A Crowning Achievement for Removing Toxic Mercury

Glenn Fox (left), John Reynolds, and Ted Baumann have developed Mercaptoplex, a polymer for removing toxic mercury from waste streams.

LIKE its namesake, the messenger of the gods, mercury is notoriously mobile in the environment. Water-soluble and toxic mercury readily leach out of landfills and even wastes solidified with cement. In recent years, environmental scientists and regulators have focused on the development of new processes to remove mercury ions from solutions more efficiently and cheaply than present methods.

The technical challenge is formidable because any method must be impervious to the corrosive nature of the waste streams that contain these ions. In addition, these waste streams can contain a variety of other metal ions (sometimes in much higher concentrations)—some of which also possess the same +2 charge as mercury ions. So an effective removal process must be selective of only mercury ions.

In response to the need for a better method for mercury removal, a team of Lawrence Livermore chemists (Glenn Fox, John Reynolds, and Ted Baumann) has designed an organic polymer called Mercaptoplex that demonstrates an unusually strong affinity for mercury ions in solution. Tests at Livermore show that Mercaptoplex extracts more than 95 percent of mercury ions and does so faster and more selectively than other techniques such as precipitation and activated carbon absorption. Originally developed for use in processing nuclear fuel rods at the Department of Energy's Idaho National Engineering and Environmental Laboratory, the molecule can also remove mercury from both industrial waste streams and public water supplies.

Mercaptoplex has demonstrated a remarkable capacity for removing mercury ions under a broad range of conditions, including those currently found in government and industrial waste streams. In addition, the molecule can be reused indefinitely after the bound mercury is removed, making the process cost-effective. Because of its ability to be recycled, the molecule minimizes the amount of secondary waste generated during extraction, a major challenge in waste treatment.

Three Molecules in One

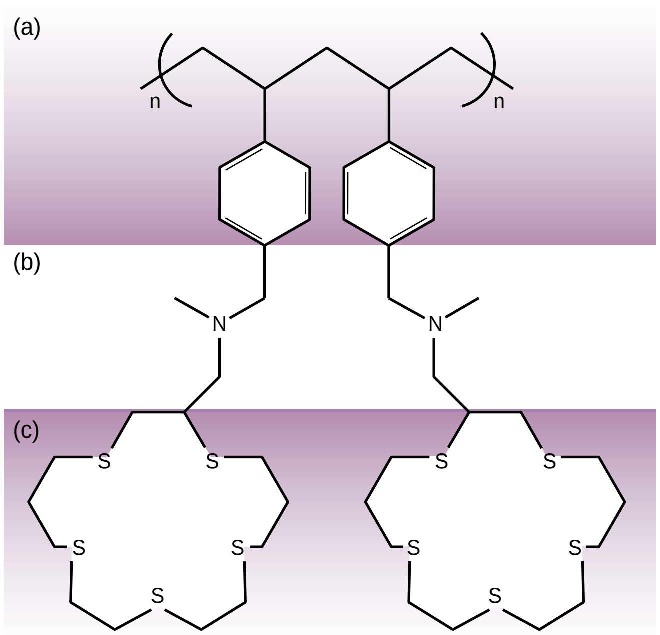
Mercaptoplex is really three molecules combined into one. The business end belongs to a class of organic compounds called crowns, which are molecular rings that contain metal-binding atoms incorporated into their carbon frameworks. The original crowns featured oxygen atoms linked together in a ring by carbon atoms. They earned their name because the molecule looks like a crown when viewed from the side.

The oxygen atoms can be replaced with sulfur atoms to form a crown that exhibits a high affinity for mercury ions, through the donation of electrons to the positively charged mercury ion. (The molecule is still called a crown in chemistry parlance, although the sulfur atoms do not confer a crown appearance.) Together, the five linked sulfur atoms of Mercaptoplex form a strong complex with a single mercury ion.

The sulfur crown is attached to the second Mercaptoplex constituent, a nitrogen-linking unit. The researchers surmise that this unit facilitates interaction between the crown and the acidic aqueous solution. It also links the sulfur-containing crown to the third component, a backbone of cross-linked polystyrene molecules (polystyrene is the chief ingredient of the ubiquitous Styrofoam coffee cup).

