Lattice thermal conductivity of $SrTiO_3/TiO_2$ superlattice nanowires

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Abstract- The present study was designed to investigate n-type perovskite oxide based superlattices as a potential materials system for thermoelectric power generation. The model based on the phonon Boltzmann transport equations with diffuse mismatch interface conditions has been used to calculate the lattice thermal conductivity of $SrTiO_3/TiO_2$ nanostructures. Result shows that in the superlattice nanowire structure the interface scattering cause the reduction in phonon thermal conductivity. . It was also found that nanowire boundary scattering provides significant resistance to phonon transport. The reduced thermal conductivity of superlattice nanowire was found to be 1.156 W/mK for d_w=0.44 nm and L=5 nm. As the diameter increases, the nanowire boundary scattering decreases, which leads to increase nanowire thermal conductivity. The obtained results suggest that, by optimizing the periodic length and the wire cross-sectional width, $SrTiO_3$/anatase TiO_2 superlattice nanowire can be a very good candidate as materials for high performance, efficient thermoelectric material. However the reduction in thermal conductivity is more effective due to the reduction in diameter of nanowire as compared to reduction in periodic length of the nanowire.

Index Terms- Boltzmann constant, phonon, superlattice, diffuse mismatch model, Nanoscale.

I. INTRODUCTION

The need of the renewable energy sources and environment friendly energy sources can be fulfill by conversion of waste heat into electrical energy. The emission of greenhouse gases and consumption of fossil fuels can be reducing through the use of thermoelectric power generators. Thermoelectric power generators are the devices which can convert waste heat into electrical energy only when the high-efficiency thermoelectric materials are used. [1] These devices convert the waste heat into electrical energy without emitting greenhouse gases. So for the efficient thermoelectric power generators it is very important to search high-performance thermoelectric materials. [3] The automobiles industries have been investigating the ever more high performance power generator devices to utilize the waste heat from the radiator of engine and exhaust systems of the future generation vehicles in generation of the electrical power.

To improve the performance of thermoelectric devices, many researches are being made to search for the potential thermoelectric materials and reduce the lattice thermal conductivity of these materials to its minimum value.[1,8]The figure of merit *ZT* is the dimensionless quantity which is defined as $ZT= S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the total thermal conductivity (i.e. lattice and electrical thermal conductivity). It is the measurement of the efficiency of the thermoelectric devices. Therefore, the improvements of the figure of merit of thermoelectric materials to reduce the consumption of fossil fuels are in great demand [2, 3, 5, 8, 10]. Nanoscale thermoelectric materials are of interest due to low in size, cheaper than bulk thermoelectric materials, low in lattice thermal conductivity [13]that can results in being improve the performance of thermoelectric devices. The reduction in the size of the thermoelectric materials comparable to the mean free path and wavelength of phonons can reduce the lattice thermal conductivity due to boundary scattering of phonons without reduction in electrical conductivity and Seebeck coefficient which results the improvement in the value of figure of merit. In semiconductors phononic transport plays an important role in the reduction of thermal conductivity. Therefore the semiconductor nanowires are the efficient thermoelectric materials if their diameters are comparable to the mean free path of phonons [4, 6, 8, 10] due to their exceptionally lower thermal conductivity than bulk materials. The superlattice structures on nanoscale size are the promising candidates for thermoelectric devices due to their periodic features [2, 6] which provide the possibility of reducing the lattice thermal conductivity and hence achieving a high figure of merit. However semiconductor based superlattices are of great interest to improve the thermoelectric performance. [16] The superlattice nanowires could be high potential thermoelectric materials due to their better interface and boundary scattering of phonons. The contribution of phonons to the thermal conduction can be reduced in nanoscale thermoelectric materials. [6]

Previous literature analysis shows that the various theoretical studies have been attempting to investigate the effects of phonon transport in superlattice structures which lead to reduce the phonon thermal conductivity. In previous paper [13], the thermoelectric figure of merit of Bi_2Te_3/Sb_2Se_3 and PbTe/PbTeSe quantum dot semiconductor superlattices along the cross plane and in-plane direction respectively were reported as improved thermoelectric materials. Moreover, the thermal conductivity of p-type LSMO/LMO superlattices in cross-plane direction at the room temperature was reported as 0.89 W/mK

which is lower than the previous reported thermal conductivities of bulk oxides. [12] The thermal conductivity of Si/Si_xGe_{1-x}($0<x<1$) superlattice nanowires were reported as lower than bulk due to its structural features which causes the phonon scattering. The low thermal conductivity of material would enhance the thermoelectric figure of merit. The deviation of the nanowire superlattice structure from its lattice structure enhances the scattering of phonons which reduce the lattice contribution to the thermal conductivity. [5] The Si/SiGe superlattice nanowires were also reported as the thermoelectric materials having thermal conductivities lower than the bulk Si nanowires of similar diameters. [17]

