

Building Bridges to the Nanoworld

Michael Roukes is not a musician, yet his conversations are seeded with references to guitar strings. Roukes is not an architect or civil engineer, either, although he often talks about building suspension bridges. Roukes is a physicist who, in his laboratories at the California Institute of Technology, is exploring the basic science behind nanofabrication, the creation of structures not much bigger than atoms or molecules. He and his colleagues are artfully carving up gallium arsenide and other semiconductors to construct some of the smallest freely suspended objects in the world. And these miniature structures are what Roukes compares to suspension bridges, guitar strings, and other oscillating mechanical systems.

These microscopic oscillators are, in Roukes' view, gateways into new physical domains. On a macroscopic scale, researchers understand reasonably well how heat and other forms of energy behave in various materials. Far below that scale, however, is largely terra incognita. But because Roukes' oscillators are so small, the slightest shifts in their energy, shape, or other physical characteristics have noticeable effects on their behavior, in the form of significant amplitude or frequency changes in their vibrations. Therefore, on these lilliputian bridges and strings Roukes will be able to trace whether heat flows differently than in macroscopic bulk materials, or how a single defect in a semiconductor crystal absorbs energy. Roukes also plans to use these structures to search for phonons, quantized lattice vibrations that are the fundamental units of heat. "We'd like to see the imprint of quantum mechanics," he says.

For the moment, this is all fundamental physics research, says Roukes, but eventually such information will be needed by nanotechnologists who dream of building electronic systems on the scale of individual molecules, or protein-sized machines that clean up pollution. Like engineers in the real world, they'll need to know how energy behaves in their tiny machines. Of a more immediate and practical nature, though, the Caltech group and their collaborators intend to use their minute oscillators to probe the nuclear or electron "spins" of just a few atoms deep within a material, an application that has intrigued some semiconductor manufacturers.

Because this research hovers in the area between applied and basic research, it has

trode pulled electrons in the lower band out of the polymer—leaving vacancies, or holes, behind them. These lower band electrons take a step around these holes, one at a time, and this shuffling forward means that the holes effectively move backward toward the negative electrode. If one of these backward-moving holes happens to move past a forward-moving electron in the upper band, the electron may seize the moment—and a chance to move to lower energy—and drop down, emitting a photon.

The conducting polymer that made this happen was poly(*p*-phenylenevinylene), or PPV. The light it gave off will never replace the light bulb, but its glow can be seen in daylight. For materials scientists, that meant the possibility of building flat display screens from other materials besides the delicate and hard-to-manage liquid crystals that currently make up those displays. If polymer LEDs could be made to emit all colors, efficiently and reliably, and were cheap and easy to make, there was a fortune to be made.

Adding color to the field. And that realization made polymer LEDs a growth industry. "The LEDs are really promising and very exciting," says Heeger, now at the University of California, Santa Barbara (UCSB). His group, and others in Europe and Japan, set out to see whether they could make the polymers truly shine. One of the first tasks was to get the LEDs to emit different colors beyond the Cambridge group's yellow-green. This is done by altering the polymer so that the energy gap between the lower and upper energy bands creates photons of the right wavelength. Tuning a polymer to emit red light, for instance, which is a low-energy photon, requires a smaller energy gap. In 1991, Heeger's group was able to tweak the internal structure of PPV and produce red light. Blue light, on the other hand, has a higher energy, so the polymer needs a bigger band gap. In 1992, Gunther Leising's group at the Technical University of Graz in Austria achieved this with a larger-gapped polymer, poly(*p*-phenylene).

But color is only one hurdle; the other is efficiency—the proportion of electrons injected into the polymer that result in an emitted photon. The first polymer LEDs produced in Cambridge had efficiencies of only around 0.01%, low compared to a light bulb, in which about 10% of the introduced electrons produce photons. One reason lies in the electrodes that attach to the polymer. The electrodes are usually made of metal and they have their

own energy bands, which don't match the bands in the polymer. And the energy bands in the most suitable metals are not at the right level for putting electrons into the upper band. The result: There are often holes in the lower band, but no upper band electrons to drop into them, and the material loses efficiency.