Strong Polystyrene Backbone

The Livermore chemists chose a backbone of polystyrene because its chemistry is well understood and its simple cross-links of divinylbenzene transform the molecule into a highly entangled and thereby insoluble repeating unit (or polymer) that does not dissolve in water. The Livermore team postulates that other materials, such as polymers of polyethylene, may also prove effective as backbones.



Two repeating units of the mercury-extraction polymer, Mercaptoplex. The molecule consists of three parts: (a) a backbone of cross-linked polystyrene molecules (n) makes the molecule insoluble in water; (b) a nitrogen-linking unit (N) facilitates interaction between the crown and acidic solutions; and (c) a "crown" of five linked sulfur atoms (S) binds to a single mercury ion in solution.

In solution, because of the entangled nature of the Mercaptoplex polymer, it is probable that neighboring crowns combine to trap mercury ions. For example, two sulfur atoms from one crown may combine with three sulfur atoms from a nearby crown to bind to a mercury ion. Studies using spectroscopic techniques are under way at Lawrence Livermore to gain a better understanding of the bonding mechanism.

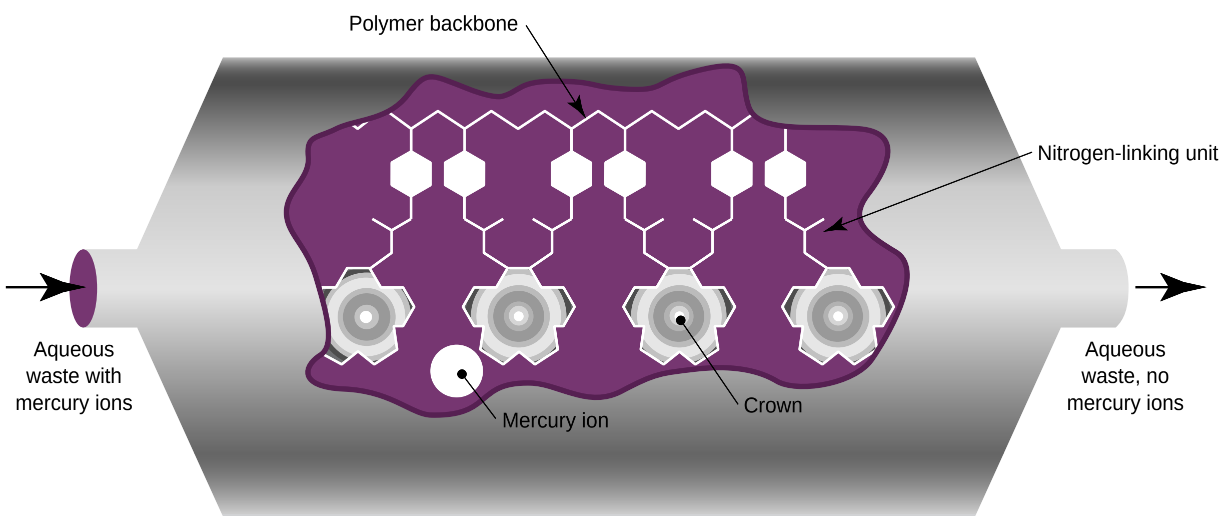
The Livermore chemists have shown that Mercaptoplex is effective at pH ranging from 1.5 (extremely acidic) to 7.0 (neutral). In contrast, precipitation, a common technique of mercury removal, requires constant pH adjustment. If the pH gets too low (too acidic), the precipitation process produces hydrogen sulfide, a highly toxic gas, and does not remove the mercury. The other popular mercury removal process, activated carbon, also requires continuous adjustment of pH.

Mercaptoplex is also faster and more selective in removing mercury than other techniques. When mixed with solutions containing mercury ions, it captures virtually all of the mercury within 30 minutes. This extraction rate is much faster than that seen in other systems, which can take up to 20 hours to do their job. Baumann says the ultimate goal is to use Mercaptoplex as packing for large columns to speed up the waste treatment process. In this design (shown on p. 19), the waste stream would simply flow through the Mercaptoplex without the need for mixing.

