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State-of-the-art of thermoelectric materials processing

I Properties and applications

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State-of-the-art of Thermoelectric Materials
Processing, Properties and Applications

Abstract

Development of new thermoelectric materials has been rapid in past few years. The goal of the work appears to be to reduce the thermal conductivity while remaining the electrical conductivity at relatively high level. Different techniques have been demonstrated in laboratory scale utilizing nanoscale tailoring. The recent development in nanoscale tailoring has based mainly on utilization of silicon. However, silicon can not be considered to be a good thermoelectric material due to its low ZT value. Thus, one can assume that better performance can be achieved by finding more appropriate materials. Also the problem of manufacturing the nanostructures in industrial scale still prevails. Thus, it is suggested that the development work should be focused on development of new efficient thermoelectric materials suitable for mass manufacturing utilizing nanoscience.

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Contents

1. Introduction

Semiconductor technology may help to overcome the challenges related to the enhanced energy efficiency by supplying means to produce locally energy from waste heat (White, 2008). It has been estimated that the majority of the world’s power is generated by systems that typically operate at efficiencies of about 40% or less, i.e., there is an enormous need for thermoelectric systems that can ‘salvage’ the energy currently lost as heat to the environment (Rodgers, 2008).

One way to improve the sustainability of our electricity base is through the scavenging of waste heat with thermoelectric generators, i.e. thermoelectric materials. Home heating, automotive exhaust, and industrial processes all generate waste heat that could be converted to electricity by using thermoelectrics. As thermoelectric generators are solid-state devices with no moving parts, they are silent, reliable and scalable, making them ideal for small, distributed power generation (Snyder and Toberer, 2008).

Thermoelectrics have long been too inefficient to be cost-effective in most applications. However, in 1990s theoretical predictions suggested that thermoelectric efficiency could be greatly enhanced through nanoscale engineering. The finding led to experimental efforts to demonstrate the theories suggesting the possibility to achieve high-efficiency materials. At the same time, complex bulk materials (such as skutterudites, clathrates and Zintl phases) have been explored and found that high efficiencies could indeed be obtained.

Improving the performance of a thermoelectric materials involve controlling the motion of phonons, which carry most of the heat, and electrons, which carry the electric current and some of the heat (Rodgers, 2008). The efficiency with which thermoelectric materials generate energy is determined by the thermoelectric figure of merit, ZT, where T is absolute temperature and Z is proportional to the electrical conductivity and the square of the Seebeck coefficient, and inversely proportional to the thermal conductivity. When ZT increases, the efficiency of energy generation ultimately approaches the Carnot limit, i.e., the maximum allowed by the laws of thermodynamics (White, 2008).

Historically, the ZT value of the best bulk thermoelectric materials has remained below or around one due to the difficulty to increase the electrical conductivity or

Seebeck coefficient without increasing the thermal conductivity (Rodgers, 2008). However, *ZT* values approaching three have been reported for nanostructured materials that exploit reduced dimensionality to lower the thermal conductivity of the crystal lattice in these structures (White, 2008). *ZT* values of three or more are required for competitive energy generation.

Figure of merit *ZT* can be increased by using nanotechnology due to the fact that phonons have mean free paths of hundreds of nanometers compared with about 10 nm or less for electrons. Therefore it is possible to restrict the movement of phonons without hindering the electron motion. Bulk silicon has a *ZT* value of about 0.01, but it has been shown that it is possible to increase the value up to 0.6 at room temperature by using silicon nanowires with diameters of about 50 nm. Further decrease of nanowires (20 nm thick and 10 or 20 nm wide) has been demonstrated to increase the *ZT* value up to 1 at 200 K (Rodgers, 2008). Further improvements in *ZT* are expected once quantum confinement effects can be harnessed to control the electronic properties of thermoelectric nanostructures. For example, *ZT* values as high as 25 have been predicted for nanostructured materials in which quantum dots are used for energy filtering, enabling the almost reversible exchange of charged particles between the hot and cold reservoirs of a thermoelectric energy generator. (White, 2008)

2. Thermoelectricity

Thermoelectricity means phenomena in which a temperature difference generates electricity or vice versa. Thermoelectric effects can be used to generate electricity, to measure temperature, and to cool or heat objects (Figure 1 and 2). Such phenomena include Seebeck effect (conversion of temperature differences directly into electricity), Peltier effect (production of temperature difference by electric current), and Thomson effect (heating or cooling of a current-carrying conductor with a temperature gradient). Since temperature gradients are essential for thermoelectricity, the basic requirements for the thermoelectric materials are that they conduct electricity but do not conduct heat too well.

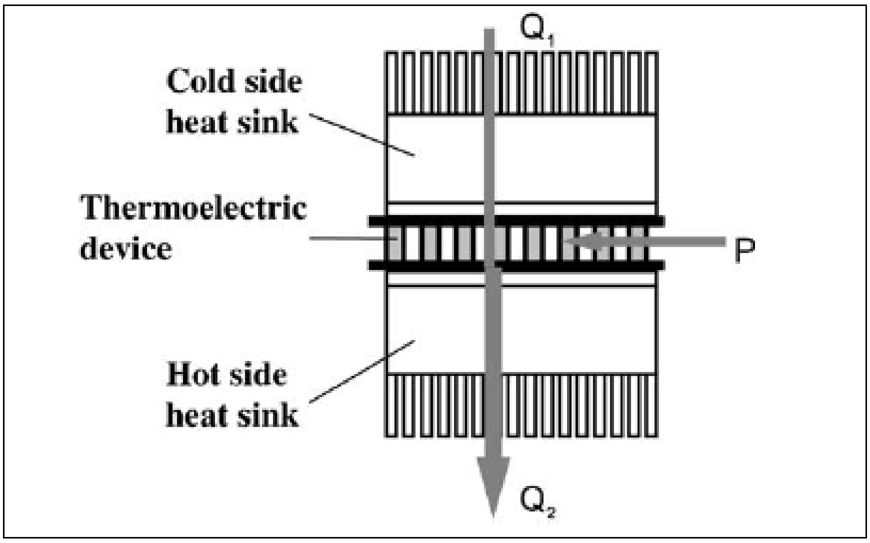

Figure 1. Arrangement for thermoelectric cooler. Q_1 is heat to be pumped, P is electrical power and Q_2 is dissipated heat (Riffat and Ma, 2003).

