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Thermal Conductivity of Nanoscale Materials: A Review

RICHA SAINI and ANKITA RANI CHAUHAN

Department of Physics, Gurukul Kangri University Haridwar, Uttarakhand, India
Corresponding author Email:- kushwaha.richa@yahoo.in
acchauhan10@gmail.com
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Abstract

Nanoscale materials are being widely used in science and technology. Rapid development in synthesis and fabrication of Nanoscale materials has created a great demand for scientific understanding of thermal conductivity in nanoscale materials. The thermal conductivity in low dimensional has been obtained by using different theoretical and numerical approaches. The low dimensional structures such as quantum well, wires and dots confined in extremely small region and have novel transport properties. Measurement methods e.g. reducing grain size, multiple Phonon scattering, BTE in 2D nanoribbons, source of coherent Phonons etc open new way for nanoscale thermal transport study. This review summarizes the development in experiments, theory and computation that have occurred in thermal transport of nanoscale materials.

Key words: Nanoscale materials; Thermal conductivity; Quantum well; Quantum wires;

Introduction

Understanding the thermal conductivity of nanostructure or nanostructures materials are of great interest in a broad scope of contexts and applications. Indeed, nanostructures and nanomaterials are getting more and more commonly used in various industrial sectors like cosmetics, aerospace, communication and computer electronics. Many new theoretical and experimental results have been reported in the past few years. But a lot of number of issues is still awaiting their conclusive resolution. The objective of this review is to provide perspective on new developments in nanoscale thermal transport that have resulted from advances in experiment, theory, and simulation over the past decade. The topics we have selected emphasize the importance of interfacial phenomena in nanoscale thermal transport and avoid topics that have been extensively reviewed by others in recent years, e.g., nanostructured thermoelectric materials[1-3] and the transport properties of isolated graphene and carbon nanotubes[4–6]. We begin our discussion with the introduction of nanostructures and then focus on thermal transport in nanostructures and finally give a theoretical review about thermal conductivity of ***nanostructures.***

What is nanostructure :

Nanostructure material can be obtained by reducing the dimensions of bulk materials. This includes materials with nanoscale grains as well as nanoporous materials that contain void on the order of a few nanometers. Also included in this category are multilayer films as well as epitaxial superlattices, which include a collection of nanometer-scale films stacked on each other. The common feature in these material is that one can identify a nanostructured unit as the building block[7]. Nanomaterials have different properties than bulk materials in many ways such as thermal transport, heat conduction, size dependence thermal conductivity, Phonon boundary, edge scattering etc. Nanostructures include: one-dimensional (1D) structures, like nanotubes (NTs) and nanowires (NWs)[8]; two-dimensional (2D) crystal lattice with only one-atom-thick planar sheets, like graphene[9]; and thin films consisting of alternating layers of two different materials, superlattices. Lattice waves, charged carriers, electromagnetic waves, spin waves or other excitation participate in thermal transport[10].

Thermal transport in nanoscale structures :

Thermal transport is an essential energy transfer process in nature. Phonon is a major part for heat conduction in semiconductors and dielectrical materials. Actually for non metallic materials phonon is most dominating heat carrier because it contribute in heat conduction is much larger than those from electrons and photons. In lattice vibration each quantum of energy is known as phonon. Phonon transport is essential for understanding heat flow in nanostructure. Various methods can be used to calculate heat flow. Earlier it believed that the phenomenon of thermal transport is to follow the Fourier's law of heat conduction $J = -k\nabla T$, where J is the heat flux in the system, ∇T is the gradient of temperature. The conductivity k is a geometry independent coefficient which mainly depends on the composition and structure of the materials and the temperature. This law had a great success to describe macroscopic thermal transport. Phonon transport in nanostructures is unique in the importance of Phonon-boundary scattering as well as confinement of Phonons in low-dimensional structures such as nanotubes and graphene. In the past two decades, rapid developments in synthesis and processing of nanoscale materials have created a great demand for understanding of thermal transport in low dimensional nanomaterials. Casimir[11] employed a radiation analogue and the Debye approximation to analyze Phonon transport in a rod in the low temperature limit where internal scattering of Phonons was negligible. Building upon Casimir's results and several other studies[12-14]. Ziman[15] developed a solution of the Phonon Boltzmann transport equation (BTE) in a rod under the relaxation time approximation. As an alternative, one can calculate the fluctuating thermal currents in a structure and relate these to the thermal conductivity through some form of the fluctuation dissipation theorem[16]. Molecular dynamics has been used successfully to understand the heat flow across interfaces and in superlattices[17-19]. This dynamic also carried out to simulate the shrinkage and relaxation methods of nanohelix[20] and to investigate the mechanical and thermal properties and response of nanoparticles on relative velocities[21]. For these applications, the method has the great advantage that it is easy to include in the model different aspects of the microscopic structure of an interface, such as the roughness[22-24] and mixing[25]. The second approach is based on the Boltzmann transport equation[26]. To solve the Boltzmann equation one therefore needs to know the Phonon dispersion relation, the group velocity, and the rate at which collisions occur. The Phonon dispersion become different in nanostructures because NW diameter reduced the dominant Phonon wavelength. This issue has been investigated by a number of studies. Some works suggested that the transition from bulk to one dimensional Phonon dispersion 20 nm diameter Si NW reduce the Phonon group velocity component along the NW axis[27,28], to be about half of the Phonon group velocity in bulk[29]. The general formula for the Phonon lifetime is given in a classic paper by Maradudin and Fein[30]. A Phonon $k_1 j_1$ can be scattered by a Phonon $k_2 j_2$ to produce another Phonon $k_3 j_3$. In this process, energy and crystal momentum are conserved. It was assumed that processes in which G = 0 are called

