by Eric J. Lerner

Big step toward molecular electronics

A Hewlett-Packard research team has advanced efforts to develop practical chips based on molecular electronics by creating the first molecular-electronic memory chip. The experimental device stored only 64 bits but achieved a storage density 10 times that of conventional silicon electronics. In addition, the chip's memory was nonvolatile (preserved with the power off) and was combined with logic elements, both of which provide advantages that are not available with silicon-based random-access memories.

During the past three years, several groups have succeeded in producing individual electronic devices, including transistors, from organic molecules such as rotoxane and from carbon nanotubes. But until now, no one had succeeded in making usable multiple-device chips or in developing techniques with the potential for mass production. Conventional lithography cannot produce the nanoscale devices needed, and no one has yet perfected self-organizing techniques that can enable molecules to form the circuits by themselves.

The Hewlett-Packard group, led by senior scientist Yong Chen, accomplished its feat by using a new imprinting process recently developed by Princeton University physicists (see *The Industrial Physicist*, October/November 2002, pp. 10–11). The work, which has not yet been published in a technical journal, is described in U.S. Patent 6,432,740. The method creates a mold out of quartz, which is then pressed into a layer of photoresist. Where the mold compresses the resist, it can be etched away. Where the resist is not compressed, it protects the underlying layer. This process allows the use of the same lithography techniques employed by the chip industry, but it yields narrower linewidths.

"It takes a couple of days to create the molds using electron-beam and optical techniques," Chen explains. "But this does not matter because using the mold to create the chip only takes a few minutes," and potentially could be done in seconds or less. In making the nanocircuits, a layer of wires is first laid down using 40-nm linewidths, which is one-third the width of the finest lines available in commercial chips. On top of this is laid a two-dimensional crystal layer of rotoxane molecules and then another layer of wires perpendicular to the first. The result is a crossbar switch consisting of about 1,000 molecules wherever the upper and lower wires cross.

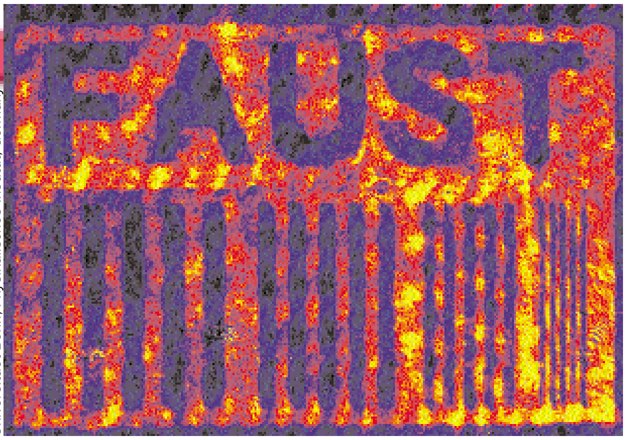
When a potential is applied to two selected wires, the rotoxane molecule switches from a conducting to nonconducting state or back again. The large difference in conductance between the two states, a factor of 10,000, is not fully understood, Chen says. A much smaller potential can then be applied to "read" the switch—to detect whether it is in a conducting or nonconducting state. Because the molecule remains in one state until switched out of it, the memory is nonvolatile and is unaffected by turning the power off.

Because each switch can work as a nonvolatile memory or as part of a logic device, the circuitry for multiplexing and demultiplexing can be built into the same chip as the memory cells. This is crucial in molecular electronics, in which many cells must feed into a few output wires.

"We see the next steps as finding better molecules and combining them more effectively with existing silicon circuits," says Chen. He expects the first commercial uses of molecular electronics to be specialized memory chips, which could reach the market in as little as five years. Such a development would eliminate the existing limits to shrinking today's silicon circuits. Eventually, molecular crossbar switches could be based on a single molecule for each switch, allowing trillions of bits to be packed into a square centimeter. Ω

Optical and scanning electron microscope images, each one-tenth the size of the previous one, show the wafer on which the 1-µm square memories were imprinted (*a*), individual memory chips with their test connections (*b*), a single memory, invisible at the center of the test structure (*c*), nanowires connected to the test pins (the memory is at the intersection of the lines) (*d*), the crossed-wire structure of the memory (*e*), and the entire 64-bit memory with a bit stored at each of the intersections of the eight vertical and eight horizontal wires (*f*).

Hewlett-Packard



Universitaet Bonn, Physikalisches Institut, Germany

High-resolution X-ray image of a tungsten test mask shows the letters FAUST with a linewidth of 120 μm and groups of lines with linewidths (l to r) of 100, 75, 50, and 25 μm.

