Temperature Rises for Devices That Turn Heat Into Electricity

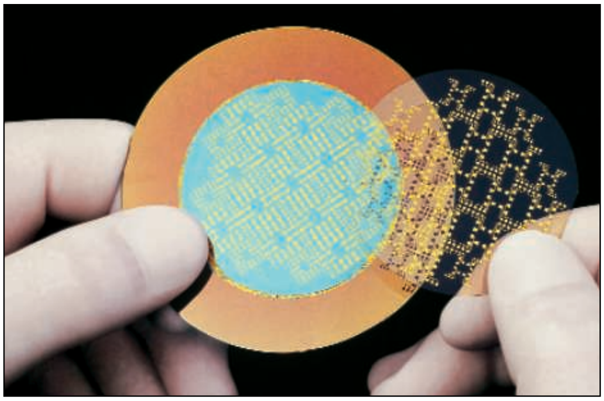
Long-sought materials that can harness waste heat and revolutionize refrigeration are on track to become more than an engineer's dream

Imagine throwing away 65% of every paycheck. Not an inviting prospect. But that's essentially what happens every time we turn on our cars, lights, and many other modern conveniences. Roughly two-thirds of the energy that is fed into these gizmos radiates away as heat without doing any useful work. In the United States alone, that's a whopping $265 billion a year worth of power that, "poof," is just gone. But, thanks to a decade of steady progress in a once sleepy field of semiconductor engineering, that may soon change. Researchers around the globe are working to improve "thermoelectric" materials that convert waste heat to usable electricity. Such chips aren't proficient enough yet to be an economical power source. But after decades of stagnation, "this field is moving very fast right now," says thermoelectric pioneer Mildred Dresselhaus of the Massachusetts Institute of Technology (MIT).

If this progress continues, it could pay big dividends by allowing everything from power plants to cars to turn some of their waste heat into power. "If you can save 10% using thermoelectrics for waste heat recovery, it means a lot," says Gang Chen, a mechanical engineer at MIT. Thermoelectrics also operate in reverse, using electricity to cool things down or heat them up. Thermoelectric chips are already used to cool everything from light-emitting diodes and lasers to picnic coolers, and researchers are pushing hard to create solid-state home refrigerators that will be free of noisy, bulky pumps and ozone-depleting gases. Many researchers hope that marrying thermoelectrics with nanotechnology will spark another round of dramatic improvements. "I think there is between 5 and 10 years of very intense research that is going to happen," says R. Ramesh, a materials scientist at the University of California, Berkeley.

Fits and starts

That's just a blink of an eye for a field that has already been around for nearly 200 years. In 1821, an Estonian physicist named Thomas Johann Seebeck discovered that when he joined two dissimilar conductors in a loop or circuit and heated one, it caused a compass needle to deflect. (Researchers later determined that the experiment produced an electric voltage that in turn created a magnetic field that tweaked the needle.) In 1834, French physicist Jean Peltier found the reverse was also true: If you fed enough electricity to a circuit composed of two different conductors, you could push electrons to carry heat from one to the other, causing the first conductor to cool while the other warmed. In the early 1900s, other investigators discovered that the key to making efficient thermoelectric materials is to boost their electrical conductivity while keeping their thermal conductivity as low as possible. That allows power to move easily through the device while maintaining the temperature difference between the junctions necessary to produce the effect. These properties were later incorporated into the thermoelectric figure of merit known as *ZT*, which researchers use to compare different thermoelectrics much as baseball fans track ERAs to compare pitchers. In particular, *ZT* depends on several factors: a material's thermopower (how much voltage is created when a temperature gradient is put across it), its electrical and thermal conductivity, and the temperature.



Cool chip. Prototype "superlattice" device, made from 1000 semiconducting sheets, can generate power or pump heat.

In the early 20th century, researchers investigated all sorts of combinations of metals for their thermoelectric potential. To their frustration, they found that in metals the two kinds of conductivity are linked: Trim the thermal conductivity, and the electrical conductivity drops as well. By the 1950s, however, researchers had shown that by engineering different semiconductor alloys they could control the thermal and electrical conductivity of their materials separately.

That was good news for would-be devicemakers. For makers of thermoelectric generators, it held out hopes of simply heating up a material and sitting back as it produced a voltage that could drive a device or charge a battery. For refrigeration experts, it held the prospect of creating solid-state coolers that worked when plugged into a standard outlet.

