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Viewpoint Paper

Thermoelectric nanowires: A brief prospective

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ABSTRACT

Nanowire structures have been investigated in order to achieve improved thermoelectric performance of thermoelectric materials. This brief viewpoint article summarizes the progress done in the last years and our vision of which are the key points to achieve a future generation of efficient nanowire-based thermoelectric devices.

1. Introduction

Thermoelectric devices are able to transform a temperature gradient into electrical current, and *vice versa*. Nowadays they are studied as an alternative energy source, which employs wasted heat produced daily in our society (in transport, factories, even computers, etc.) into usable electricity. Nevertheless, the main drawbacks that the thermoelectric devices present are: (a) their low efficiency, which is due to a poor thermoelectric performance of the available materials and (b) their high cost per Watt produced. The latest improvements in thermoelectricity have been closely related with nanostructuration [1]. One path that has been investigated is the fabrication of low dimensional structures at the nano-scale with thermoelectric materials. Among these nanostructures, nanowires stand out for several reasons. First of all, there are different fabrication techniques that allow the obtaining of high quality nanowires of different thermoelectric materials, such as vapor liquid solid processes or template assisted electrochemical deposition (widely used for chalcogenide materials). Secondly, these structures are a good approach to the single-dimensional case, which simplifies the theoretical simulations. Thirdly, they provide a way of increasing the surface to volume ratio in a controlled way and thus increase the diffusive phonon scattering, which should revert into an increase of the figure of merit.

2. Thermoelectric enhancement through dimensionality reduction

The thermoelectric efficiency is related to the thermoelectric figure of merit, which depends on different parameters of the material: $ZT = S^2 \cdot \sigma \cdot T/(\kappa_e + \kappa_L)$, where T is the temperature, S is the Seebeck coefficient, σ the electrical conductivity, and κ_e and κ_L the electronic and lattice thermal conductivities, respectively. In classical mechanics, S, σ, and κ_e are linked, and thus they cannot be tailored independently. Nevertheless, in 1993 a theoretical work from Hicks and Dresselhaus predicted that for low dimensional structures, such as thin films (two dimensions) or nanowires (one dimension), a great enhancement of the figure of merit could be observed [2]. This effect was based on the quantum confinement of the electronic states, which provides a way of increasing one of the classically interrelated parameters without affecting the others (see Fig. 1a). This theory has been demonstrated recently to be an oversimplification of what is happening in low dimensions, mainly because only one sub-band dominated all the transport properties in the initial model. Recently, a more detailed theory [3], which takes into account the effects of multiple sub-bands (see Fig. 1b) has been published. This theory is in good agreement to the measured thermoelectric power factors in nanowires and even bulk. It also accounts for a great enhancement of the nanowire efficiency at very small nanowire diameters, but it presents a different trend for larger diameters, related to the weaker confinement of the electronic states.

Dresselhaus predictions pioneer and triggered the research in the field of thermoelectric toward nanostructuration. It has been

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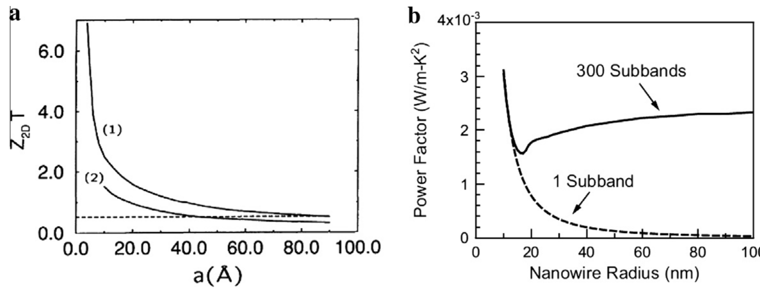

Figure 1. (a) Theoretical figure of merit versus the film thickness (1) and nanowire diameter (2) for bismuth telluride as predicted by the theory of Dresselhaus [2]. (b) Theoretical power factor versus the nanowire radius for InSb calculated for 1 and 300 subbands [3].