Better X-ray imaging

X-ray imaging is widely used for nondestructive testing of products, especially those made from metals. Ideally, such imaging should give high spatial resolution to detect small flaws, be sensitive to high-energy X-rays so that thick pieces can be tested, and have high sensitivity. But with existing X-ray methods, these requirements tend to be in conflict. For example, X-ray film absorbs relatively few high-energy X-rays. So for adequate sensitivity, large grains are required, which precludes high spatial resolution. And because of the need for developing, no film can be used in real-time applications. Flat-panel detectors, which avoid time-consuming film development, have a resolution of only 100 μm at best. And although combinations of scintillators and image intensifiers can overcome some of these problems, they are complex and expensive to make.

Now, a team of physicists at the University of Bonn in Germany has demonstrated a new method of X-ray recording that can deliver high resolution with good density even at high X-ray energies (*Appl. Phys. Lett.* **2002**, *81*, 1567). The technique begins with the creation of a simple hologram of a grating on a photorefractive material, which changes its refractive index in response to light or other radiation. The hologram is created in iron-doped lithium–niobate crystals by interfering two beams from a visible-light laser operating at the 532-nm wavelength. When the hologram is exposed to X-rays, parts of the pattern are erased. A laser reference beam is then reflected from the hologram, generating an image in visible light of the X-ray exposure, which is recorded by a charge-coupled-device camera. The process is fully reversible because the pattern can be erased by exposure to white light, and the X-rays do no lasting damage to the lithium–niobate crystal.

In experimental tests, the researchers obtained resolutions of 25 μm, a resolution limited by the diffraction of the optics. In theory, resolution is limited only by the wavelength of the optical light used, in this case 0.5 μm. In addition, the method allows the use of X-rays higher than 100 keV because the lithium–niobate crystal can be made thick enough to absorb high-energy X-rays without loss of resolution.

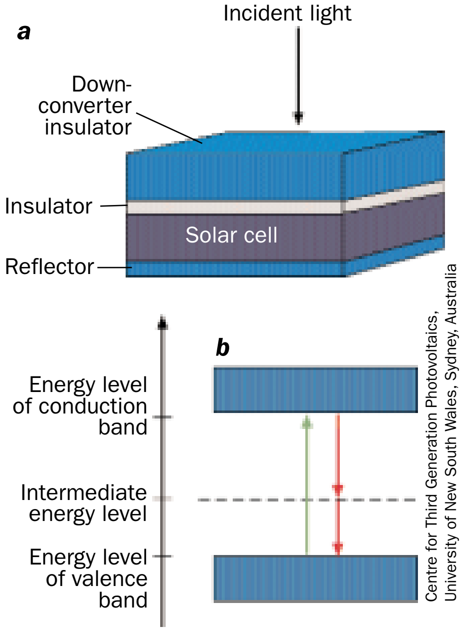
At the moment, the sensitivity of the method is about 0.01 that of X-ray film, but Karsten Buse, one of the researchers, believes that by optimizing the crystal's doping level and oxidation–reduction state, sensitivity can be improved considerably. And the new method will provide real-time digitized images, a major advantage over films for quality-control purposes. Ω

Solar-cell efficiency

The sun's energy comes to us as a wide spectrum of wavelengths, which limits the efficiency of solar cells. A solar cell works by converting a photon of light into an electron–hole pair, which can then generate a potential. But because each pair has a fixed amount of energy, defined by the solar-cell material's energy gap, photons that have higher energies than this gap are partially wasted because some of their energy goes into heat. Photons with energy less than the bandgap do not contribute at all to electricity production. As a result, the maximum theoretical efficiency of solar cells is only around 30%.

One way to increase solar-cell efficiency is to get photons with more than twice the bandgap energy to produce two electron–hole pairs. A collaboration of scientists from the University of New South Wales in Sydney, Australia, and the University of Karlsruhe in Germany has shown, in theory, a way of doing this by first splitting the photons, which converts them to lower energies (*J. Appl. Optics* **2002**, *92*, 1668). With appropriate down-conversion materials, this technique could lift solar energy efficiency to as high as 39.6%, a substantial improvement. Existing solar cells could, in theory, also be improved in efficiency by 20% with this method.

Any three-level system—that is, a system with an energy level between the conduction and valence bands—can be used to reduce the energy of photons. A photon is absorbed by pushing an electron from the valence band to the conduction band. A lower-energy photon is emitted as the electron jumps down to an intermediate energy level created by an impurity doping. A second photon is then emitted when the elec-