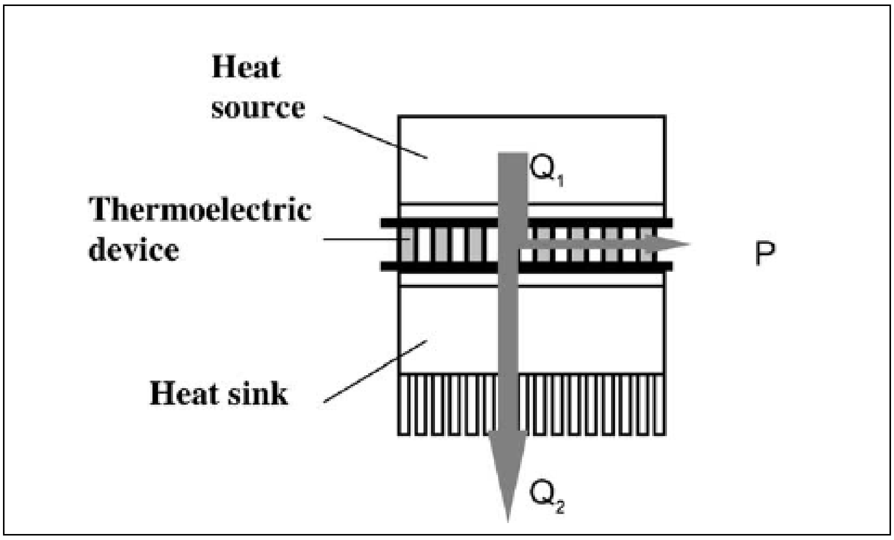

Figure 2. Arrangement for thermoelectric power generation. Q_1 is heat supplied from the heat source, P is the generated electrical power and Q_2 is the dissipated heat (Riffat and Ma, 2003).

In the Seebeck effect, a temperature difference between two different metals or semiconductors produces a voltage of several microvolts per Kelvin difference. One such combination, copper-constantan, has a Seebeck coefficient of 41 μV/K at room temperature. The Seebeck effect is commonly used in a device called a thermocouple (because it is made of a coupling or junction of materials, usually metals) to measure a temperature difference directly or to measure an absolute temperature by setting one end to a known temperature. Several thermocouples when connected in series are called a thermopile, which is sometimes constructed in order to increase the output voltage since the voltage induced over each individual couple is small.

If the temperature difference ΔT between the two ends of a material is small, then the thermopower of a material is defined as $S = \frac{\Delta V}{\Delta T}$ (unit V/K), where ΔV is the thermoelectric voltage difference between the terminals. The thermopower, or thermoelectric power, or Seebeck coefficient of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. Typical values of S for good thermoelectric bulk materials are hundreds of μV/K, negative or positive. The term thermopower is a misnomer, since it measures the voltage or electric field induced in response to a temperature difference, not the electric power. An applied temperature difference causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a classical gas that expands when heated. Mobile charged carriers migrating to the cold side leave behind their oppositely charged and immobile nuclei at the hot side, thus giving rise to a thermoelectric voltage (thermoelectric refers to the fact that the voltage is created by a temperature difference). Since a separation of charges also creates an electric potential, the build-up of charged carriers onto the cold side eventually ceases at some maximum value, since there exists an equal amount of charged carriers drifting back to the hot side as a result of the electric field at equilibrium. Only an increase in the temperature difference can resume a build-up of more charge carriers on the cold side and thus, lead to an increase in the thermoelectric voltage. Incidentally, the thermopower also measures the entropy per charge carrier in the material.

The thermopower of a material, represented by S (or sometimes by α), depends on the material's temperature and crystal structure. Typically metals have small thermopower because most metals have half-filled valence bands. Electrons (negative charges) and holes (positive charges) both contribute to the induced thermoelectric voltage, thus, cancelling each other's contribution to the voltage and making it small. In contrast, semiconductors can be doped with an excess amount of electrons or holes and, thus, can have large positive or negative values of the thermopower depending on the charge of the excess carriers. The sign of the thermopower can determine which charged carriers dominate the electric transport in both metals and semiconductors.

Superconductors have zero thermopower, since the charged carriers produce no entropy. This allows a direct measurement of the absolute thermopower of the material of interest, since it is the thermopower of the entire thermocouple as well. In addition, a measurement of the Thomson coefficient, μ, of a material can also yield the thermopower through the following relation $S = \int \frac{\mu}{T} dT$.

The thermopower is an important material parameter that determines the efficiency of a thermoelectric material. A larger induced thermoelectric voltage for a given temperature gradient will lead to a larger efficiency. Ideally one would want very large thermopower values since only a small amount of heat is necessary to create a large voltage. This voltage can then be used to provide power.

ZT is a dimensionless figure of merit for thermoelectric materials and equals to (Bulusu and Walker, 2008),

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

where S denotes Seebeck coefficient, σ means electrical conductivity (unit A V^{-1} m^{-1} = Ω^{-1} m^{-1}), T is temperature and κ denotes thermal conductivity (unit W K^{-1} m^{-1}).