Hopes rode high in the 1950s and '60s that researchers would be able to create thermoelectrics that generate large amounts of power. And *ZT*s rose from a middling 0.2 or 0.3 to about 1 for materials such as bismuth telluride. Unfortunately, despite the development of thermoelectric generators for spacecraft that use heat generated by radioactive elements to produce a trickle of electricity, practical applications needed higher *ZT*s than even semiconductors could provide. "From the 1960s to the 1990s there was not much development," Chen says.

But that story began to change in the early 1990s with the rise of nanotechnology. In the mid-1990s, Dresselhaus's group and another team led by physicist Gerald Mahan at Pennsylvania State University, University Park, independently determined that if thermoelectric materials could be made on the nanoscale, their *ZT* should shoot up dramatically, potentially even above 6. "For *ZT*, the expectation is if we could get above 5, it would enable a wide range of applications," including solid-state refrigeration and power generation aboard cars, says Heiner Linke, a physicist at the University of Oregon, Eugene. "Now there is a new pathway to approach that."

Walking the path

As with the previous era's focus on semiconductors, the ability to walk that path depends on independently controlling the electrical and thermal behaviors of a material. Dresselhaus and Mahan's simulations suggested that this control would come about by limiting at least one dimension of a thermoelectric material to the nanoscale. That means crafting thermoelectrics either out of stacks of thin planes or, better yet, out of long, thin wires. This approach, they found, would bring several benefits. First, confining electrons in one or more dimensions allows researchers to tune their electrical properties and make them more con-

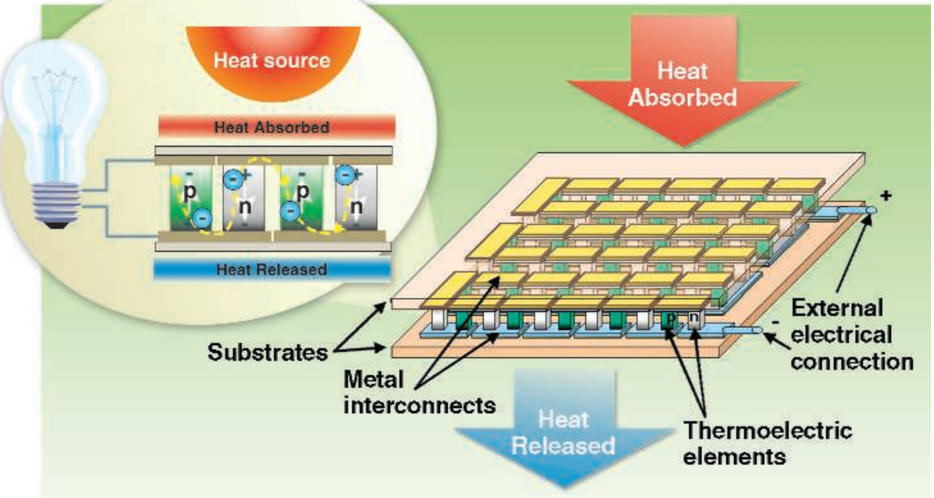
CREDIT: JOHN THEILGARD/RTI INTERNATIONAL

Published by AAAS

ductive. If controlled properly, that same confinement could also lower the material's thermal conductivity. In this case, vibrations of a crystalline lattice, called phonons, carry heat through a material. A critical measure is the so-called mean free path: the average distance that the phonons as well as electrons travel in these materials before reflecting off one surface and traveling in another direction. If researchers create materials in which one dimension is smaller than the mean free path of the phonons but larger than that of the electrons, then the electrons will zip through the material with few collisions, while the phonons will slow to a crawl, knocking into obstacles wherever they look.

Over the past couple of years, experimenters have begun making impressive strides toward harnessing those ideas. In the 11 October 2001 issue of *Nature*, for example, Rama Venkatasubramanian and his colleagues at the Research Triangle Institute in Research Triangle Park, North Carolina, reported creating a chip-based semiconductor sandwich thermoelectric with a *ZT* of 2.4, more than twice that of the commonly used bulk semiconductor bismuth telluride. The sandwich, made with computer-chip manufacturing techniques, consists of ultrathin layers of two alternating semiconductors, bismuth telluride and antimony telluride. The interfaces between these alternating layers, the researchers found, acted like additional speed bumps to slow the progression of phonons as they attempted to travel along with the electrons vertically through the sandwich. In their *Nature* paper, Venkatasubramanian's team reported crafting tiny computer chip–sized refrigerators capable of cooling a room-temperature heat source by as much as 32°C. Since then, Venkatasubramanian says that his team has data suggesting that they may be able to increase the *ZT* to over 3.5, although the work is not yet published. And for now, Venkatasubramanian says, his team is focusing on making working modules for cooling chips and other applications.