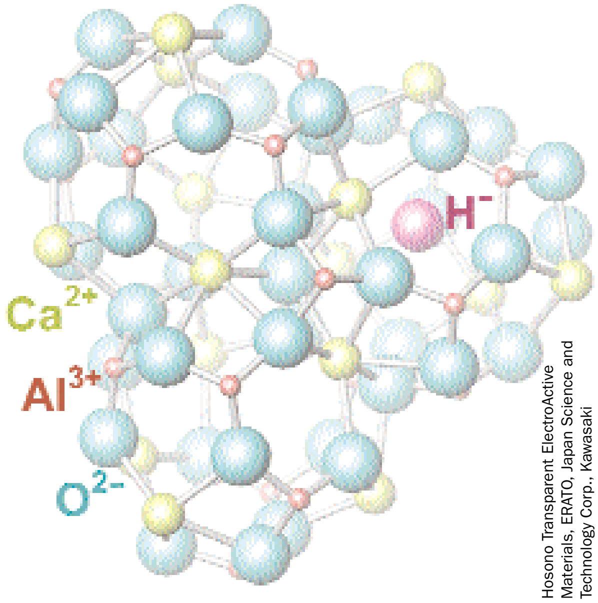
Centre for Third Generation Photovoltaics, University of New South Wales, Sydney, Australia

With a down-converter on a solar cell (*a*), high-energy photons are absorbed by a band-to-band transition (green arrow, *b*). The two-step recombination of the generated electron–hole pair via the intermediate level (red arrows) is accompanied by the emission of two lower-energy photons, which can both be used for the generation of electron–hole pairs.

tron jumps back to the valence band. For an ideal down-converter for solar cells, the bandgap of the converting material should be just twice the bandgap of the solar cell, and the impurity level must be just halfway between the valence and conduction bands.

The best efficiencies, the team found, occur when the down-converter material is placed on the rear surface of the solar cell, in front of a mirror that bounces radiation back into the cell. This minimizes the amount of energy lost by absorption in the down-converter. However, even with a front-surface converter, energy efficiency can be improved by 20%. The advantage of a front-surface converter is that one could coat it onto existing solar cells. The researchers found that using a material with a high refractive index for the down-converter aided efficiency because it enabled more emitted photons to be directed into the solar cell.

"There are a number of compounds that can be used for efficient down-conversion," explains Thorsten Trupke of the University of New South Wales, one of the team members. "Aluminum arsenide and gallium phosphate are two possibilities, as is lithium gadolinium fluoride, when doped with europium. The next step is to carry out experiments to determine what efficiency is actually achieved." Ω



Hosono Transparent ElectroActive Materials, ERATO, Japan Science and Technology Corp., Kawasaki

When H^- ions are incorporated into the subnanometer-sized cages of the transparent insulating oxide $12CaO \cdot 7Al_2O_3$, subsequent irradiation of the material with ultraviolet light results in a conductive state.

Transparent circuits

Transparent circuits are essential in several display technologies, including liquid crystals, plasma screens, and electroluminescence displays. Each of these devices has a light-producing or light-modifying material sandwiched between two transparent electrodes. But the combination of transparency and conductivity is rare, for fundamental reasons. Good conductors exclude electric fields and thus very effectively filter out the electromagnetic fields of light.

Until recently, the only material sufficiently conductive and transparent enough for these devices was indium tin oxide (ITO). But that material is expensive to make, and forming it into circuits along with insulating materials such as glass or quartz requires a complex lithographic process.

Now, a Japanese research team at the Japan Science and Technology Corp. in Kawasaki and the Tokyo Institute of Technology campus in Yokohama has developed a way to convert a transparent insulator into a conductor with flashes of UV radiation, opening up the possibility of less expensive and more flexible transparent circuits (*Nature* **2002**, *419*, 462). The team uses a calcium aluminum oxide called C12A7 ($12CaO \bullet 7A_{12}O_3$), which consists of units that each contain 12 atomic cages just 0.4 nm across. Heating the crystals to 1,300° C for 2 h in a mixture of hydrogen and nitrogen causes negatively charged hydrogen ions (atoms with one additional electron) to enter the cages.

As long as the extra electrons are trapped on the hydrogen ions, the whole substance remains an insulator. But when exposed to UV radiation from a xenon lamp, the extra electrons are excited and jump off the hydrogen ions to the crystal lattice, leaving behind trapped hydrogen molecules. The electrons are then relatively free to move about and the material becomes a conductor. The change is permanent and results in a 3 billionfold increase in conductivity. Potentially, this means that circuits can be written in one step simply by exposing the material to UV light through a mask that protects the areas that are to remain insulating.

However, the conductivity of the converted material is still 1,000 times less than that of ITO. "We are currently making an effort to improve the conductivity," says Katsuro Hayashi of Japan Science and Technology Corp.'s exploratory research group, one of the team's members. "But we have already achieved an easier processing method and higher transmission of light than for ITO."

The material could also be used for that Holy Grail of high-density memories, three-dimensional holographic memories. Theoretically, such three-dimensional memories could be far denser than current memories, which all rely on storing data on surfaces. Interference between two coherent UV sources could produce a pattern of conductivity that could be read out electronically. The team is currently doing experiments on such holographic memories, which, using the present material, would be permanent read-only types. In addition, the team is developing the necessary fabrication processes to turn the new material into a practical alternative route to transparent circuits. Ω