In the present study the main aim is to examine the low thermal conductivity of semiconductor oxide based superlattice nanowire. We choose $SrTiO_3$ and anatase TiO_2 as potential candidates for thermoelectric applications. The complex oxide thermoelectric material $SrTiO_3$ is a potential candidate for thermoelectric devices because of environment friendly nature, non-toxicity and high temperature stability. But the thermal conductivity of bulk counterparts is ~12 W/mK at room temperature which is still a very large thermal conductivity. [19] So $SrTiO_3$ nanowire structures could significantly reduce thermal conductivity due to interface and boundary scattering and provide a pathway to improve thermoelectric figure of merit *ZT*. [18]The naturally occurring anatase phase of Titanium dioxide (TiO_2) is most photoactive which shows as a promising and low-cost material for the alternative energy source. [20, 21] TiO_2 is suitable for thermoelectric applications due to its low value of thermal conductivity. [22, 24] In this paper, we use a model based on Boltzmann transport equation with diffuse mismatch interface conditions to study phonon transport in semiconductor oxide based $SrTiO_3/TiO_2$ superlattice nanowire at room temperature. The scattering of phonons in semiconductors are taken into account. The simulation results for the thermal conductivity of $SrTiO_3/TiO_2$ superlattice nanowire at room temperature can be calculated by using the parameters such as bulk phonon mean free path, volumetric specific heat, phonon group velocity, thermal conductivity of the bulk materials at room temperature in the phonon Boltzmann transport equation (BTE) with Diffuse mismatch model (DMM) interface conditions. In the present report, we will first introduce the background physics of thermal conductivity, then go through the simulation details, and finally present the results and discussion.

II. THEORETICAL BACKGROUND FOR THERMAL CONDUCTIVITY

Theoretically, the solution of Boltzmann transport equation gives the value of thermal conductivity of nanomaterial. [15] Boltzmann transport equation with diffuse mismatch model is the fundamental equation for the theoretical study of the phonon transport ignoring electrical transport. [7] The diffusive scattering of phonons at the rough interface and boundary of the materials could be analyze through the simplest Boltzmann transport equation based on diffuse mismatch model with diffuse interface boundary conditions. Nanowire material having two different nanodots materials say X and Y when arranged alternately form the superlattice structure of nanowire having periodic length $L=L_X+L_Y$. Boltzmann transport equation based on Diffuse Mismatch Model (DMM) predicts the interfacial transport of phonons experience completely diffusive and elastic scattering between the interfaces of two different materials. [28]

Fig. 1. The superlattice structured nanowire in which X=$SrTiO_3$ and Y= anatase TiO_2

III. SIMULATION DETAILS

The diffuse mismatch model is the low temperatures model typically applied at temperatures above Debye temperature. The Debye temperatures for the materials considered in this work are 758K and 513K for bulk anataseTiO2 [25] and SrTiO3 [18], respectively. We therefore assume the DMM to be applicable at room temperature for both materials. [28]

For the diffusive nanowire boundary for phonons, the lattice thermal conductivity k_{SL} of superlattice nanowires is given by [29]

$$\frac{L}{k_{SL}}=\frac{L_X}{k_X}+\frac{L_Y}{k_Y}+4\left(\frac{1}{C_X v_X \tau_{XY}}+\frac{1}{C_Y v_Y \tau_{YX}}\right)\left(1+\frac{\tau_{XY}+\tau_{YX}}{2}\right)+\frac{3}{d_w}\left(\frac{L_X}{C_X v_X \alpha_X}+\frac{L_Y}{C_Y v_Y \alpha_Y}\right) \quad (1)$$

where *k*, *C*, and *v* are the lattice thermal conductivity, volumetric specific heat capacity, and phonon group velocity of the bulk material (*X* or *Y*), τ_{XY} (or τ_{YX}) is the phonon transmission from *X* to *Y* or *Y* to *X*, which means the probability of transfer of energy of phonons from *X* to *Y* or from *Y* to *X*, through the interface. α_X(or α_Y) is a geometric factor which is given by [23],

$$\alpha=\frac{N^3-N}{N^3\left[\ln\left(\frac{2L}{Nd_w}\right)+0.5\right]} \quad (2)$$

, where *L* is the total length of nanowire, *N* is the number of segments of nanowire, d_w is the nanowire diameter. It only depends on the aspect ratio L_X/d_w (or L_Y/d_w) of the nanodots *X* and *Y*, its values lie between 0.75 and 1 for cylindrical wires.