Normal (N) processes, and those for which $G\neq 0$ are Umklapp (U) processes. Early work on phonon lifetimes was summarized in review articles by Klemens[31] and Carruthers[32], and in a book by Ziman[15].

Some important work done on Phonon transport for longitudinal and fast transverse acoustic Phonons, the rate τ^{-1} of this process varies as ω^5 [33]. This assumes that the wave number is small compared to the wave number at the Brillouin zone boundary. For slow transverse Phonons, the rate varies as ω^5. when the wave vector lies in some directions, but in other directions the decay rate is zero because there is no solution to the conditions of conservation of energy and momentum[34,35]. Some work also investigated on alloy nanojunction of ferromagnets crystal, phase field matching theory was using to analyze the scattering effect and transport properties for spin wave incident from hcp cobalt leads across a ferrimagnetically ordered 19 cobalt gadolinium alloy nanojunction[36], in addition strain dependent phonon properties and thermal conductivity of LJ argon and silicon. It was shown that with increasing of strain thermal conductivity of LJ argon decrease exponentially while thermal conductivity of silicon remains constant under compressive strain and decrease with increasing tensile strain[37]. A discussion of the lifetime of optical Phonons at zero temperature has been given by Klemens[38] Herring[39] has shown that for longitudinal Phonons, again with $\omega \ll k_B\ T/\hbar$ and $\tau^{-1} \propto \omega^{\alpha}\ T^{5-\alpha}$ where α is an integer, which is larger than 1 and dependent on the symmetry of the crystal. The lifetime is determined by the collisions of the longitudinal Phonon with a transverse Phonon and producing a transverse Phonon of different polarization. These collisions are called Herring processes. Phonon lifetimes have been calculated for the nearest-neighbor central force model of a fcc crystal with one atom per unit cell. This model has the advantage that the harmonic and anharmonic forces are each described by only one parameter. These parameters can be related to the Debye temperature and the Gruneisen constant C. The Phonon lifetime based on this model was first considered by Maradudin *et al.*[40] and later investigated in more detail[41]. A strain dependent lifetime was studied and it was found that the mode averaged lifetime decrease exponentially as the systems moves from compression to tension for LJ argon and for silicon the lifetime increase anormalously[37]. From the experimental and theoretical investigations, it is clear that the concept of Phonon transport in low dimensional systems is not well understood and it is hard to predict value of thermal conductivity of nanostructures on a particular assumption. Because transport behave is different with every single change in structure. In some cases the transport is increase while on the other hand it decreases by making a small change. So there is a number of challenges in this field to be worked out. The researchers can found many research oriented work in nanomaterials for further applications to make the nano world more reliable and interesting.

Thermal conductivity of nanostructures :

In recent years, much effort has been devoted to investigate the heat conduction in low dimensional nanostructures by numerical method by different workers. These studies show that nanostructures are most promising platform to verify fundamental thermal transport theories. Carrying these numerical and experimental investigations thermal conductivity of different nanostructures has been investigated. In the absence of electron- phonon interaction, the low temperature thermal conductivity of solids can be accounted for in terms of three scattering process viz., boundary scattering, Point defect scattering and Phonon- Phonon scatterings[42]. Many microstructural effects on Phonon-mediated thermal transport were largely worked out in the 1950s and 1960s by Klemens[43,44], Callaway[45,46] and others[15]. Thermal conductivity for Phonon scattering by anharmonicity has created a great interest for researchers and investigated mostly using the Phonon Boltzmann equation, first derived by Peierls [47], in the relaxation time approximation assumptions but did not explain the kinetic theories which enumerated by Hardy[48], Allen and Ford[49]. Using this transport equation and equation of motion method for non-equilibrium Green's functions, is used by many workers to derive an expression for transport coefficient[50,51]. These analyses led to expressions for the thermal conductivity in terms of the Phonon relaxation times for different Phonon scattering processes integrated over the Phonon energy distribution. There are several important results pertinent to nanostructured materials that follow directly from the Klemens- Callaway model[47] and the form of the relaxation times. First, in the absence of any defects and at intermediate temperatures, below 2 to 5 times the Debye temperature T_D, the thermal conductivity decreases approximately as $1/T$ and asymptotes to a temperature independent value given by k_{min}. Microstructural defects, including point defects, anti-site defects, and grain boundaries, all decrease the scattering time with contributions that are independent of temperature.