Electrical and thermal contacts between the thermoelectric materials and surroundings are also very important in practical applications (da Silva and Kaviany, 2004). Both electric and thermal resistances of interfaces must be minimized in order to obtain optimal performance. Interfacial effects can be a major limitation for thermoelectric performance especially in column-type film structures. Thermal and electrical resistances of the interfaces are partly caused by fabrication non-idealities, such as impurities, variations in the crystal size and orientation, and defects in the interface.

However, even an ideal interface between two materials has finite thermal and electric resistances caused by mismatch between the properties of the two materials. Thermal resistance depends on differences in, e.g., density of states, mass density, Debye frequency, and speed of sound, and electrical boundary resistance is caused, e.g., by differences in the band structures of the materials.

3. Materials

Bulusu and Walker (2008) reviewed models for thermoelectric materials presented since the discovery of the Seebeck effect. According to Bulusu and Walker (2008) the first thermoelectric materials were metals, but in the middle of the 20th century semiconductors were noticed by Ioffe (1957) due to their high Seebeck coefficient and because heat conduction is dominated by phonon transport. Positive feature in metals is relatively high ratio of electrical to thermal conductivity. However, modern thermoelectric materials are essentially semiconductors.

Semiconductors are classified by their electrical resistivity at room temperature (Kittel, 2005). The values are in the range of $10^{-2}\ldots10^{9}$ ohm-cm and they are strongly dependent on temperature. Highly purified semiconductors exhibit intrinsic conductivity, which is different to impurity conductivity of less pure or doped specimens. The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band. The extremes in the bands are conduction band edge and valence band edge. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band. Both the electrons in the conduction band and in the vacant orbitals and holes left behind in the valence band contribute to the electrical conductivity. Large mean atomic weight of semiconductors corresponds to lower thermal conductivity (Ioffe, 1957; Bulusu and Walker, 2008). This is because increase in density causes sound velocity in crystal to decrease, which leads to a decrease in thermal conductivity.

Bismuth telluride (Bi_2Te_3) and its alloys are good thermoelectric materials below room temperature. Above room temperature the relatively narrow band gap causes mixed conduction due to both electrons and holes. This leads to reduced Seebeck coefficient. Bismuth telluride can be alloyed with Sb_2Te_3 or Bi_2Se_3, which reduces thermal conductivity considerably. Pseudo-ternary system of Bi_2Te_3-Sb_2Te_3-Sb_2Se_3 has also been formed (Bulusu and Walker, 2008). Problems with tellurium arise, since it is scarce, toxic and volatile at high temperatures. Therefore the use of tellurium is limited (Terasaki, 2005).

Lead telluride (PbTe) was found to have good thermoelectric properties at temperatures in the range of 300–700 K. Similar materials are such as PbS and PbSe, which belong to chalcogenides system. Chalcogenide is chemical compound including at least one chalcogen (“ore former”) ion (usually S, Se or Te) and electropositive element. Lead chalcogenides have a FCC structure and are polar semiconductors with a mixed ionic-covalent bond with the electrons travelling mainly in the cation (Pb) sublattice and the holes in the anion chalcogenide sublattice. PbTe has high mean atomic weight and a multi-valley band structure. The band gap at 300 K is 0.32 eV, which produces higher Seebeck effect than that of bismuth telluride. Also its thermoelectric figure of merit (*ZT*) is higher when the temperature is raised although it has better lattice thermal conductivity than bismuth telluride. (Bulusu and Walker, 2008)

PbTe- SnTe system have been studied since 1961. Lead telluride forms isomorphous solid solutions with lead selenide and tin telluride, which leads to lower thermal conductivity and improved *ZT* values. Band gap goes to zero at $Pb_{0.4}Sn_{0.6}Te$ and therefore lower compositions of tin telluride are required to ensure adequate band gap leading to *ZT* values near 1 for n-type PbTe-SnTe alloys at 700 K. Another system that gives similar properties are TAGS, i.e. $AgSbTe_2$ and GeTe. (Bulusu and Walker, 2008)

SiGe alloys are superior materials for thermoelectric generation (Bulusu and Walker, 2008). Silicon has a large band gap and therefore silicon rich alloys, such as Si0.7Ge0.3, are suitable for high temperature applications because problems with minority carrier dominance do not arise. The large phonon scattering ensures low thermal conductivity without affecting the electron mobility (Bulusu and Walker, 2008). ZT values for some of the practical thermoelectric materials are presented in Figure 3 (Terasaki, 2005).

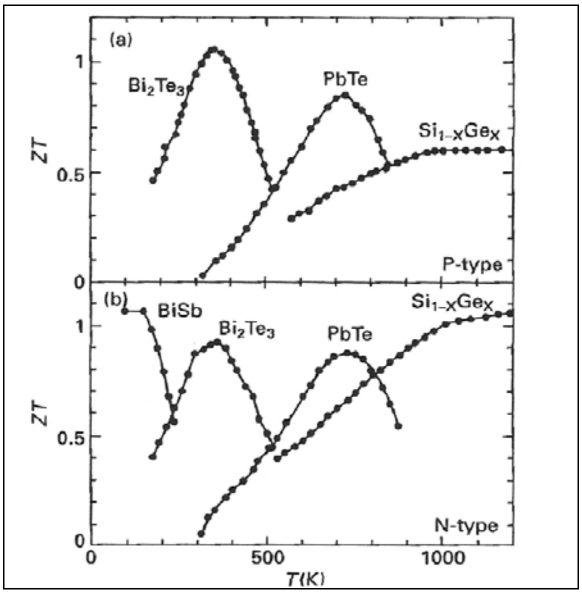

Figure 3. The figure of merit ZT for various thermoelectric materials (Terasaki, 2005).