Fox notes that because typical mixed waste streams (those combining both toxic and radioactive materials) contain a variety of other metal ions, such as aluminum, iron, cadmium, and lead, removal of mercury requires a highly selective process. The chemists have tested Mercaptoplex in solutions of mercury ions ranging from 4 to 200 parts per million and when concentrations of other ions outnumber mercury by 100 to 1. In every case, Mercaptoplex has selectively removed mercury with an efficiency of 95 percent or greater. (Baumann says mercury removal is probably greater than 99 percent, but the amount of mercury left in solution after treatment is too small for the chemists to measure accurately.)

Recycling Is a Big Advantage

Because Mercaptoplex is insoluble in water, it can be easily separated from solution by filtration once the extraction



Schematic of column treatment of mercury waste using Mercaptoplex.

is complete. The mercury can then be recovered, and the Mercaptoplex regenerated by a variety of treatments. One method developed by the Livermore team is to use chloroform solutions of diphenylthiocarbazone to strip the bound mercury from the polymer. Under these regeneration conditions, the diphenylthiocarbazone has an even greater affinity for mercury ions than does the sulfur crown. Once rinsed and dried, Mercaptoplex has been used to effectively treat additional volumes of mercury. The team is investigating other methods of stripping the mercury ions from the polymer such as electrochemically reducing the ions to the safer metallic mercury.

In comparison to Mercaptoplex, other techniques typically require additional treatment steps and generate large amounts of secondary waste. Precipitation generates mercury sludges that require further treatment. Activated carbon columns loaded with mercury are rarely regenerated, and the spent columns require additional processing.

At the Idaho National Engineering and Environmental Laboratory, where mercaptoplex was first used, mercury is used as a catalyst to treat spent fuel rods from U.S. Navy submarines. The Livermore process is also applicable at other DOE sites that need selective and cost-effective treatments for mixed waste.

The process should prove useful in treating industrial waste streams and water supplies that contain mercury. For example, the Livermore team has discussed the process with representatives from the bleach manufacturing and oil industries, who must meet strict federal regulations concerning mercury levels in their waste streams.

By simple substitution of the sulfur atoms, the molecule can be tailored to target other metal ions, such as cadmium, silver, and lead, commonly found in mixed waste streams and water supplies. “There is a lot of synthetic chemistry you can do with crowns,” says Fox, “such as modifying the number of noncarbon atoms in the ring to better bond to the ion in the solution of interest. In this way, chemists can target a particular metal pollutant through careful molecular design.”

—Arnie Heller

Key Words: activated carbon, crown polymers, Idaho National Engineering and Environmental Laboratory, Mercaptoplex, mercury, precipitation.

For more information contact Glenn Fox (925) 422-0455 (fox7@llnl.gov).

Flat-Panel Displays Slim Down with Plastic

Plastic substrates for flat-panel displays are flexible, transparent, and lightweight.

FOR years, manufacturers of electronics with flat-panel displays have dreamed of using plastic as a cheaper, more compact, more rugged, and far more lightweight alternative to glass. The Department of Defense is particularly interested in ultrathin yet flexible screens as standard equipment for the Pentagon's "information warrior" of the next century. With plastic displays, soldiers could hang satellite navigation system displays on their belts or keep electronic maps rolled up in a back pocket.

The most advanced type of flat-panel displays, used in most portable computers, is active-matrix liquid-crystal displays. In this display, each of the million or so tiny screen pixels is controlled by thin-film transistors (TFTs) that act as tiny on/off electrical switches. By turning on and off dozens of times a second, the TFTs permit continuously changing images of words, pictures, and video.

Currently, TFTs for active-matrix displays are manufactured onto a rigid glass substrate in a process that involves baking glass sheets at temperatures of up to 600°C. This conventional process is far hotter than any plastic can withstand without deforming and melting. But now a team of Lawrence Livermore researchers is showing how TFTs can be manufactured on top of thin, flexible plastic sheets instead of glass by keeping manufacturing temperatures at or below 100°C.

The work was carried out by a group of electrical engineers, physicists, and materials scientists in the Device and Process Group in the Information Science and Technology Program of the Laser Programs Directorate. The research is part of a larger effort by Livermore scientists and their Department of Energy colleagues to apply laser-based processing techniques to current U.S. semiconductor production problems. The plastic substrate project, now in its third year, is funded by the Defense Advanced Research Projects Agency's High-Definition Systems Program, which sponsors development of new display concepts that address the issues of lighter weight, improved ruggedness, lower power, higher resolution, and easier use.

