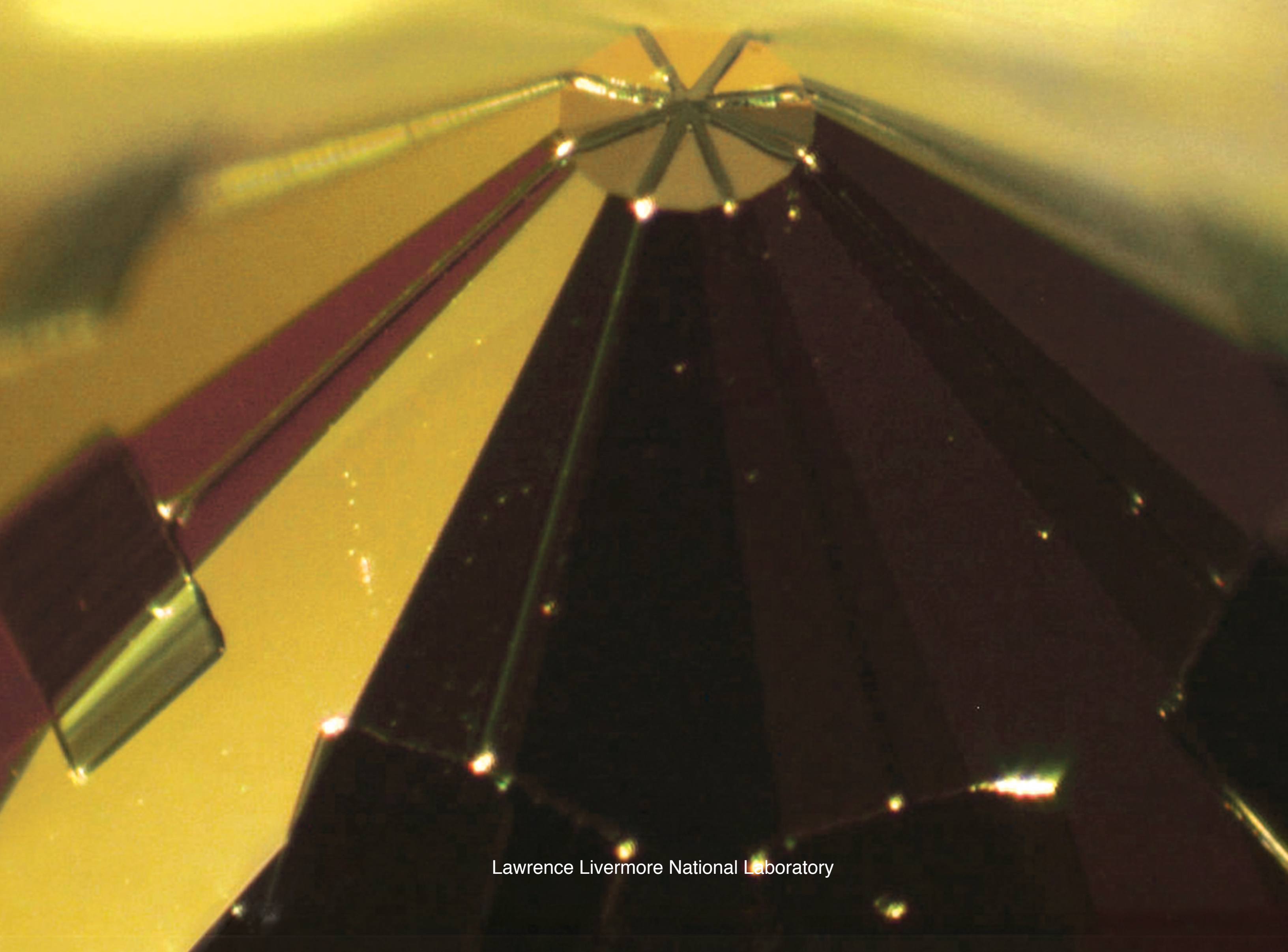
Three Dimensional on the Nanoscale

New micro- and nanolithographic techniques are expanding Livermore's current expertise in three-dimensional lithography.



Making smaller and smaller micro- and nanodevices requires a tool for precisely adding and removing material. Standard lithographic "writing" processes, combined with chemical deposition and etching, can do the job for very small objects, if they are flat. However, the world isn't flat, and neither are most of the things in it.

In the 1980s, Livermore needed a tool to write electronic circuitry on tiny, three-dimensional (3D) devices. Laboratory engineers applied laser technology to create a 3D lithographic system, which they dubbed laser pantography (LP).