As the thermal conductivity due to anharmonic phonon scattering decreases with increasing temperature, all forms of microstructural defects have a greater apparent effect in lowering thermal conductivity at lower temperatures than at the higher temperatures, decreasing the observable temperature dependence. In the extreme, when the minimum conductivity is reached, they can result in a temperature-independent conductivity over a very large temperature range. We will return to this point later in discussing grain size effects and high-defect concentrations.

For many materials, the simplest approach to nanostructuring is to reduce grain size. Grain boundaries act as obstacles to the movement of Phonons through a material by scattering Phonons and lower the thermal conductivity by decreasing the time between Phonon scattering events[52]. In practice, the mean-free-path for Phonon scattering cannot be smaller than approximately half the Phonon wavelength and, in turn, smaller than the inter-atomic spacing, as pointed out by Roufosse and Klemens[53].

As the thermal conductivity due to Anharmonic Phonon scattering decreases with increasing temperature, all forms of microstructural defects have a greater apparent effect in lowering thermal conductivity at lower temperatures than at the higher temperatures, decreasing the observable temperature dependence[52]. Wang and Mingo[54] recently presented BTE solutions for nanowires of different cross sections and 2D nanoribbons with two diffuse edges, and verified the accuracy of the Matthiessen's rule only for the nanowire case, because diffuse boundary scattering alone does not lead to a finite mean free path in 2D nanoribbons. The axial thermal conductivity of different nanowires structures, the thermal conductivity of thin films[55] and periodic nanoporous membrane structures[56] along the in-plane direction have been obtained with the use of suspended micro-devices with built in resistance thermometers[57]. The effect of pore size and shape was studied and found that thermal conductivity of empty MOFs decrease with increasing pore size. In contrast in larger pores ,the thermal conductivity does not change with increasing gas density because longer gas molecule resulting in a lower frequency of gas crystal collision and less gas induced phonon scattering[58]. TDTR techniques have also been employed to measure the cross-plane thermal conductivity of nanowire arrays[59]. The theoretical framework of Casimir and Ziman can explain well the suppressed thermal conductivity found in InAs nanowires[60], Bi_2Te_3 nanowires[61], SnO_2 nanobelts[62] and Si nanowires[63] grown by a vapor liquid solid (VLS) method with a diameter larger than about 30 nm, as well as Bi nanowires, In Sb nanowires[64] and SiGe nanowires[65] when additional impurity and defect scattering were considered. Martin *et al.*[66] employed first order perturbation theory, also referred as the Born approximation, to calculate the volumetric scattering rate caused by this perturbation. Their results suggest that the thermal conductivity in the surface roughness scattering dominant regime is proportional to $(D/s)^2$. Some other formulations also carried out by authors *e.g.* electrical and thermal conductivities on the joule heating of one-dimensional conductor was investigated by solving the coupled non-linear steady state electrical and thermal conduction[67]. Establishing a scaling law, the temperature of SWNT(single wall nano tube) under pulsed laser with Gaussian spot studied and it was concluded that the maimum temperature rise is inversely proportional to the incident laser power[68]. Thus, the temperature dependent thermal conductivity studied by different methods, models and experimental techniques shows its variations according to thermal transport methods for different materials and structures.

Conclusion

In this review we have discussed recent experimental and theoretical method studied on thermal transport in nanostructures. We discussed the scattering process due to anharmonicity, micro-structural defects, point defects, grain boundaries. It was shown that the grain boundaries decrease the scattering time so that its resist the movement of Phonon and decrease the thermal conductivity which is independent of temperature, whereas the anharmonic Phonon scattering decrease with increasing temperature. Thermal conductivity also effected by grain size defects and high defect concentrations. Thermal conductivity and thermal transport in nanoribbons, nanowires, nanotubes, thin films, nanoporous membranes in plane and cross plane structures also investigated using different methods and techniques has been discussed here. Although a lot of work has been done on nanostructures by several authors but many unsolved problems e.g. conductivity, reliability improvement, decrement of energy or power loss, enhacement of working periods etc. is left to be worked on. Besides challenges in study of thermal transport in nanoscale, theoretical models can deal with these problems in an ideal way. The theoretical capabilities suggest future research opportunities to work in low dimensional system and handle large and complex nanostructures in theoretical models.

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