Lowest conductivity appears in amorphous state and opposite in crystalline state. By setting the mean free path of the phonons equal to that in the amorphous state the smallest possible lattice conductivity can be achieved (Bulusu and Walker, 2008). The resulting materials are called phonon glass and electron crystals (PGEC). These materials have a very complex structure and include materials like borides (YB_{68}) and silver-thallium compounds. Since long range order does not exist, the atoms or molecules rattle and act as phonon scattering sites, which reduce thermal conductivity.

Skutterudites ($ReTm_4M_{12}$) are complex materials containing rare earth elements (Re), transition metals (Tm) and metalloids (M). Binary skutterudites have chemical formula of $ReTm_4M_{12}$, where Re is rare earth element, Tm is transition metal and M is metalloid. Binary skutterudites have the chemical formula of TmM_3 and relatively high thermal conductivity, but the Seebeck coefficient is also relatively large. The crystal structure of binary skutterudites has two large empty spaces in each unit cell. When the empty space is occupied by relatively heavy rare earth element, the result will be reduced thermal conductivity due to rattling of the heavy element within loosely bound lattice. The figure of merit (*ZT*) has been found to be higher than unity at 700 K.

New class of thermoelectric materials was introduced by Ohta (2007) based on a metal oxide: a two-dimensional electron gas (2DEG) in $SrTiO_3$. The 2DEG demonstrates a Seebeck coefficient *S* that is enhanced by a factor of ~5 compared with the bulk and an optimized *ZT* that reaches 2.4, twice that of conventional thermoelectric materials. Other new oxide materials developed in Japan are such as Na_2CoO_4, $CaMnO_3$, $(ZnO)(In_2O_3)$, ZnO and $CuAlO_2$ (Sugihara, 2005).

The listed oxide thermoelectric materials appear promising, since they are chemically stable at high temperatures and they have high oxidation resistance. They are also non-toxic (Koumoto et al., 2006). Especially Na_2CoO_4 has been reported to show unusually high Seebeck coefficient at room temperature, i.e., 100 µV/K (Terasaki, 2005). Most of the oxide thermoelectric materials show low electron mobility and have therefore been dismissed (Terasaki, 2005). These poorly performing oxides are reported to be those of Mn and Ni, as well as Cu in $Bi_2Sr_2CaCu_2O_8$. Koumoto et al. (2006) reviewed oxide thermoelectric materials, including Na_xCoO_2 -materials. General problems with oxide thermoelectrics was reported to be weak mechanical strength, high contact resistance at interfaces of oxides and electrodes.

4. Possibilities with nanotechnology

Other PGEC materials include inorganic clathrates (A_8B_{46}) where B represents either gallium or germanium or their combination. Gallium and germanium atoms form an open crystal acting as an electron crystal. Clathrate ("lattice") is a material which is a weak composite, with molecules of suitable size captured in spaces which are left by the other compounds. Guest atoms are selectively incorporated nanocavities in the crystal and vibrate independently thereby scattering phonons. The group of materials shows promise for thermoelectric applications above 600 ºC (Bulusu and Walker, 2008). Alloy of Pb-Sn-Sb-Ag-Te (LAST) with nano-sized inclusions was developed as n-type thermoelectric material having *ZT* values around 1.7.

Superlattices have been found as structures which improve *ZT* (Venkatasubramanian et al., 1997; 2001). The alternating layers of materials can be manufactured from good thermoelectric materials. Superlattice consists of several alternating nanosized layers, each less than five nanometers thick (Figure 4). These layers block the travel of atomic vibrations that produce heat flow but still let the electrons to flow as current. Adding interfacial phonon scattering sites, the thermal conductivity can be reduced. Fabrication methods include lithography and electroplating, which are widely used in semiconductor industry. The superlattice structures appear to be more than twice as efficient as previous bulk thermoelectric materials. However, serious difficulties will be met due to phenomena taking place in nanoscale. The biggest problem is reported to arise with electrical conductivity due to contact resistance and difficulties in predicting thermal conductivity (Venkatasubramanian et al., 1997; 2001). The problem requires mastering of electron-hole-phonon transport in nanoscale (Bulusu and Walker, 2008).