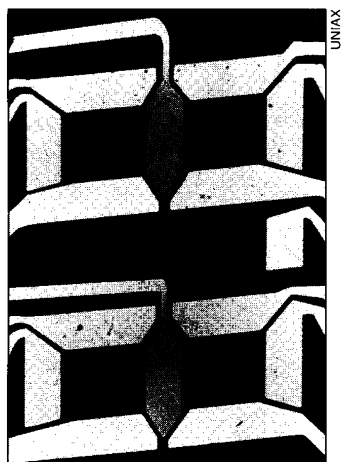
Researchers are trying to solve this problem with different polymers and different electrode materials. Last October, Friend's group reported the highest efficiency yet attained: around 4%. They achieved it by constructing a two-layer LED out of two different polymers. One layer, from a family of conjugated polymers called poly(cyanoterephthalylidene)s, has energy bands closer to those in metals such as aluminum, making it easier to insert electrons into the upper energy band. The second layer is PPV, from which electrons are pulled into an indium tin oxide (ITO) contact, creating holes for the electrons to drop down into.

This bilayer arrangement also helps to bring electrons and holes together, since they tend to congregate at the junction between the two polymers. There's a slight energy band mismatch between the two materials, which hangs up both lines of electrons at the junction for a few extra fractions of a second, increasing the probability that an electron will find a hole. And an efficiency of 4% creates ample brightness for use in flat screen displays.

Lighting the way to market? These initial successes don't mean plastic displays will be on display any time soon. In particular, there's one large unsolved puzzle: how to make polymer LEDs last longer. Some polymers only glow for a few minutes before fading, others may last hundreds of hours, but to be useful to industry they must glow unfailingly for tens of thousands of hours. Researchers are still hunting for the reasons why the plastic LEDs fade so quickly; among the prime suspects are overheating and degrading the polymer with too high a current, and oxidative reactions between the polymer and the electrode which damage the material. But it's a tough problem. Says Philips' Braun, "I'm optimistic—but I'm not going to hold my breath."

Yet that optimism, as well as the patience, now pervades the field, since the other problems with LEDs were solved with time. Friend and Heeger have already set up companies for bringing commercial application of these polymers to light.

—Daniel Clery



Plastic light. Conducting polymers can be made to emit light in a pattern.

also piqued the interest of the physics community. "I think there will turn out to be very interesting physics. I envy Mike the capability to do it," says University of Oregon physicist Stephen Gregory, who has pursued some of the same ideas, but with larger graphite wire oscillators. "This is neat stuff," agrees Harold Craighead, director of Cornell University's National Nanofabrication Facility.

To build what he calls "laboratories on a chip," Roukes starts with small, thin multi-layer semiconductor wafers, perhaps 2 inches in diameter and twenty-thousandths of an inch thick. Using beams of electrons and ion bombardment, scientists chisel the outlines of tiny bridges and other shapes in the top layer of the wafer, and then use semiconductor-dissolving chemicals to eat away at material just beneath the spans. Caltech electrical engineer Axel Scherer, a long-time Roukes collaborator, has used these techniques to make structures that are a fraction of a micron long and have diameters below 100 angstrom—a nanorecord.

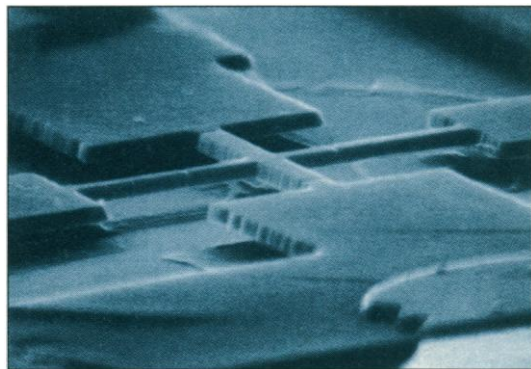
It's a record with string instruments. "Think of them as nanometer-scale guitar strings," says Roukes, referring to Scherer's creations. In the human-sized world, part of the reason a plucked string's note slowly fades out is that billions of crystal defects within the string soak up energy. On this level, it's hard to figure how much energy is absorbed by each defect—and it isn't terribly important. But as devices shrink, the energy-absorption of single defects looms larger—it could affect the performance of the entire device.

