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prostate, followed by epithelial neoplasia, and a similar process was observed in the forestomach. These findings suggest the existence of a TGF-β–induced signaling pathway that is initiated in the stroma and terminates, either directly or indirectly, in epithelial cells. That TGF-β indirectly promotes tumors by stimulating stromal reactivity and fibrosis is well established (*17*), but the fascinating discovery of Bhowmick *et al.* is that TGF-β signaling can act as an indirect tumor suppressor. Moreover, the fact that loss of TβRII in stromal fibroblasts leads so quickly and so inexorably to

epithelial carcinoma provides a clear counterexample to the assumption that mutations in epithelial cells are the required initiating factors for carcinoma. Thus, far from being a mere "landscaper," the tissue microenvironment is a powerful regulator of tumor induction as well as tumor suppression—a role that clearly merits not only further exploration, but also respect!

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MATERIALS SCIENCE

# Thermoelectricity in Semiconductor Nanostructures

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With the widespread use of semiconductors in microelectronics and optoelectronics, it is hard to imagine that the initial excitement was due to their promise not in electronics, but in refrigeration (*1*). The discovery in the 1950s that semiconductors can act as efficient heat pumps led to premature expectations of environmentally benign solid-state home refrigerators and power generators containing no moving parts. Except for specialized applications, however, the vision of widespread use of thermoelectric energy–conversion devices has remained elusive. At issue are some fundamental scientific challenges, which could be overcome by deeper understanding of charge and heat transport in semiconductor nanostructures. Lyeo *et al.* (*2*) report in this issue an experimental technique that could improve our grasp of these phenomena, while Hsu *et al.* (*3*) report the synthesis of a new class of materials that could potentially be used for power generation.

Thermoelectric materials are ranked by a figure of merit, *ZT*, which is defined as $ZT = S^2\sigma T/k$, where *S* is the thermopower or Seebeck coefficient, σ is the electrical conductivity, *k* is the thermal conductivity, and *T* is the absolute temperature. To be competitive compared with conventional refrigerators and

generators, one must develop materials with *ZT* > 3. Yet in five decades the room-temperature *ZT* of bulk semiconductors has increased only marginally, from about 0.6 to 1 (see figure). The challenge lies in the fact that *S*, σ, and *k* are interdependent—changing one alters the others, making optimization extremely difficult. The only way to reduce *k* without affecting *S* and σ in bulk materials is to use semiconductors of high atomic weight such as Bi_2Te_3 and its alloys with Sb, Sn, and Pb. High atomic weight reduces the speed of sound in the material, and thereby decreases the thermal conductivity. Although it is possible in principle (*4*) to develop bulk semiconductors with *ZT* > 3, there are no candidate materials on the horizon.

It is, therefore, encouraging to see Hsu *et al.* (*3*) report on page 818 that
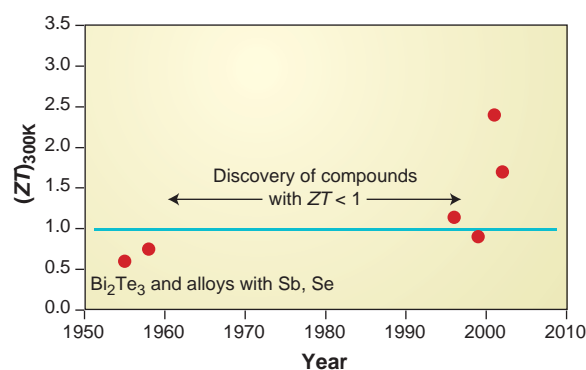
Thermoelectric improvements. History of thermoelectric figure of merit, *ZT*, at 300 K. Since the discovery of the thermoelectric properties of Bi_2Te_3 and its alloys with Sb and Se in the 1950s, no bulk material with $(ZT)_{300K} > 1$ has been discovered. Recent studies in nanostructured thermoelectric materials have led to a sudden increase in $(ZT)_{300K} > 1$.

$AgPb_mSbTe_{2+m}$ has $ZT \approx 2$ at 800 K for $m = 18$. Although the temperature may be too high for refrigeration, it is appropriate for power generation. What is interesting, however, is the discovery that this material contains regions 2 to 4 nm in size that are rich in Ag-Sb and are epitaxially embedded in a matrix that is depleted of Ag and Sb. Presumably, the electronic band structure and vibrational properties of these nanoregions are different from those of the surrounding material, suggesting quantum confinement. However, several questions remain: Are there quantum effects in these nanostructures and, if so, do they play any role in raising the *ZT* of the material? Is the acoustic impedance of the nanodots very different from that of the matrix and, if so, do they scatter acoustic phonons and thereby reduce thermal conductivity? How does the structure and size depend on *m*, and are there ways to maximize *ZT*?

Over the past decade, these questions about quantum effects have received increasing attention, and their answers hold promise (*5*, *6*) in increasing *ZT*. In the past 3 years, reports have suggested that nanostructured thin-film superlattices (*7*) of Bi_2Te_3 and Sb_2Te_3 have *ZT* ~ 2.4 at room temperature, whereas PbSeTe/PbTe quantum dot superlattices (*8*) have *ZT* ~ 1.3 to 1.6. Seen historically, this is a huge jump over an extremely short period (see figure). What is the underlying science? In semiconductors, electrons and holes carry charge, whereas lattice vibrations or phonons dominate heat transport. Electrons (or holes) and phonons have two length scales associated with their transport—wavelength, λ, and mean free path, ℓ. By nanostructuring semiconductors with sizes comparable to λ, sharp edges and peaks in their electronic density of

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states are produced, whose location in energy space depends on size. By matching the peak locations and shape with respect to the Fermi energy, one can tailor the thermopower S. Furthermore, such quantum confinement also increases electronic mobility, which could lead to high values of σ. Hence, quantum confinement allows manipulation of $S^2\sigma$ that is otherwise difficult to achieve in bulk materials.