Livermore engineers still use LP for 3D patterning and are now adding other sophisticated 3D lithographic techniques. Together, these techniques will be useful for fabricating experimental targets at the National Ignition Facility (NIF). (See *S&TR*, July/August 2007, pp. 12–19.) NIF targets are small spheres, the size of a poppy seed, or about a millimeter in diameter. Design specifications for targets are extremely stringent, in part because of the high temperatures, pressures, and energy densities the targets will face inside the NIF target chamber. Entirely new materials and fabrication techniques, including 3D micro- and nanolithography, are needed to meet these specifications.

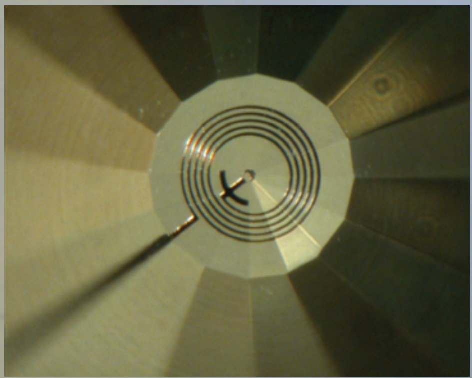
"NIF is the driver of our current focus on 3D micro- and nanolithography," says Anantha Krishnan, director of the Laboratory's Center for Micro- and Nanotechnology. "We are building on Livermore's history of expertise in 3D lithography."

The impetus for LP was the Strategic Defense Initiative of the 1980s. Today, it is finding very different uses. For example, LP is used to pattern coils in portable nuclear magnetic resonance spectrometers for detecting weapons of mass destruction and in catheters for treating stroke and heart attack patients. In addition, LP is used to pattern tungsten microprobes on the walls of diamond anvil cells, which compress a material to extremely high pressures. (See *S&TR*, December 2004, pp. 4–11.) Equation-of-state experiments with diamond anvil cells tell researchers how materials behave under extreme conditions. To create the probes, researchers use LP to pattern wires from the tip of the diamond down the steep walls, a process that is impossible to mimic with standard 2D lithography.

Grayscale lithography and projection microstereolithography (PμSL) are being added to the Laboratory's 3D micro- and nanolithography repertoire. Both methods were developed elsewhere and are being customized at Livermore to meet the needs of NIF. The Laboratory is also enhancing the performance and resolution of the PμSL technique.

A Look Back

LP was developed to support a number of creative research programs at the Laboratory. Under the Strategic Defense Initiative, Livermore researchers delivered many new materials and technologies—such as lighter-than-air aerogels—for Brilliant Pebbles and other facets of the missile shield program. They applied LP technology to fabricate metal interconnects on multiple electronic chips. These devices were designed for use as sensors and other control systems aboard the tiny Brilliant



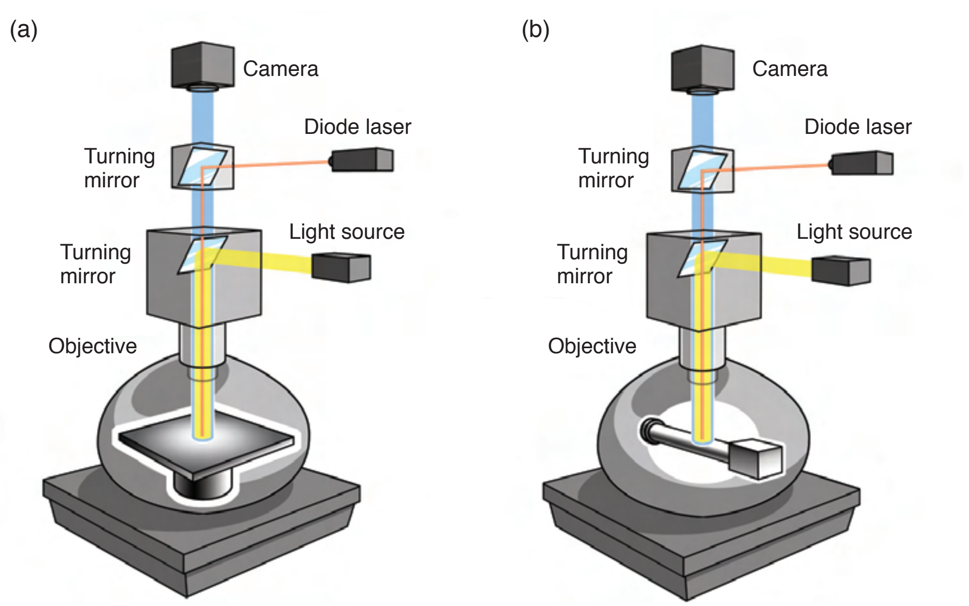
A designer diamond anvil is made by lithographically fabricating tungsten microcircuits on the diamond's flattened tip.

