circumstances, the effect of ax changing on ZT values is significantly greater than the influence of az changing on ZT values, for n-type and p-type nanowires in [110] direction. Nanowires may obtain the best thermoelectric performance, when ax>az. Besides, ZT values in [015] direction have more dramatic step change relative to those in [110] direction, with the change of ax and az for n-type and p-type nanowires.

Based on data comparison, it is found that the thermoelectric properties of Bi_2Te_3 rectangular nanowires are evidently superior to those of the square nanowires. The best *ZT* value of n-type rectangular nanowires in [110] direction is 47.9, which is 89% higher than that of n-type square nanowires in [110] direction, while the best *ZT* value of p-type rectangular nanowires is 65.2, 57% higher than that of p-type square nanowires. By contrast, the growing rate of *ZT* values for n-type and p-type rectangular nanowires is smaller, just about 30% of that for the square nanowires in [015] direction.

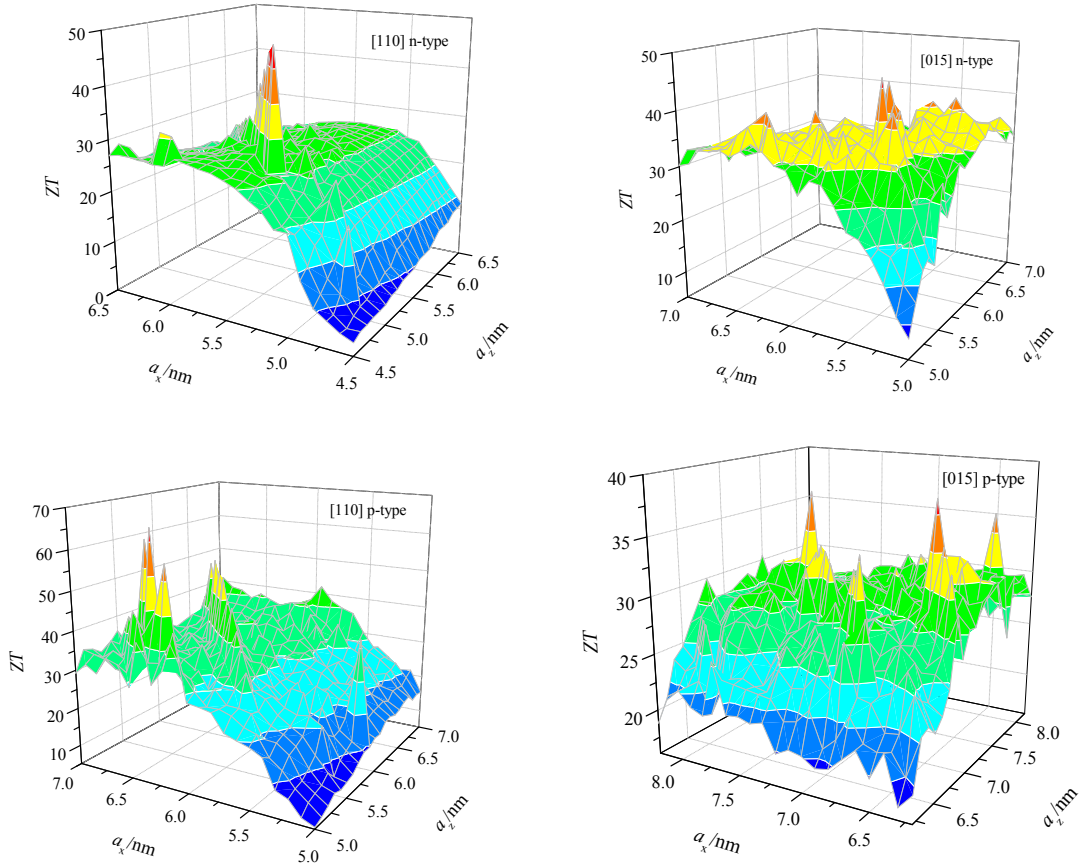

Figure 3 Schematic diagrams of the relationship between *ZT* values and the side length for Bi_2Te_3 rectangular nanowires in normal temperature (300K)