demonstrated that controlling the morphology, crystallinity, orientation, composition, etc., at the nanoscale is a good way to reduce thermal conductivity in these materials. The research in nanostructured thermoelectrics has helped to better understand the electron and phonon transport properties. From that moment on many groups focused on fabricating nanowires of the smallest diameter possible, along with the control of other parameters which deeply correlate with the thermoelectric performance, such as: crystallinity, stoichiometry, control of defects (twinning, dopants, scattering centers, etc.) using different techniques. For example template assisted electrochemical deposition of chalcogenide materials [1,4] has achieved Bi_2Te_3 nanowire diameters as small as 15 nm [5], and highly textured nanowires [6], Chemical Vapor Deposition (CVD) [7], or vapor liquid solid (VLS), Bi_2Te_3 [8]. Silicon nanowires have been grown by lithographic techniques combined with molecular beam epitaxy (MBE) [9], or by chemical etching to obtain rough silicon nanowires [10], achieving single crystalline Si/SiGe superlattice nanowires [11]. Each technique, after optimization, provides different crystal qualities, doping levels, and types of grain boundaries, which can help with the reduction of thermal conductivity, but can reduce electrical conductivity. Also, a good understanding of the influence of all those parameters is required. Moreover, the crystal orientation is crucial in anisotropic materials, where there is one more favorable orientation to maximize the thermoelectric efficiency. In order to optimize all those parameters, one has to gain an in-deep understanding of the processes that govern this type of materials at the nanoscale. In most cases, when the transport properties of the nanowires were measured, an increase in the figure of merit has been found [12,13]. Some results arouse values larger than the theoretically expected ones, such as for silicon nanowires, which increase from the bulk value of $ZT \sim 0.01$ at room temperature [14] to 0.25 for nanowires of 20 nm diameter [9] and 0.6 for rough silicon nanowires of 50 nm in diameter [10]. The most accepted explanation for this increase is the higher surface to volume ratio, which enhances the diffusive phonon scattering and thus reduces the thermal conductivity of the lattice [15]. Similar results have been found for other nanowires, where the diameters are not small enough to achieve quantum confinement, but whose thermal conductivity is affected by the nanostructure [12,16]. Other quantum effects theoretically predicted, such as the resonance effect of coherent phonons in core–shell GeSi nanowires [17] and the decoupling between electrons and phonon transport also in these structures with surface disordered [18] have to be demonstrated experimentally. Regarding experimental work, core–shell SiGe nanowires have shown how related are the carrier concentration and the thermoelectric power factor, but no quantum confinement at room temperature was found [19]. Actually, the quantum confinement effects have not been confirmed experimentally, except maybe for few works such as InAs nanowires, where a great enhancement of the thermoelectric Power Factor, that is, $S^2 \cdot \sigma$, was found [20]. Nevertheless, a more recent work justified this enhancement not by the one-dimensional sub-band model quantum confinement, but by quantum-dot states that appear inside the nanowires [13]. Another important effect to be taken into account is the surface states and how they affect the conductivity in small radius nanowires, where there is a high surface to volume ratio, along with the phenomena of topological insulating surface states that appear in most chalcogenides [21,22]. The research is focused now to demonstrate how these two effects, thermoelectricity and topological insulators [23], affect each other, and how important those surface states are for the smaller diameter nanowire performance.

3. Measurement of nanowires' properties

There are many difficulties in the measurement of the transport properties at the nano-scale, but in recent years there has been a huge effort in obtaining repetitive and reliable measurements to evaluate their figure of merit [24]. Among the difficulties, some are obvious, such as the experimental challenge that is the actual size of the structures, which makes necessary the use of specific systems that allow either nanometer resolution or enough sensitivity to detect the properties of the nanowires, or the placing of nanowires in the device. In general, the available techniques can be divided in single nanowire and whole nanowire array measurements.

Single nanowire measurements involve certain experimental challenges, such as avoiding nanowire surface oxidation, which is of great importance due to the high surface to volume ratio in these structures, and can affect their transport properties, the contacts, etc. In the case of measurement systems based on microchips with two [25] or four point contacts [26,27], micro-heaters, and so on, the contact resistances or the way the contacts are made are also a key parameter, which is usually difficult to evaluate. These micro-structures are usually not easy to fabricate, the accuracy of the temperatures at the nanoscale and thermal isolation are also tricky. Therefore, reproducibility is difficult, which makes it really important to develop a metric to evaluate the goodness of the measured parameters. Other ways of measuring single nanowires are based on Scanning Probe techniques (SPM) [24], such as measuring the electrical conductance of a nanowire along its length with Kelvin Probe Microscopy [28], or optical methods like micro-Raman or micro-luminescence of single nanowires [29].

In the case of nanowires embedded in a matrix, the whole array can be measured like a thin film or a bulk sample [30,31] or with SPM systems, which have high spatial resolution [16]. Optical based systems such as the photo-acoustic or photo-thermal techniques have also been used for the measurement of nanowire arrays [32]. All these techniques have the advantage of being non-destructive, with no need of dissolving the matrix in which the nanowires are placed, avoiding oxidation of the surface. But there are some drawbacks too, such as the complexity of the