It is entirely possible, though, that the increase of ZT may be less dependent on quantum confinement of electrons and holes, and more on phonon dynamics and transport. For example, if the size of a semiconductor is smaller than the mean free path of phonons and larger than that of electrons or holes, one can reduce thermal conductivity by boundary scattering without affecting electrical transport. Although charge transport in thermoelectricity is almost monoenergetic (energy levels within a few kT around the Fermi energy), heat transport by phonons is broadband over the Brillouin zone. Many bulk thermoelectric materials are alloys because alloy scattering of the short-wavelength acoustic phonons suppresses thermal conductivity without substantially altering $S^2\sigma$. However, the mid- to long-wavelength phonons remain largely unaffected and conduct heat in alloys. Can one beat the alloy limit? It is possible that embedded nanostructures (*3*, *7*, *8*) in semiconductor alloys could scatter the mid- to long-wavelength phonons as well because of the similarity in sizes, and thereby reduce the thermal conductivity below the alloy limit (*9*). Given all these possibilities, it is unclear which effect can be exploited most readily to increase ZT. What is clear, though, is

that if one has to increase ZT beyond 3, it is imperative that how charge and heat transport (*10*) occur in semiconductor nanostructures be understood.

Lyeo *et al.* (*2*) report on page 816 a technique called scanning thermoelectric microscopy (SThEM) that can probe thermoelectric transport at nanoscales. By heating a sharp metallic tip to about 10 K above the temperature of a sample and bringing them in contact under ultrahigh vacuum, they create a temperature gradient within a localized region in the sample right under the tip. The thermoelectric effect in this sample region creates a potential difference, which can be measured between the tip and the sample. By scanning the tip laterally, one can map out the thermopower profile in a sample. Lyeo *et al.* demonstrated this by mapping out the thermopower of a *pn* homojunction. Because *p*- and *n*-doped semiconductors have positive and negative thermopowers, respectively, a *pn* homojunction produces a large swing in thermopower over a length scale that is on the order of the depletion region. What is remarkable is that they showed the spatial resolution to be on the order of 2 to 4 nm in highly doped semiconductors, which creates the possibility of probing semiconductor nanostructures for thermoelectricity. Interestingly, this resolution is on the order of the nanostructure size discovered by Hsu *et al.* (*3*) in $AgPb_{18}SbTe_{20}$.

Although arguments for SThEM have been made with thermoelectrics in mind, the reported results on a *pn* homojunction have important ramifications in electronics and optoelectronics as well. The continuous reduction in field-effect transistor size requires the fabrication of doped sources and drains with extremely sharp *pn* junc-

tions. What has remained difficult is to accurately map out the dopant profiles with nanometer spatial resolution. Techniques such as scanning capacitance microscopy have been used in the past; however, the need for an external bias can introduce band bending, which requires deconvolution. For thermoelectric probing, in contrast, this problem is largely eliminated, making it an ideal approach. The demand for sharp electronic interfaces is even more severe in optoelectronic devices, where heterostructures of quantum wells and quantum dots are currently being used in lasers, light-emitting diodes, and photodetectors. Here again, thermoelectric probing could provide a means to map out the electronic band structure without introducing band-bending effects.

Over the past decade, researchers in thermoelectricity have leveraged their knowledge of band gap engineering from electronics and optoelectronics to create nanostructured thermoelectric materials and devices. Lyeo *et al.* (*2*) show that through SThEM, the converse could be true as well—thermoelectricity could be used to facilitate the next generation of electronics and optoelectronics.

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PHYSICS

Pas de Deux for Atomic Electrons

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An atom with many electrons is like a complex ballet, displaying an often chaotic interplay of orbits. Owing to the effects of quantum mechanics, the lowest energy orbits (or ground states) of many-electron atoms are stable. Excited states of the atoms do experience interactions, however, in which one of the electrons is liberated while the other falls to a lower state. The connection between these so-called autoionization processes and the classical or-

bits is generally obscured by the same quantum effects that stabilize the ground states, but in an experiment reported by Pisharody and Jones on page 813 of this issue, the connection is greatly clarified (*1*).

In classical mechanics, a multielectron atom is similar to a planetary system [for a nice description of the classical planetary three-body problem, see (*2*)]. There are some differences, particularly the fact that the gravitational forces coupling planets with each other and with the Sun are always attractive, whereas the electrons in an atom all are attracted to the nucleus but repel each other. The classical orbits of these two systems have many similarities, in-

cluding the presence of chaos (i.e., a sensitivity to initial conditions that leads to wildly different outcomes). There are also collisions between planets or electrons that can throw them free of their respective systems. We observe in nature that our solar system is relatively stable, and furthermore that the ground states of multielectron atoms are stable. The reasons for this stability are different in the two cases. In the solar system the planets are in nearly circular orbits, each with a different radius, so that they are never very near each other. The gravitational force between each pair of bodies is proportional to the product of their masses, and because the planetary masses are much smaller than that of the Sun, the coupling with the Sun is much stronger than the planets' mutual attraction unless they get very close together indeed. Were the planets to have very eccentric orbits so that they crossed, the probability of

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