That's where Roukes' nano-scale guitar strings come in. They're so small that they have a few defects at most. If "plucked" by applying an electrical impulse, they'll vibrate with a certain amplitude until a defect absorbs a distinct parcel of energy. "The hope is we'll be able to do a form of defect spectroscopy, watching the amplitude change by a discrete amount," says Roukes. That understanding of individual defects might, in turn, help engineers create more efficient semiconductor circuits and other crystalline devices. "One would like to understand the [energy] loss mechanisms in solids, to get rid of them or take advantage of them," says AT&T Bell Labs physicist Bernard Yurke.

These nanostructures will also be used to study the flow of heat in a world where quantum mechanics holds sway. The width of Scherer's semiconductor spans can be far smaller than the wavelengths of phonons. That, says Roukes, constrains thermal energy so that it basically travels in just one dimension: along the length of the bridge. This phenomenon is similar to the confinement of electrons with electrostatic fields into so-called quantum wells, wires, and dots

(*Science*, 29 November 1991, p. 1306).

The motivation for investigating one dimensional heat flow can be compared to that of car makers, who must keep in mind how thermal energy moves through the materials of their engines, since overheating has an impact on the engine's longevity and efficiency. Similarly, future nanoengineers hoping to design atomic-sized motors and other devices must be able to predict how heat travels within their creations. Right now, they can't, because few have investigated



Under construction. Microscopic bridges like these, which are 4 microns across, can pave the way for novel nanoscale devices.

whether this nanoregime differs from the macroscopic world. "If our hope is to ultimately make atomic size structures, this will be a serious problem," asserts Roukes.

Not only does Roukes plan to turn up the heat on his nanobridges, he also intends to take it away. At normal temperatures, the bridges' thermal energy causes them to oscillate naturally. By cooling the spans down to millikelvin temperatures, Roukes can suppress these heat-derived fluctuations. But they'll still vibrate at ultrahigh and microwave frequencies, because of an unremovable parcel of energy called "zero-point energy." That's a phenomenon of quantum mechanics implied by Heisenberg's uncertainty principle, which asserts that no oscillator can ever be completely at rest.

With only zero-point motion as background noise, these chilled oscillators could provide the most sensitive force or displacement detectors ever, since the slightest energy boost would increase the oscillator's amplitude. "We can see a single quantum of mechanical energy added," predicts Roukes. This sensitivity, says Bell Lab's Yurke, could even allow the first direct detection of individual phonons. It's hard to predict now how that skill would be put to practical use, say investigators, but it would nonetheless be an impressive feat of fundamental research.

Roukes' sensitive structures may be of more immediate benefit in a novel kind of magnetic resonance imaging (MRI) that could probe a few atoms beneath the surface of semiconductors and examine the inner

shape of a cellular protein. That would be welcome, since "there really exist no high-resolution sub-surface probes," explains P. Chris Hammel, a magnetic resonance expert at Los Alamos National Laboratory.

The idea for this new type of MRI was proposed in 1992. In that year, physicist and orthopedist John Sidles at the University of Washington suggested a way to bypass the traditional insensitivity of MRI, which requires a lot of material—biological or otherwise—to induce a signal detectable on an electromagnetic field. Sidles had calculated that when the electron or nuclear "spins" of just a small number of atoms couple with a magnet implanted on a minute oscillating cantilever, it produces a resonance that should exert a barely detectable mechanical force on the cantilever (*Science*, 7 August 1992, p. 750). Investigators are trying to bring that design to life, but true atomic resolution demands an exquisitely delicate cantilever.

The freestanding structures made by Caltech should prove ideal, says Hammel, because they are lightweight and shed energy very slowly, making the resonance easier to detect. Together, the Caltech and Los Alamos researchers are working to create microchip-sized instruments that explore the inner workings of superconductors or peer into semiconductors for buried interfaces and defects. The latter application has attracted interest from industrial groups like the semiconductor consortium Sematech. "This will be making an impact in a short time," predicts an excited Hammel. Not bad for plucking a few microscopic guitar strings and building some bridges that are invisible to the naked eye.

—John Travis

ADDITIONAL READING

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