On 27 September 2002, Ted Harman and colleagues at MIT's Lincoln Laboratory added their own new twist, reporting another type of layered semiconductor called a quantum dot superlattice in which they grew layers of nanometer-sized islands of an alloy of lead, selenium, and tellurium in layers of lead telluride. Those superlattices displayed a *ZT* of 2 at room temperature. But just a year later, Harman reported at the Materials Research Society meeting in Boston that his team had created a similar superlattice with a *ZT* of 3 when tested at 600 K. Not only do the islands help scatter phonons and therefore reduce the thermal conductivity of the material, but Harman says he suspects they



Dynamo. Heat drives electrons (*inset*) through a thermoelectric module to generate power.

also force electrons to have tightly controlled amounts of energy. As a result of that restriction, the quantum dot superlattices boast a high density of electrons at a particular energy level, a condition favorable to increasing the conductivity of the material.

Dresselhaus says the new superlattices are impressive but have a long way to go before making it out of the lab. "This has to be consolidated and put into practice on a much higher level," Dresselhaus says. Even more daunting, says Mercouri Kanatzidis, a chemist at Michigan State University in East Lansing, is turning such tiny devices into the bulk materials needed for large-scale applications such as generating power from a car's or factory's waste heat.

But Kanatzidis's team has progressed at least partway to a solution. In the 6 February issue of *Science* (pp. 777, 818), they reported creating a bulk crystalline semiconductor made from silver, lead, selenium, and tellurium with a *ZT* of 2.2 when working at 800 K. Although that temperature is far too high to be of much use in household refrigerators, the material—or its future kin—may be of use in turning waste heat to power in, say, hot engines. Such materials "could be of very significant interest to the automotive industry," says Mark Verbrugge, who directs the materials and process lab at GM's R&D Research Center in Warren, Michigan. Thermoelectrics aren't quite ready to break open the heat-recovery business, he says, but they are getting a lot closer: "We've seen some significant materials changes in the last few years."

The good news, Dresselhaus and others say, is that materials engineers and nanotechnologists have a few more tricks up their sleeves that could boost *ZT*s even higher. One, says physicist Terry Tritt of Clemson University in South Carolina, is simply to try more combinations of materials when making bulk semiconductor alloys. Researchers have spent decades testing two-member alloys such as bismuth telluride and antimony telluride, but they've only recently begun testing three- and four-member alloys, such as Kanatzidis's recent success story.

Another approach now being hotly pursued, says Dresselhaus, is combining the success of the superlattices with nanowire semiconductors. Several groups around the globe, such as one led by Lars Samuelson at Lund University in Sweden, have recently begun growing nanowire superlattices: materials consisting of wires composed of alternating semiconductors abutting one another like boxcars in a train. As with the chip-style superlattices, the numerous interfaces between the different semiconductors should slow heat transport in the materials, while electrons should still zip through the wires, thereby giving them a high *ZT*. But so far that's been difficult to confirm, partly because hooking these wires up to tiny circuits to test their *ZT* is a considerable challenge.

Going the next step and turning forests of these nanowires into devices has been even harder. One hurdle here, Venkatasubramanian points out, is that any matrix material that holds these nanowires must be as good a phonon blocker as the nanowire superlattices themselves so heat leaking from one side of the device to the other doesn't just bypass the nanowires and slip through the matrix. Although these challenges haven't been solved yet, groups around the globe are now bearing down and expect results soon. If successful, they will undoubtedly act as a double espresso for this once sleepy field and perhaps awaken entirely new industries in energy recovery and solid-state refrigeration.

–ROBERT F. SERVICE

CREDIT: JAMES LIM AND JEFF SNYDER/JPL/CIT; INSET: N. KEVITIYAGALA/*SCIENCE*, ADAPTED FROM J. LIM AND J. SNYDER