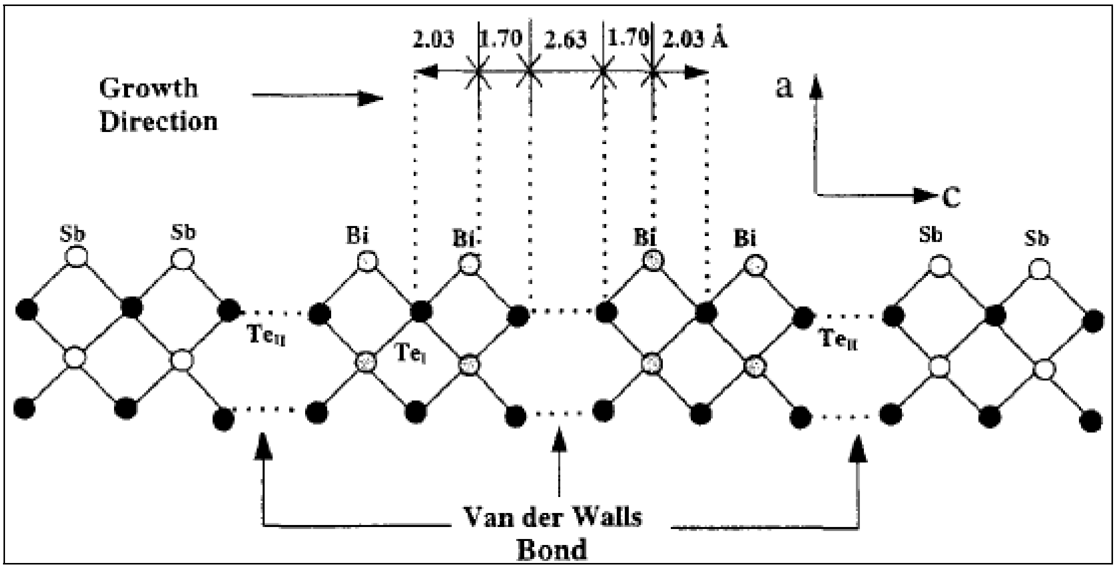

Figure 4. Crystal structure of layered Bi_2Te_3/Sb_2Te_3 material along the growth direction. Van der Waals bonding exists along the c-axis (Venkatasubramanian et al., 1997).

Ezzahri et al. (2008) compared the behaviour of bulk thin films of SiGe and superlattice thin films of Si/SiGe as microrefrigerators. They observed that although superlattice has enhanced electrical properties (larger thermoelectric power factor), the maximum cooling of thin film refrigerators based on SiGe alloys are comparable to that of superlattices. This is considered to be due to larger thermal conductivity of superlattices as compared to bulk SiGe thin films. Bulk thin films are also easier to grow by using methods such as chemical vapour deposition. Si-based microrefrigerators as well as other devices are attractive for their potential monolithic integration with Si microelectronics.

Nanowires can be used for blocking free movement of phonons. Boukai et al. (2008) reported efficient thermoelectric performance from the single-component system of silicon nanowires for cross-sectional areas of 10 nm X 320 nm and 20 nm X 320 nm (Figure 5). By varying the nanowire size and impurity doping levels, *ZT* values representing an approximately 100-fold improvement over bulk Si were achieved over a broad temperature range, including *ZT* < 1 at 200 K.

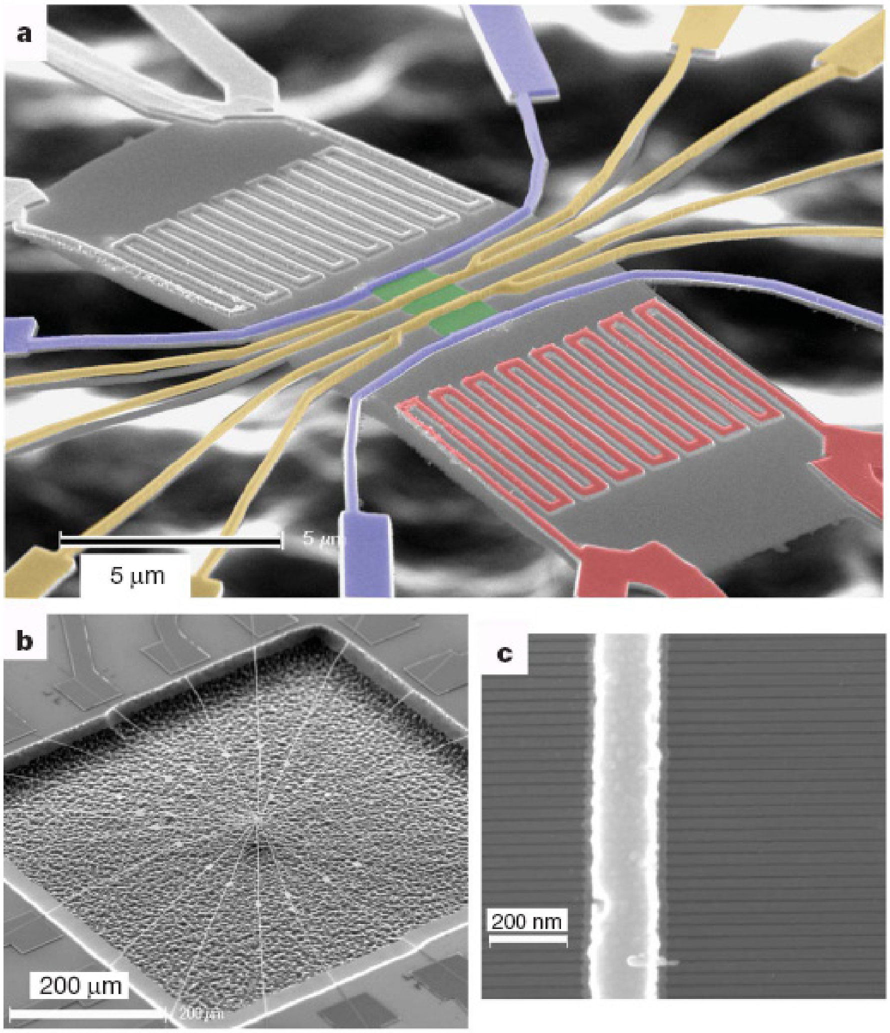

Figure 5. Scanning electron micrographs of the measurement arrangement of Boukai et al. (2008). a) Electrical connections suspending the device, b) overview of the suspension arrangement and c) 20 nm wide Si nanowires with a Pt electrode.

Similar results have been reported by Hochbaum et al. (2008). They synthesised electrochemically large-area, wafer-scale arrays of rough Si nanowires that are 20–300 nm in diameter (Figure 6). These nanowires have Seebeck coefficient and electrical resistivity values that are the same as those of doped bulk Si, but those with diameters of about 50 nm exhibit 100-fold reduction in thermal conductivity, yielding $ZT = 0.6$ at room temperature. For such nanowires, the lattice contribution to thermal conductivity approaches the limit for amorphous Si, which cannot be explained by current theories.