Pebble satellites, whose goal was to home in on an incoming missile and intercept it. At that time and until well into the 1980s, LP was the only 3D lithographic system available and one of just a few laser writing systems.

Several major corporations were interested in putting LP to work. "IBM wanted to use LP's 3D capabilities for writing circuitry on the side of stacked, multichip modules to reduce problems with inductance," says Vince Malba, program leader for 3D lithography at Livermore. Texas Instruments, Hewlett-Packard, Micron Technology, and Honeywell also partnered with the Laboratory to develop advanced 3D interconnect capabilities using LP. Micron Technology expressed considerable interest in commercializing the technology for dynamic random access memory (DRAM). "However, semiconductor companies like Micron could increase DRAM densities faster and less expensively than we expected to do with LP, which was a new tool," says Malba.

In the 1990s, LP was used in two major weapons-related programs: the W87 Life-Extension Project and enhanced surveillance for the Department of Energy's Stockpile Stewardship Program. The W87 Life-Extension Project involved refurbishing the W87 warhead, the warhead design with the most modern safety features in the stockpile. The goal was to extend the lifetime of the weapon to beyond 2025. The Laboratory developed and certified the engineering design of the W87 modification through a combination of nonnuclear experiments, flight tests, physics and engineering analyses, and computer simulations. A number of miniaturized electronic devices used for telemetry and flight tests were fabricated with LP.

After nuclear weapons testing ended in 1992, nonnuclear experiments, testing of weapon components, and computer simulations became the primary tools for ensuring that the nation's nuclear stockpile remains safe, secure, and reliable. Surveillance of the nuclear stockpile was enhanced. During the middle to late 1990s, LP was used to fabricate microscale actuators and sensors for monitoring the health of nuclear weapons in the stockpile.



The laser pantography system can be configured either as (a) a mill for patterning flat surfaces or (b) a lathe for patterning cylindrical surfaces. The light source allows for the camera image to be seen on a computer screen.

A Hot New LP

Over the years, Livermore engineers have improved LP with new exposure tools, chemical processes, and control systems. The LP system today has a motion control system whose accuracy is better than 1 micrometer. The system can function either as a lathe or as a five-axis mill. A 405-nanometer diode laser acts as the "cutting" tool, which exposes the photoresist coating. The mill configuration patterns noncylindrical substrates.

The lathe setup—known as the LaserLathe™—is used to pattern cylindrical objects. Any design can be patterned on a compound curvature surface with the LaserLathe's programmable multiaxial controller.

When a coil or wire must be fabricated on a tube, the tube is first exposed to an oxygen plasma to roughen the surface and remove impurities prior to sputter deposition. A coating about 50 nanometers thick of titanium is laid down, followed by a copper layer of about 200 nanometers. This "seed" layer creates a conductive surface on which a positive electrodeposited photoresist can be electroplated. The photoresist is exposed with the computer-controlled laser and then chemically developed to form the desired patterned mask. Copper is electrolytically deposited through the photoresist mask, after which the mask is chemically removed. The sputtered copper is removed from the field with a proprietary solution that etches sputtered copper faster than plated copper. Finally, the titanium is chemically removed, leaving a microcoil firmly adhered to the tube.

The challenge lies in getting the photoresist onto a 3D surface. In the manufacture of computer chips, depositing photoresist is usually accomplished by spinning the chips. To coat more complicated parts that are not flat, Livermore uses the self-limiting electrophoretic process. "Electrodeposition of photoresist makes 3D lithography possible," notes Malba.

The photoresist is a colloidal suspension of polymer, surfactant, sensitizer, and plasticizer. During the electroplating process, anionic micelles—the surfactant molecules dispersed in the colloid—move toward an anode in the presence of an electric field. The micelles "fall apart" on the conductive substrate, coating it. Because the coating is a dielectric material, its thickness is uniform, which inhibits further deposition as its thickness increases. The thickness of the photoresist, from 5 to 30 micrometers, is controlled by the plasticizer content and temperature setting. The sensitizer diazonaphthoquinone changes the polymer solubility as a function of absorbed light. Adding the sensitizer lowers the polymer's solubility, while photolysis increases it. At 35°C, 1 percent sodium carbonate (an electrolyte) develops an image in 2 to 3 minutes.