3.3 Effects of doping concentration on *ZT* values for Bi_2Te_3 rectangular nanowires

Because of the band structure of Bi_2Te_3 nanowires directly affected by doping concentration, the doping concentration is one of the parameters, which have important influence on *ZT* values of Bi_2Te_3 nanowires. There are four schematic diagrams of the relationship between *ZT* values and the doping concentration for four types of Bi_2Te_3 rectangular nanowires in normal temperature (300 K), as shown in figure 4. It is illustrated from the figure that *ZT* values of all types of nanowires gradually decline after the step increase, with increase of the doping concentration. When the doping concentration gradually increases from $3\times10^{17}cm^{-3}$, *S* increases, as well as σ. At the same time, the carrier mobility decreases with the increase of the doping concentration, increasing the chance of scattering carriers. Hence, *ZT* values may have step increase. With further increase of the doping concentration, it is certain that the impurity band results in the energy gap narrowing. σ increases, as well as κ, while σ/κ drops dramatically. So, *ZT* values gradually decrease. Take p-type Bi_2Te_3 rectangular nanowires in [110] direction for example. There are three distinct step changes, especially the biggest change at $43\times10^{18}cm^{-3}$. *ZT* values change from 53.4 to 67.1, when the doping concentration changes from $43\times10^{18}cm^{-3}$ to $44\times10^{18}cm^{-3}$. Based on the data calculation, κ_e decreases due to the step change, respectively at the doping concentration of $20.56164\times10^{18}cm^{-3}$, $38.97994\times10^{18}cm^{-3}$ and $43.75214\times10^{18}cm^{-3}$. Hence, the step change of *ZT* values is caused by that of κ_e, which is similar to other types of nanowires.

It is worth noting that there is biggish error in the calculation and analysis above for n-type nanowires in [110] direction. When sectional dimensions determined, the *ZT* value changes from 47.9 (n=$50\times10^{17}cm^{-3}$) to 50.9 (n=$25\times10^{17}cm^{-3}$). Analytical error of the other three types is lesser, which can leave out. It can be found that the adjustment of the doping concentration is an effective way to improve the thermoelectric performance to some extent. However, the acquisition of the best

thermoelectric properties doesn't only depend on the adjustment of the doping concentration.

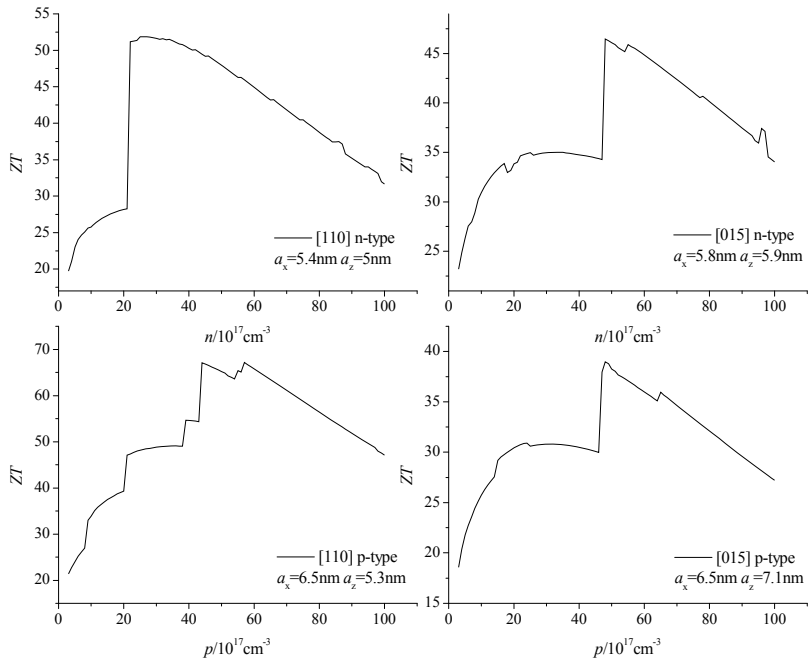

Figure 4 Schematic diagrams of the relationship between *ZT* values and the doping concentration for four types of Bi_2Te_3 rectangular nanowires in normal temperature (300K)