Bulk Si is a poor thermoelectric material. However, by greatly reducing thermal conductivity without affecting much the Seebeck coefficient and electrical resistivity, Si nanowire arrays show promise as high-performance, scalable thermoelectric material.

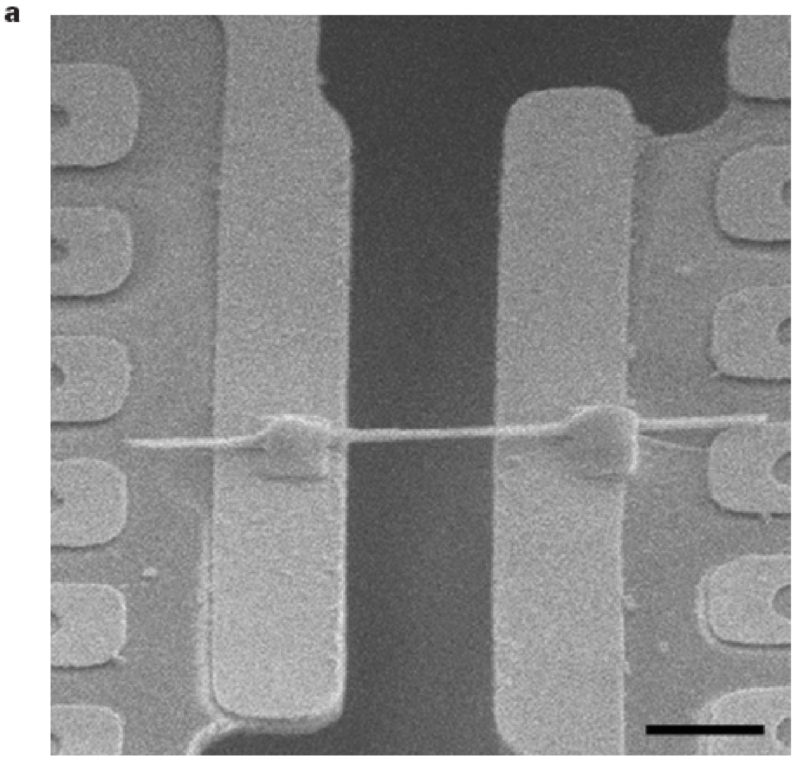

Figure 6. A scanning electron micrograph of Pt-bonded rough Si nanowire (Hochbaum et al., 2008).

Harman et al. (2002) have synthesized arrays of quantum dots each only a few nanometers in diameter. The materials were PbSeTe-based quantum dot superlattice structures grown by molecular beam epitaxy. Harman et al. (2002) demonstrated improved cooling values relative to the conventional bulk $(Bi,Sb)_2(Se,Te)_3$ thermoelectric materials using a n-type film in a one-leg thermoelectric device test setup, which cooled the cold junction 43.7 K below the hot junction temperature of 299.7 K (Figure 7). The typical device consists of a substrate-free, bulk-like (typically 0.1 mm in thickness, 10 mm in width, and 5 mm in length) slab of nanostructured PbSeTe/PbTe as the n-type leg and a metal wire as the p-type leg.

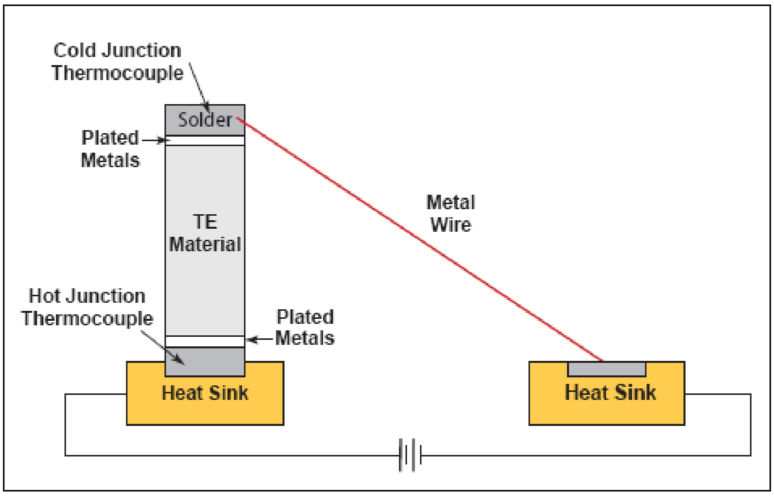

Figure 7. Schematic presentation of the thermoelectric cooling device setup (Harman et al., 2002).

5. Processing methods for thermoelectric materials

There exist several methods for fabrication of novel nanostructured thermoelectric materials (Bhushan, 2004), such as electrochemical deposition, electron beam and nano-imprint fabrication, molecular beam epitaxy, vapour deposition, VLS (vapour-liquid-solid) method, quantum structure nanofabrication using epitaxy on patterned structures, quantum structure nanofabrication using strain-induced self-assembly, several scanning probe techniques, physical and chemical self assembly methods and template methods. It is not practical to discuss all of them, since not all methods can be considered to be possible to use in industrial scale today.

Xiaofeng and Burda (2005) synthesized Bi_2Se_3 heterostructure nanowires and PbTe nanorods via novel sonoelectrochemical method in an aqueous solution at room temperature. By using electrochemical analysis they discovered that the ligand to cation ratio played a very important role in the determination of the product purity. Sonoelectrochemical setups provide sufficient parameters to finetune the structures of the products. Xiaofeng and Burda (2005) suggest that besides Bi_2Se_3 and PbTe, sonoelectrochemical technique can also be applied in the synthesis of other promising nanomaterials. Thus, the method can be a very powerful tool for nanoscale manufacturing.