Guiding Catheters

In a collaborative effort with researchers from the University of California (UC) at San Francisco, Livermore engineers are using LP for patterning magnetized microcatheters. (See the figure at right.) Computerized interventional magnetic resonance, developed in 2001, helps surgeons remotely guide a catheter to collapsed veins and arteries.

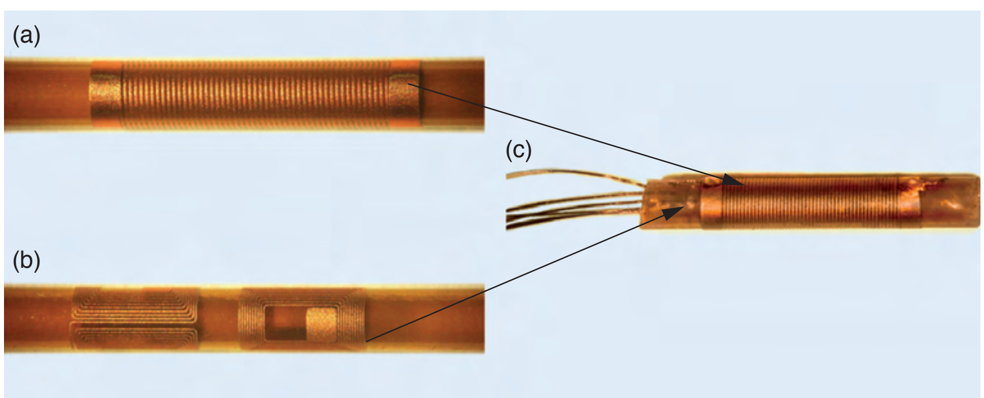
Coils patterned on the tips of catheters create magnetic moments when energized by direct current pulses. In the presence of an external magnetic field, these magnetic moments cause the catheter to bend. Having one helical coil and two saddle coils perpendicular to one another allows the catheter tip to be bent in any direction. The surgeon can thus remotely manipulate the catheter through complex anatomy to reach a particular blood vessel branch.

"Early attempts at manufacturing catheter tips required hand-winding fine copper wire into coils," says Malba. A helical solenoid can readily be made using this method, but hand-winding a saddle coil is quite difficult. Hand-wound saddle coils are one-of-a-kind products because of the difficulty in reproducing the number of turns, the pitch of the wire, and the coil's orientation with respect to other coils. In addition, even very fine wire adds appreciably to the diameter of the catheter tip.

Fabricating saddle coils directly on polyimide tubing with microlithography makes the coils more precise and reproducible, with much smaller line widths than can be attained with hand-winding. Additionally, coils can be precisely oriented with respect to each other, guaranteeing their perpendicular orientation. Livermore's work with UC San Francisco has involved simulations of heating and coil design as well as development of fabrication tools and manufacture of both helical and saddle coils.

Recent experiments showed that the current required to deflect the catheter tip has the potential to cause damaging heating effects to the patient. Raising the temperature of the blood even a few degrees could result in blood coagulation or vessel-wall damage. The team is experimenting with manufacturing procedures and materials that should eliminate these possible heating effects. The simplest change is to increase the thickness of the electroplated copper, thereby decreasing the coil's resistance and, consequently, the heat generated per ampere. Says Malba, "Making this change will require significant modifications to the microcoil manufacturing process. But ultimately it will result in a factor of two reduction in the heat generated."

A complementary approach is to remove the heat as it is generated with a constant saline flow through the catheter. However, the polyimide tubes used as the substrate for the microcoils are poor thermal conductors and would not provide an adequate thermal path to the flowing saline. The team has experimented with ceramic tubes, which have better thermal conductivity. Thus far, results show a substantial reduction in temperature elevation. "Combining thicker copper windings with flowing saline should eliminate the possibility of heat damage," says Malba.