Laser Pulses Fast, Precise

The novel Livermore transistor fabrication process combines well-established, low-temperature deposition techniques with excimer lasers that produce pulsed beams of ultraviolet light. These lasers are a much more powerful version of the instruments that are used in eyesight correction surgery to literally vaporize corneal tissue without damaging surrounding tissue. In fact, the lasers are so precise they can make precise notches in human hair that can be exactly and repeatedly duplicated. The Livermore team takes advantage of the laser's extreme precision and ultrafast operation to melt, crystallize, and dope (add impurities to) the silicon layers forming the TFTs at substrate temperatures lower than the melting temperature of plastic.

The Livermore team chose one of the most common plastics for the substrate: polyethyleneterephthalate (PET), more commonly known as polyester. Thin (175 micrometers), cheap, flexible, transparent, and rugged, PET is used for many other purposes, including the Mylar for viewgraphs. Standard 10-centimeter-diameter wafers are cut from 61-centimeter-wide rolls of PET. Onto these plastic circles are applied the materials fundamental to integrated circuits: an insulator (silicon dioxide), semiconductor (crystallized silicon or polysilicon), dopants of selected elements, and metal connectors.

The process begins with a thin layer of silicon dioxide deposited on the plastic wafer through a conventional process called plasma-enhanced chemical-vapor deposition that produces uniform films of molecules. Next, the team uses sputter deposition to apply an amorphous layer of silicon atoms to the substrate. Both of these layers are applied at a relatively cool temperature of about 100°C to keep the plastic intact.

The excimer laser irradiates the amorphous silicon layer from 3 to 10 times at an ultraviolet (UV) wavelength of 308 nanometers. Each pulse lasts only 35 nanoseconds (billionths of a second) while melting the amorphous silicon. The result (shown on p. 22) is a highly ordered, polycrystalline layer of silicon atoms some 40 nanometers thick. (This transformed silicon, typically called polysilicon, permits electrons to move more easily through its highly ordered lattices.)

Plastic Doesn't Melt

During the melting process, the fleeting UV laser energy is absorbed mainly in the top 10 nanometers of the amorphous silicon layer before it diffuses downward into the plastic. That localization of the laser energy, together with the silicon dioxide layer that acts as a thermal barrier, keeps the plastic substrate from heating and melting.

Although the silicon layer melts at 1,400°C, the plastic barely notices the heat from the deposited laser energy. The team's understanding of the physics and chemistry of the laser processing steps is aided by advanced simulation work done at Livermore.

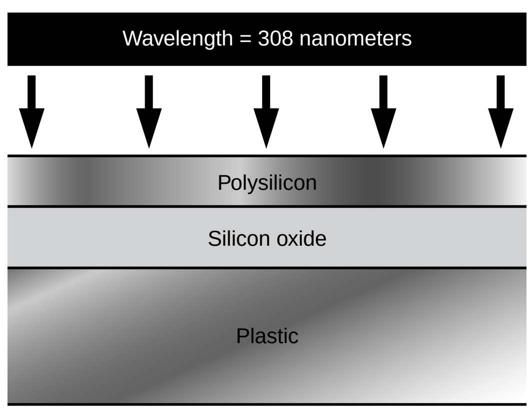
The laser beam is adjusted to cover from 1 to 11 square millimeters at the wafer surface. Covering the entire wafer takes about one minute. In contrast, traditional processes require baking glass sheets in high-temperature furnaces for many hours.

The next steps are modified, lower-temperature versions of traditional semiconductor processing involving photolithography, which uses a sequence of photomasks. These masks act as photographic negatives do, allowing light to imprint a pattern on the wafer. The pattern defines the areas to be removed through etching, doped with impurities, and deposited with aluminum connectors.

