Thermoelectric Structured Systems with Nanophonic Metamaterials

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Keywords: Thermoelectric systems, Nanophonic metamaterials, Thermal conductivity, Electrical conductivity, Cooling devices, Phonon spectrum.

Abstract. This work is aimed at analysis of methods for the developing of new thermoelectric systems including those based on the so-called locally resonant "nanophonic" metamaterials. These materials, with their experimental realization, are intended for use in thermoelectric systems, since they have a large value of the thermoelectric Q-factor $ZT$. The increase in $Q$ is achieved by reducing the thermal conductivity of the material, which leads to an increase in the value of $ZT$, if the electrical conductivity remains the same. The reduction in thermal conductivity, without corresponding reduction in electrical conductivity, is achieved by choosing a configuration of thermoelectric materials consisting of a thin film with a periodic set of columns mounted on a free surface. Such a configuration qualitatively changes the base phonon spectrum of a thin film due to the hybridization mechanism between local column resonances and underlying lattice scattering. Numerical methods are used to study changes in the phonon spectrum and, as a consequence, a change (decrease) in the value of thermal conductivity depending on variations in the system architecture.

Introduction

The functioning of modern high-performance electronic components that form the basis of computer systems is accompanied by significant heat generation, especially when operating in forced modes. As a result, the effective operation of such components requires adequate cooling means. Similar problems arise when creating various optoelectronic devices. To support optimal temperature conditions, special cooling devices are usually used - coolers based on traditional radiators and fans.

Despite the fact that the parameters of traditional coolers are constantly improving, recently the issues of miniaturization of such devices due to the continuous miniaturization of electronic components have become acute. Special means of cooling electronic elements based on thermoelectric effects in semiconductors have also appeared on the computer market. In particular, according to experts, semiconductor thermoelectric modules, the cooling properties of which are based on the Peltier effect, are extremely promising for creating the necessary operating conditions for computer components.

As is known, the thermoelectric conversion efficiency is determined by the formula $ZT = \sigma S^2 T / \chi$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\chi$ is the thermal conductivity, $T$ is the absolute temperature of the converter.

Thus, materials with high electrical conductivity and low thermal conductivity are the best thermoelectrics. Back in the middle of the last century, A.F. Ioffe showed that semiconductors are the best thermoelectrics [1]. Their advantage is the ability to control electrical conductivity and the type of main carriers by alloying. Because of the use of semiconductor alloys in the 1960s, significant success was achieved in the field of improving the thermoelectric figure of merit.

But, despite fairly active research in different countries of the world, until the end of the 20th century, the value of the $ZT$ parameter in the best semiconductor thermoelectrics was able to increase from $ZT = 0.75$ only to $ZT = 1.0$ at room temperatures. This circumstance significantly limits the scope of thermoelectricity. If it were possible to increase the $ZT$ value to 2.0 - 3.0, then this would increase the efficiency of thermoelectric converters to 20%, and $ZT = 3.0 - 4.0$ creates the possibility of real competition for refrigeration units.
Thus, one of the most important tasks of thermoelectricity is to increase the value of ZT.

In a solid, heat can spread through various mechanisms:

1. Heat is transferred by the same carriers that are responsible for the transfer of electric charge. The corresponding thermal conductivity $\chi_{el}$ is the electronic thermal conductivity.

2. Heat is transmitted through vibrations of the crystal lattice (phonons). The corresponding thermal conductivity is the lattice (phonon) thermal conductivity $\chi_{ph}$. The first mechanism prevails in metals, since they are characterized by an abundance of carriers, and the lattice is quite plastic. In semiconductors, the opposite picture is observed. Generally speaking, in solid semiconductors (for example, in silicon and germanium), phonon thermal conductivity is several orders of magnitude greater than electronic thermal conductivity. For example, in silicon, the lattice thermal conductivity is 400 times greater than the electronic one.

Although, on the other hand, the ratio of thermal conductivities in soft semiconductors is much smaller (for example, in bismuth telluride $\text{Bi}_2\text{Te}_3$ it is approximately four). Thus, in the general case, the thermal conductivity coefficient is $\chi = (\chi_{el} + \chi_{ph})$. In the research community, there is a constant struggle to increase the thermoelectric figure of merit of ZT materials, and, in particular, by lowering the thermal conductivity while maintaining the electrical conductivity.