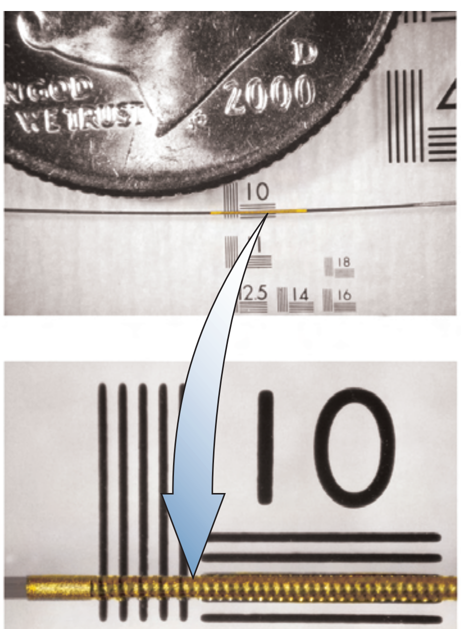


For the magnetic resonance imaging microcatheter, laser pantography was used to fabricate (a) a helical coil and (b) two perpendicular side-by-side saddle coils. (c) The saddle coil tube is placed inside the helical coil tube to produce a magnetized catheter tip that will bend in any direction when in the presence of an external magnetic field.

Identifying Chemical Signatures

The team also has been contributing for several years to work on sensors for portable nuclear magnetic resonance (NMR) used in onsite identification of signatures from nuclear, chemical, and biological weapon agents, narcotics, explosives, toxins, and poisons. NMR is a powerful technique for revealing the identity of chemical molecules. However, to date, NMR is significantly less sensitive than mass spectrometry or other spectroscopic techniques. In addition, when sample sizes are very small, which would be the case with trace quantities from a warfare agent, NMR's lack of sensitivity makes it even less useful.

One solution to increasing sensitivity is creating a much more powerful small helical radio-frequency (RF) coil, which is at the heart of any magnetic resonance system. Many techniques have been tried since the mid-1990s to reduce the coil size. Hand-winding works well, but the process is slow, tedious, and not reproducible. Other more easily reproducible fabrication methods resulted in coils that were less sensitive than their hand-wound cousins.



The latest microcoils for a portable nuclear magnetic resonance chemical sensor measure just 100 micrometers in diameter.

Using the LaserLathe, Malba's team has had great success in fabricating RF coils with adjustable widths and line spacings. The team's first RF microcoils were fabricated on tubes ranging from 1.3 millimeters down to 850 micrometers. The latest, third-generation microcoils are just 100 micrometers in diameter. Line widths are 20 micrometers with 100 turns in the coils.

A challenge with small magnets, however, especially low-cost ones, is that they tend to generate inhomogeneous magnetic fields, which conceal much of the useful spectral information. Because the goal of this work is a portable, readily available NMR detector, cost is a critical factor. Livermore engineers and chemists teamed up with researchers from Lawrence Berkeley National Laboratory and UC Berkeley to produce such a probe. They explored various designs to improve the magnetic field, including combining an RF coil with a shim coil. Shim coils reduce the overall probe size and improve durability.

The optimal design proved to be a helical coil connected to a coaxial cable placed within a ceramic tube. The tube is patterned with shim coils connected to twisted pair cables. The shim coils are visible in the completed probe assembly, shown in the figure at the top of p. 17. The team's tabletop system uses a commercial, single-resonance RF spectrometer, the first such portable spectrometer available. The system runs on a laptop computer with software for instrument control and data processing. The device is being tested at both the Laboratory and UC Berkeley. "We have improved the sensitivity of the latest probe design to less than 10 parts per million," says Malba. "We expect the latest improvements to result in 1-part-per-million detection, the desired benchmark."

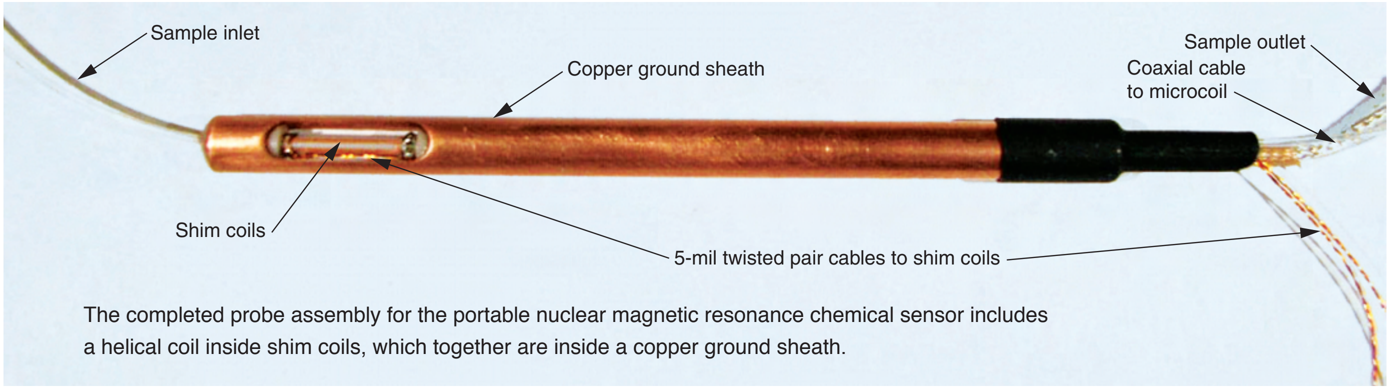
New Kids on the Block

Joining the well-established LP at Livermore are grayscale lithography and, more recently, PμSL. Engineer Chris Spadaccini is leading both development projects.