Xiao et al. (2008) presented a review on recent progress in electrodeposition of thermoelectric thin films and nanostructures (Figure 8). Although there exist reports and articles demonstrating the improvement of efficiency through nanoengineering, the successful application of nanostructures will be determined by a cost-effective and high through-put fabrication method. Xiao et al. (2008) suggest that electrodeposition is such a method.

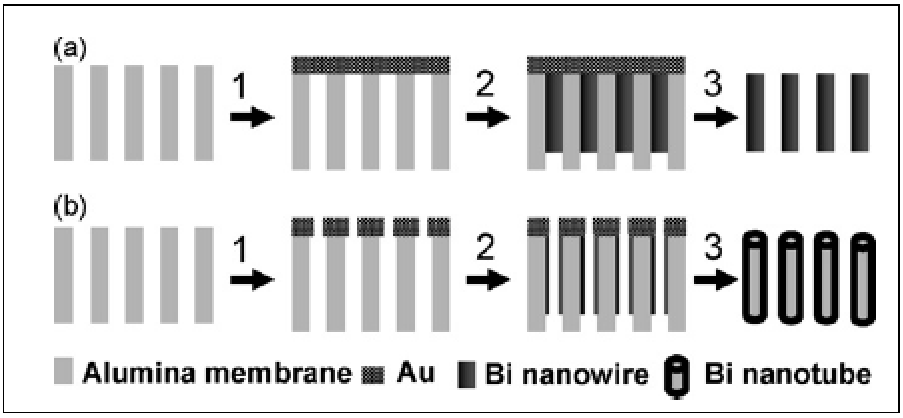

Figure 8. Fabrication process of the Bi nanowires (a) and Bi nanotubes (b). The steps are as follows: 1) sputtered gold seed layer, (2) electrodeposited Bi nanowires or nanotubes inside the nanochannels and (3) removed gold layer and alumina membrane to release Bi nanowires or nanotubes (Xiao et al., 2008).

Especially interesting technique for producing industrial products appears to be atomic layer deposition (ALD). ALD can be used to produce 1–2 nm thick material layers, which makes the method suitable to produce superlattice structures. Atomic Layer Deposition (ALD), also known as Atomic Layer Epitaxy, is a CVD like process where the coating is formed as a result of alternate saturated chemical reactions on the surface resulting in self-limiting growth of the coating. Hence, the thickness and composition of the coating can be very precisely controlled and large areas can be uniformly coated with the ALD technique.

6. Characterization and measurement of physical properties

The materials and components manufactured can be characterized using scanning (SEM) and transmission electron microscopy (TEM), as well as atomic force microscopy. The crystallographic structure and purity of the materials may be characterized using X-ray diffraction measurements.

Measurement of thermoelectric properties requires nearly as much complexity as building an entire device (Snyder and Toberer, 2008). Commercial test benches are not available and, thus, measurement requires ad hoc laboratory test setup. One method to determine the thermoelectric figure of merit, *ZT*, is to measure separately the electrical conductivity, the Seebeck coefficient, and the thermal conductivity, and determine *ZT* using Eq. (1). Techniques and difficulties of those measurements are described, e.g., by Tritt (2005). Such a method has been used, e.g., by Hochbaum et al. (2008) and Boukai et al. (2008) to determine *ZT* of nanowires. Another possibility is to utilize Harman technique, in which *ZT* is determined directly from two voltage measurements when a DC current is applied: one immediately after applying a DC current, and another in steady state after the Peltier effect has cooled the sample to steady-state temperature (Tritt, 2005). A variation of that method has been used, e.g., by Keyani & Stacy (2006) to measure *ZT* of an array of nanowires. Other possibilities for direct measurement of *ZT* have been suggested, too (Min and Rowe, 2001; Dilhaire et al., 2002). Methods for thermoelectric measurements have been described also by, e.g., Harman et al. (2002), Bhushan (2004), and Sugihara (2005).

In ceramic materials thermal conductivity is usually measured with laser flash method, which is the most popular method to measure thermal conductivity of thermoelectric materials at ranges from room temperature up to 1000 K (Sugihara, 2005).

An interesting phenomenon of embrittlement due to neutron irradiation produces also Seebeck effect. This is utilized in the method called STEAM (Acosta and Sevini, 2004). The STEAM measuring system consists of a measurement chain, and an inhomogeneous circuit formed by two copper blocks at different temperatures over which the sample is positioned, the former at room temperature and the latter at 80ºC. When one of the blocks is heated, a temperature difference (ΔT) is established between the two sample's tips, causing the thermal flux across the specimen and therefore the Seebeck effect. The Seebeck coefficient, or absolute tension, of a pure metal may take values ranging from one to a few tens of µV/ºC depending on the imposed temperature difference, the chemical composition of the conductor and its microstructure. When the latter changes, as a consequence of neutron irradiation (formation of vacancies, copper precipitates and segregation phenomena), the thermoelectric power also changes for some classes of materials and its change can be correlated to the change in mechanical properties of the aged material.

7. Potential applications for energy harvesting

Energy system comprises of energy sources, transformation, distribution, use and energy related services (Savolainen et al., 2008). As a whole the energy system is very complex. There exist several major energy sources, as well as transformation technologies and distribution methods. Also the energy related services (i.e. use) are numerous.

Local energy supplies are becoming increasingly important for applications such as environmental monitoring with wireless sensor networks, implantable medical devices and traffic control systems. Ideally, these networks should be powered by local sources of electricity (based on energy extracted from the environment) rather than batteries, which are expensive to replace. Especially, mobile solutions and different stand alone systems can benefit local energy scavenging methods. Such applications would include different vehicles, mobile electronics as well as autonomous and/or ubiquitous instruments and systems.