In Equation (1), first and second terms account for scattering of phonons in pure bulk materials. Third term shows the contribution of interface scattering of the nanowire and fourth term shows the contribution of boundary scattering in nanowire in the lattice thermal conductivity of superlattice nanowire.

The transmission probability using the diffuse mismatch model, τ_{XY} is given by

$$\tau_{XY}=\frac{C_Y v_Y}{C_X v_X+C_Y v_Y} \quad (3)$$

and $\tau_{YX}=1-\tau_{XY}$.

Equation (1) can then be rearranged as

$$\frac{L}{k_{SL}}=\frac{L_X}{k_X}\left(1+\frac{4}{3}\frac{\Delta_X}{L_X}+\frac{\Delta_X}{\alpha_X d_w}\right)+\frac{L_Y}{k_Y}\left(1+\frac{4}{3}\frac{\Delta_Y}{L_Y}+\frac{\Delta_Y}{\alpha_Y d_w}\right) \quad (4)$$

Where Δ_X and Δ_Y are the mean free paths of phonons in bulk materials *X* and *Y*, respectively, which are derived from kinetic theory, [1, 3, 4, 8]

$$k=\frac{1}{3} C v \Delta, \quad (5)$$

Where *k* is the thermal conductivity *v* is the velocity of sound, *C* is the volumetric heat capacity, and Δ is the mean free path of the phonons.

The effective phonon mean free path Δ_{eff} for one segment (say *X* or *Y*) in the superlattice nanowire is given by

$$\Delta_{X,eff}^{-1} = \Delta_X^{-1} + \frac{4}{3L_X} + \frac{1}{\alpha_X d_w} \quad (6)$$

The corresponding effective thermal conductivity k_{eff} in each segment is given by,

$$k_{X,eff} = (\Delta_{X,eff} / \Delta_X)\, k_X, \quad (7)$$

Finally the expression of the lattice thermal conductivity k_{SL} can be expressed in terms of effective thermal conductivity of individual nanodots (*X* and *Y*). [29]

$$\frac{L}{k_{SL}} = \frac{L_X}{k_{X,eff}} + \frac{L_Y}{k_{Y,eff}} \quad (8)$$

IV. RESULTS AND DISCUSSION

The calculation of thermal conductivity of *n*-type $SrTiO_3/TiO_2$ superlattice nanowires can be done by keeping the length of the nanowire fixed at 300 K which is below the Debye temperatures of the bulk $SrTiO_3$ and TiO_2. The periodic length for superlattice nanowires is $L=L_{SrTiO3}+L_{TiO2}=10$ nm having equal length segments, diameter of the nanowire is taken as 5 nm. The lattice thermal conductivity of $SrTiO_3/TiO_2$ superlattice nanowire is calculated using the equation (8), the thermal properties of the bulk $SrTiO_3$ and bulk TiO_2 are taken through the various references. Kinetic theory of gas describes the thermal conductivity $k=\frac{1}{3} C v \Delta$ as a function of volumetric heat capacity, average phonon velocity and phonon mean free path[8] .Using bulk data of $SrTiO_3$ and TiO_2 from the references, this equation allows to find the value of bulk phonon mean free path of $SrTiO_3$ and TiO_2. The geometric factor α is taken as 0.75. For the various length segments and diameter we find the value of lattice thermal conductivity of $SrTiO_3/TiO_2$ superlattice nanowires. We can find the value of phonon mean free paths of bulk $SrTiO_3$ and anatase TiO_2 from kinetic theory, [1, 3, 4, 8]

$$k=\frac{1}{3} C v \Delta \quad (9)$$

Where *k* is the thermal conductivity *v* is the velocity of sound, *C* is the heat capacity, and Δ is the mean free path of the phonons. The typical value of volumetric heat capacity C for anatase TiO_2 is 2.76×10^6 J/m^{3}K. The sound velocity of anatase crystal is applied here as the group velocity of phonons and a mean value of 4181 m/s. The thermal conductivity of bulk anatase TiO_2 is 8.5 W/mK [26] and the parameters for SrTiO3 are its volumetric heat capacity is 2.78×10^6 J/m^{3}K. [27] The group velocity of phonons in bulk $SrTiO_3$ is 5500 m/s [18] and the bulk thermal conductivity is 12 W/mK .[19] The values of mean free path of phonons in anatase TiO_2 and $SrTiO_3$ are calculated to be 2.2nm and 2.35nm respectively from the equation (10). By putting all these values we can find the value of effective thermal conductivity of $SrTiO_3$ and anatase TiO_2 and finally we can find the value of the thermal conductivity of superlattice nanowires.