3.4 Effects of the temperature on *ZT* values for Bi_2Te_3 rectangular nanowires

Whether from the definitions of the *ZT* value and the reduced chemical potential, or from the band structure, the mobility and thermal conductivity of Bi_2Te_3, those are related to the temperature. Therefore, temperature has vital meaning to the thermoelectric properties of Bi_2Te_3 nanowires. Figure 6 shows the schematic diagrams of the relationship between the *ZT* values and the temperature for four types of Bi_2Te_3 rectangular nanowires. As shown in the figure, the *ZT* values of four types all reach the maximum near the room temperature (300K), 50.9 ([110] n-type, 300 K) , 65.3 ([110] p-type, 300 K), 47.2 ([015] n-type, 300 K) and 38.1 ([015] p-type, 300 K) for respectively. *ZT* values may decline, with the increase or the decrease of the temperature. What causes the phenomenon? When the temperature rises from 200 K, *S* gradually increases. Besides, the specific heat of the lattice is approximate a constant, while the phonon density increases proportionally. The scattering among the phonons exacerbates, and then the mean free path shortened. It leads to the decline of the thermal conductivity and the gradual increase of the *ZT* value. With the temperature rising continuously, the relatively narrow band gap makes the conduction mixture of electrons with the electron holes after the *ZT* value reaching the maximum, which results in the decrease of the Seebeck coefficient. Besides, the ratio of σ to κ fluctuates slightly, as a result of small *ZT* values. It is remarkable that *ZT* values drop dramatically with the increase of the temperature, after the *ZT* value reaching the maximum. Then, the value presents the tendency of oscillation drop, which is the main reason for the step changes of κ_e. Take the n-type nanowires in [110] direction for example. There is a phase step of κ_e at 309.1787 K, from 2.137 W/ (K·m) to 4.234 W/ (K·m). With the increase of the temperature, κ_e has complex and frequent step changes, which makes the oscillation of *ZT* values diminished. In addition, due to the mobility of electrons higher than that of holes, p-type nanowires have greater trend of rising or falling, compared with n-type nanowires.

Above all, for various types of Bi_2Te_3 nanowires, it is highly possible to obtain the best thermoelectric performance in normal temperature but very difficult to improve the *ZT* values of

nanowires by adjusting the temperature.

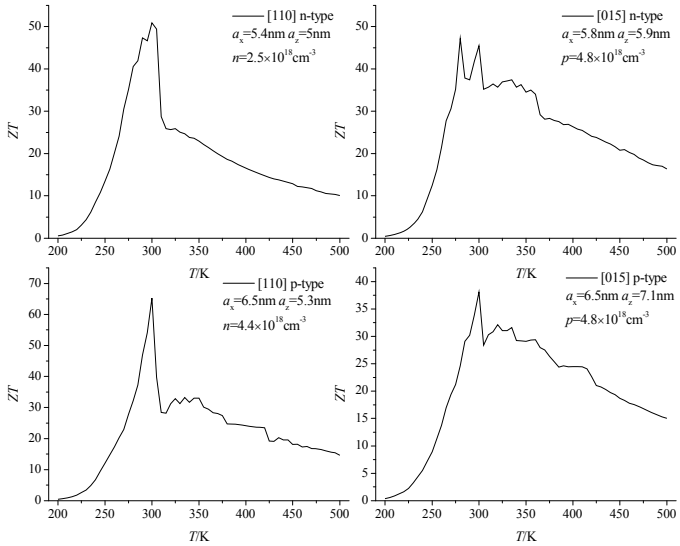

Figure 5 Schematic diagrams of the relationship between *ZT* values and the changes of temperature for four types of Bi_2Te_3 rectangular nanowires

4 Conclusions

Based on the Boltzmann equation established, the analysis is carried out to research how these parameters have influences on *ZT* values, including the band structure, the size of nanowires, the doping concentration and the temperature, using the similar relaxation time associated with the size and energy. Conclusions are drawn as following.

1) *ZT* values of Bi_2Te_3 nanowires show the trend of decrease after the initial increase with the decline of the side length through the theoretical calculation. On this basis, there are different levels of the step oscillation in this range of the side length, due to the discretization of energy levels from the quantum size effect.

2) In the same condition, with the change of the doping concentration and the temperature, the maximum of *ZT* values can be obtained, featuring in the same phase step. This is the result of the correlation of doping concentration and temperature with the band structure.

3) It is illustrated from the theoretical calculation that it is feasible to improve the thermoelectric performance of Bi_2Te_3 nanowires. The size of nanowires can be determined based on the change of *ZT* values with the size. Then, the improvement of the *ZT* value may be obtained, when the doping concentration of Bi_2Te_3 materials is adjusted to the optimum value.

Acknowledgements

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