Hybrid vehicles are optimized for low fuel consumption. This is done by means of separating the engine from direct power train by using electrical power transmission (Savolainen et al., 2008). This requires efficient energy recovery and storage, in which thermoelectric materials may prove useful. Electricity consumption when driving in electric mode is estimated to be 0,2 kWh/km, i.e. 4 kWh/20 km (Savolainen et al., 2008). This would require 20 m^2 photovoltaics panel per one electric or hybrid car. The problems arise in winter time when sun does not provide enough energy. This could be overcome by developing efficient thermal power systems (scavenging and storaging) to support photovoltaics (Savolainen et al., 2008).

It has been suggested that the first applications for new thermoelectric materials could be a device for siphoning off electrical power from the heat in automobile exhaust (Venkatasubramanian et al., 2001). Eventually such a device could be used to supplement power from electric and fuel cell engines or provide a conventional vehicle with most of its electricity needs, running everything from its radio to its air conditioner. Other sources for thermal energy in hybrid vehicles are breaking action during deceleration (Savolainen et al., 2008).

Venkatasubramanian (2001) also envisions the materials use in microelectronics. The heat build-up in today's ultra fast microchips is, in particular, a problem in making smaller and faster devices. Tiny patches of the films precisely positioned on microelectronic chips could be used to spot-cool only the components needing it. Similar problems persist in embedded industrial electronics and optoelectronics.

Within process industry one can find several heat sources and heat exchangers which could be used as energy sources for process instruments. Other specific industrial components are electric motors, which are the major industrial energy users. Also friction in mechanical equipment provides heat to the environment.

Thermoelectric materials will most likely appear first in specialty applications, but if efficiency can be improved, then whole other areas of technology will be available as well from refrigerators to turbine power generators. Also as the price of fossil fuels increases, the electric and hybrid vehicles become more attractive, and thermoelectric systems may provide additional energy capacity.

Another possibility for local electricity generation is solar energy (photovoltaics), which appears probably the most promising technology. At present, further reductions in the cost of solar energy from photovoltaic systems are limited by the supply of silicon but it is expected to achieve cost parity with grid-based power supply in 2012. Silicon-based photovoltaics have experienced exponential reductions in cost over the last 40 years. Yet, the performance of silicon-based photovoltaics can further be enhanced (White, 2008). However, photovoltaics cannot be adopted in places where the sun is seldom seen. Also if energy is being lost as heat the thermoelectric materials are suitable means for energy harvesting. Thus, thermoelectric materials can be adopted as back up system and to enhance the efficiency of photovoltaics panels.

A third possibility to extract electricity locally from the environment is to exploit vibrations. A great deal of energy is wasted in the form of mechanical vibrations, and it has been demonstrated how this energy can be harvested from the linear or rotational motion of a test mass in microelectromechanical systems (MEMS). However, the power density scales as volume to the power of 4/3, so the power density reduces as devices get smaller. Power density is also proportional to the cube of the vibration frequency, which makes it difficult to generate energy from low-frequency vibrations. Despite these challenges, power levels from tens of microwatts to tens of milliwatts can be generated at vibrational frequencies between 10 Hz and 1 kHz, and commercial versions of these technologies are beginning to appear on the market. Piezoelectric materials are also able to convert mechanical or strain-based energy into electricity and such generators based on piezoelectric ZnO nanowires have been described. This approach has the advantage that it can harvest mechanical energy over a broad range of frequencies, and the unique properties of piezoelectric nanostructures may also have applications in novel sensor and information-processing devices (White, 2008).

Technologies that can generate energy, or harvest it from the environment, are part of a larger electronic system that must be designed up-front with the idea of energy harvesting in mind. In particular, system design must take into account the fact that the electrical power produced by harvesting technologies is very low, so it is important not to waste any power through poor design. It is also important to note that no single energy source is likely to be able to power something as potentially ubiquitous as a node in a wireless sensor network. Systems should therefore be designed to take advantage of energy harvesting from several sources including photons (photovoltaics), waste heat (thermoelectrics), mechanical vibrations (MEMS) and thin-film battery technologies (White, 2008).

As a very promising application for novel thermoelectric materials appear to be measurement and monitoring of irradiation embrittlement, as well as recovery during annealing of components. Irradiation embrittlement is a phenomenon causing metallurgical changes and takes place in nuclear reactor pressure vessels due to neutron irradiation. Acosta and Sevini (2005) and Sevini et al. (2006) reported that utilization of Seebeck-Thomson effect (a method called STEAM – Seebeck and Thomson effects on aged materials) that takes place in thermoelectric materials gives better results than resistivity measurement. Combination of the two would give even better results. They conclude that there exists a relationship between the change of the Seebeck coefficient and the hardness changes due to embrittlement. Resistivity measurements data are less correlated, which can mean that the technique is promising but needs improvements to the experimental set-up. They also report that the use of standard specimens, more sensitive instrumentation and better electric contacts would even improve the situation.

8. Summary

Development of new thermoelectric materials has been rapid in past few years. What is lacking is thorough understanding how the materials can be tuned to optimize their properties. More specifically, which materials are optimal when materials properties are adjusted in nanoscale? There exist several potential materials groups for development. The recent development in nanoscale tailoring has based mainly on utilization of silicon. However, silicon can not be considered to be a good thermoelectric material due to its low ZT value. Thus, one can assume that better performance can be achieved by finding appropriate materials. Another major drawback is problem with manufacturing in industrial scale. Thus the development work should be focused on development of new efficient thermoelectric materials suitable for mass manufacturing utilizing nanoscience.

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