Fig.2. Relationship between diameter of nanowire and thermal conductivity of $SrTiO_3$/anataseTiO_2

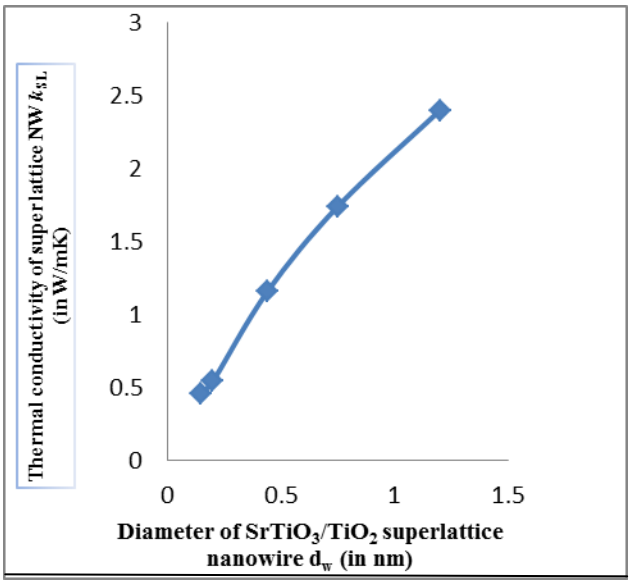
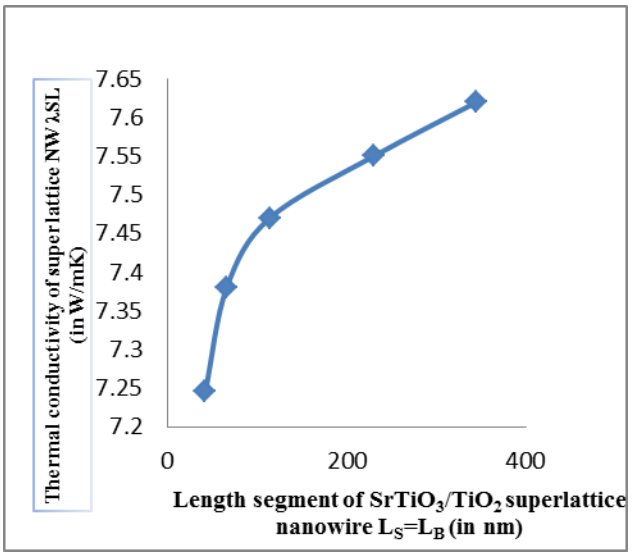


Fig.3. Relationship between Length segment and thermal conductivity of $SrTiO_3$/anataseTiO_2



V. CONCLUDING REMARKS

The thermal conductivities of $SrTiO_3/TiO_2$ superlattice nanowires having equal length periods and each nanowire material has length segments of 5 nm but having different diameters of 0.15 nm, 0.2 nm, 0.44 nm, 0.75 nm and 1.2 nm were measured at room temperature and the thermal conductivities of $SrTiO_3/TiO_2$ superlattice nanowires having different length periods and each nanowire has equal length segments of 42 nm, 66 nm, 114 nm, 230 nm and 345 nm keeping the diameters of 10nm remains constant were measured at room temperature. The graph between the thermal conductivity and diameter of the superlattice nanowire keeping its length segment constant and the graph between thermal conductivity and length segment of superlattice nanowire keeping its diameter constant are plotted

which shows that if the total length of the superlattice nanowire is fixed, reducing the period length will lead to decreased effective thermal conductivity due to the increased number of interfaces. The reduced thermal conductivity of superlattice nanowire was found to be 1.156 W/mK for d_w =0.44 nm and L =5 nm, which is very much less than the thermal conductivities of bulk $SrTiO_3$ and bulk anatase TiO_2 both at room temperature.

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