The first and obvious way to increase this is to optimize the properties (optimization of the concentration of charge carriers; optimization of the band gap; optimization of the chemical composition) of materials that determine the thermoelectric figure of merit. This method allows to increase, although in most cases insignificantly, the thermoelectric properties of traditional thermoelectric materials, which are well studied and for which physical models have been developed that can purposefully determine the directions of optimization of material properties.

The second way is associated with the creation of fundamentally new thermoelectric materials, which is a much more complex material science task than the optimization of the properties of traditional thermoelectrics. The search for materials that have both low thermal conductivity (glass) and high electrical conductivity (crystal) is based on the Slack model [2], which proposed using substances containing weakly bound atoms or molecules (phonon glass - electronic crystal) as an effective thermoelectric material. Such atoms or molecules, called “retlers”, can freely rotate or oscillate within a limited volume, effectively scattering phonons and thus reducing lattice thermal conductivity. High electrical conductivity will be provided by a covalently bonded framework with a low polarity of chemical bonds. In other words, Slack’s idea is aimed at independent optimization of thermal conductivity and electrical conductivity in order to achieve maximum thermoelectric figure of merit. Among the materials that are actively studied as “phonon glass - electronic crystal”, it is necessary to note semiconductor clathrates [3] and filled scutterudites [4]. However, the progress achieved along this way is still small.

A promising direction in the field of developing effective thermoelectric materials is the creation of various nanostructures, such as quantum dots, nanoscopes, superlattices, bulk nanocomposites [5,6].

The increase in thermoelectric figure of merit in nanomaterials is associated with two physical phenomena:

- A decrease in lattice thermal conductivity due to the appearance of numerous interfaces in nanomaterials, which are effective scattering centers for phonons but have little effect on electron transport;

- An increase in the band gap in nanomaterials with a simultaneous increase in the density of states near the Fermi level; although in this case the electrical conductivity decreases, but the thermo-EMF increases, which under certain conditions can lead to an increase in the power factor.

Such nanostructuring can be an effective way to reduce the lattice thermal conductivity by reducing the average phonon mean free path due to scattering on the corresponding inhomogeneities. In particular, there are some studies that report the possibility of a significant decrease in thermal conductivity in thin films with the structure of superlattices in the $\text{Bi}_2\text{Te}_3 / \text{Sb}_2\text{Te}_3$ material.

A fundamentally new concept to reduce thermal conductivity is the concept of Davis and Hussein described in [7]. It consists in creating an array of nanoscale columns on the surface of a sheet of thermoelectric material, such as silicon, to form what the authors call “nanophononic metamaterial.”
The atoms that make up the miniature columns vibrate at different frequencies. Davis and Hussein used a computer simulation complex, to show that the vibrations of the rods will interact with the vibrations of the phonons, slowing down the heat flux without affecting the electrical conductivity.

**Computational Methods Used in the Work**

Study of silicon-based systems (thin films with non-parallel surfaces and mounted on them with a periodic set of silicon columns of increasing height and variable cross-sectional sizes; thin films with one or more folds of the boundary and periodic sets of silicon columns installed on them; thin films with rods separated on the section) were carried out in the present work, following the procedure described in [7]:
- Alignment and evaluation of model configurations of arrays of silicon atoms in the columns;
- Calculations and fitting of nominal boundaries in the system using the Broden—Fletcher—Goldfarb—Shanno algorithm [8];
- Description and assessment of the adequacy of the interaction between silicon atoms using the empirical anisotropic Tersoff potential [9,10]; assessment of the adequacy of the interaction;
- Carrying out parametric calculations of the dynamics of the crystal lattice using the General Utility Lattice Program (GULP) software package [11];
- Calculations of the thermal conductivity in the system will be carried out using the Callaway—Holand model [12,13] with partial use of the Bloch method of plane wave decomposition;
- Assessment and verification of the adequacy of the thermal conductivity in the system;

Similar studies have been carried out for systems based on silicon-germanium alloy.

**Summary**

The results obtained in this work are in good agreement with the results of [8] for silicon structures. It is determined that taking into account the non-parallelism of the surfaces of the silicon film within 1 degree practically does not affect the final result of the calculations. For the practical implementation of the studied thermoelectric structures, it is supposed to use methods developed in the authors' work [14].

**Acknowledgement**

This research was financially supported by the Russian Foundation of Basic Research (Project №19-07-00456).

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