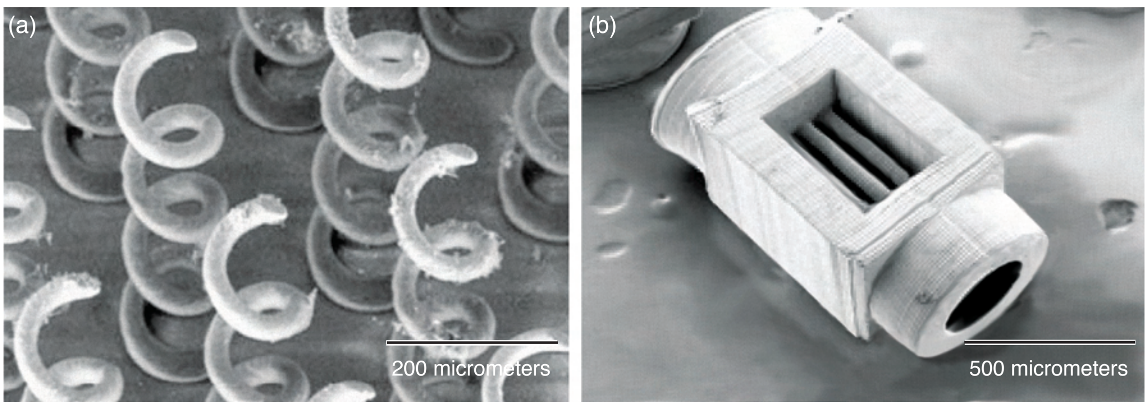
Grayscale lithography is a modification of conventional 2D photolithography. (See *S&TR*, October 2006, pp. 18–26.) That process, which involves exposing a coated, masked silicon wafer to ultraviolet light, is typically all or nothing, so all features have a uniform height. In grayscale lithography, the light's intensity can be adjusted to produce 3D photoresist profiles with varying shapes. After chemical etching, the profiles can be transferred to a substrate. Spadaccini anticipates using these 3D structures not only for NIF targets but also to create microoptical devices.

In addition, Spadaccini expects to start work soon on PμSL research that is directed primarily toward target fabrication for ignition and high-energy-density experiments on NIF. Spadaccini will be working with Malba, engineers Robin Miles and Todd Weisgraber of Livermore, and Nicholas Fang of the University of Illinois at Urbana–Champaign and its Center for Nanoscale Chemical-Electrical-Mechanical Manufacturing Systems.

PμSL has already produced objects such as microscale coils and a bioreactor. Thus far, the technique has a resolution limit of about 400 nanometers. Spadaccini's goal is to reduce this limit to less than 50 nanometers. His team aims to fully understand the physics and chemistry of the PμSL process and the physical and chemical properties that limit its resolution. The team will also explore PμSL's use for a range of materials, including



The completed probe assembly for the portable nuclear magnetic resonance chemical sensor includes a helical coil inside shim coils, which together are inside a copper ground sheath.



Projection microstereolithography can produce objects such as (a) microscale coils and (b) a bioreactor. (Scanning electron micrographs courtesy of Nicholas Fang, University of Illinois at Urbana–Champaign.)

graded-density foams and highly porous metallic foams that are being considered for NIF targets. In addition, PμSL will be augmented with “superlenses” and digital holographic nanolithography, new processes designed to improve resolution as well as the speed with which objects can be fabricated.

Within the next few years, NIF experiments will require hundreds of targets. Researchers throughout the Laboratory are working to replace the current labor-intensive target fabrication process with a high-throughput production process to meet NIF’s needs. PμSL and Livermore’s other 3D fabrication tools will play an important role in making this happen.

—Katie Walter

Key Words: grayscale lithography, LaserLathe™, laser pantography (LP), magnetic resonance imaging, National Ignition Facility (NIF), nuclear magnetic resonance (NMR), projection microstereolithography (PμSL).

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