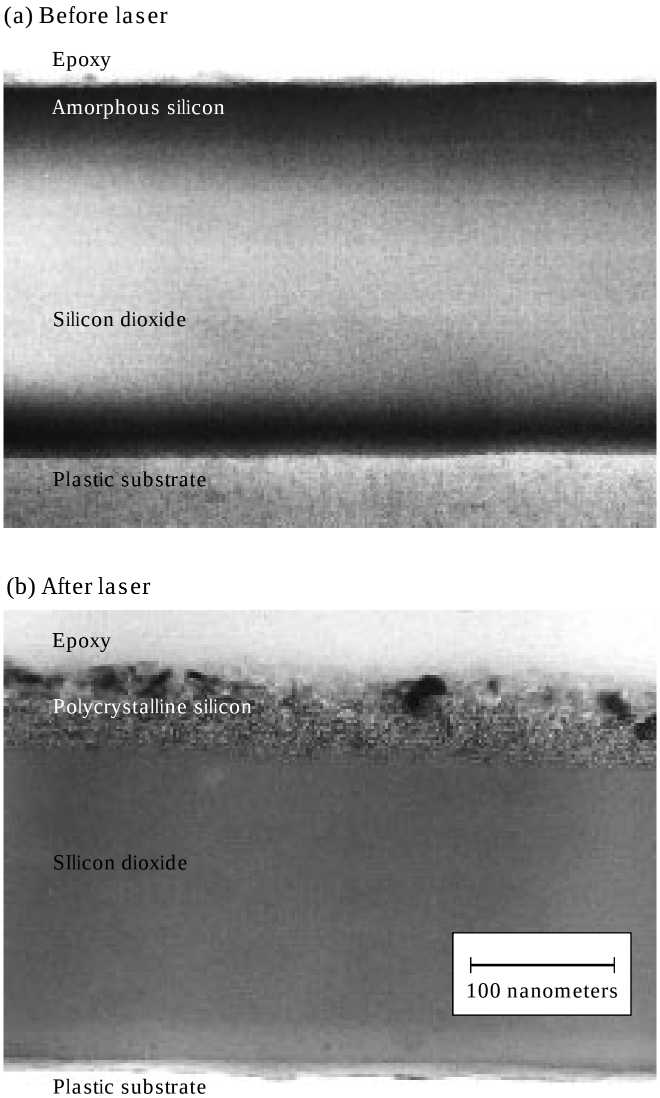
The doping with boron and other elements is accomplished using another pulsed excimer laser in a technique also developed at Livermore. First, a thin layer of doping atoms is deposited using plasma-enhanced chemical-vapor deposition. Then repeated laser pulses drive the atoms deep into the polysilicon. (Doping allows the polysilicon, which is essentially an insulator, to conduct electricity by giving up or attracting electrons.)

Switches Ready for Connection

The result is a 10-centimeter-diameter array of several hundred simple switches ready to be joined to its neighbors and to a liquid-crystal-display system. The Livermore team is continuing to refine the low-temperature manufacturing process. In particular, it is working to achieve TFTs that permit electrical current with higher "mobility," or speed. The bigger the display, the higher the desired mobility.



An excimer laser irradiates a layer of amorphous silicon atoms at a wavelength of 308 nanometers for about 35 nanoseconds. The process is repeated up to 10 times.



Electron micrographs show how the excimer laser pulses transform the amorphous silicon layer into a 40-nanometer-thick layer of polycrystalline silicon.

The research has progressed sufficiently that discussions are taking place with U.S. flat-panel-display manufacturers to license the technology. It is anticipated that an industry–Livermore project to develop a complete prototype would combine Livermore's plastic "backplane" of TFT-driven picture elements, or pixels, with liquid crystals or organic light-emitting materials furnished by a display manufacturer.

Display manufacturers are particularly interested in the potential to manufacture large displays inexpensively, particularly with a roll-to-roll continuous manufacturing technique much like the roll-to-roll printing process. In this scenario, the plastic would roll through processing stations similar to those of a printing press, and finished displays would be cut to size.

The Livermore breakthrough may well make possible within a few years a new generation of ultralight, flexible, and inexpensive displays. Applications could include notebook and desktop computer displays, instrument panels, video game machines, videophones, mobile phones, hand-held PCs, camcorders, satellite navigation systems, smart cards, toys, and a new generation of electronic devices for which flat-panel displays have been too heavy or too costly. Indeed, it looks as if plastic flat-panel displays will be used by everyone, from couch potatoes to information warriors.

—Arnie Heller

Key Words: active-matrix liquid-crystal display, amorphous silicon, Defense Advanced Research Projects Agency, enhanced chemical-vapor deposition, excimer laser, flat-panel display, liquid-crystal display, polysilicon, sputtering, thin-film transistor (TFT).

For further information contact Tom Sigmon (925) 422-6753 (sigmon1@llnl.gov).