A common adage goes, “thin is beautiful.” To a growing number of researchers—and intrigued companies—the saying is especially true for a unique class of materials called multilayers. Composed of alternating layers of two different materials as thin as a few atoms, multilayers offer extraordinary strength, hardness, heat resistance, and unexpected new properties. At Lawrence Livermore National Laboratory, researchers are pioneering entirely new applications for these materials, which many now believe to constitute an essentially new state of matter.

Multilayers’ alternating layers can vary in number from a few to more than 200,000. Individual layer thicknesses range from a few atoms to a few thousand atoms, corresponding to a maximum structure thickness of about 10 millionths of an inch. The repeat distances in the multilayers, that is, the thickness of two adjacent layers, can be purposely selected to be identical to the interaction lengths characteristic of important physical properties (e.g., magnetic interaction lengths) to yield new properties. In this context, says Laboratory material scientist Troy Barbee, Jr., one of the pioneers of modern multilayer technology, “it is generally accepted that one should expect the unexpected when multilayers are fabricated and experimentally characterized.”

Multilayers are part of a larger, established scientific field of so-called designer or “nanostructured” (from nanometer, a billionth of a meter) materials...
multilayers cannot be used in x-ray imaging devices because x rays are substantially absorbed by the materials. As a result, their high nonmagnetic nature, and more environmentally friendly materials, copper–zirconium multilayers could be used to replace beryllium–copper alloys commonly used in springs and tools.

**Seeing the Sun in New Ways**

One of the most important applications of multilayers is astronomical imaging. High-performance multilayers have been used as mirrors to focus light in the x-ray, soft x-ray, and EUV regions. Images taken by telescopes using multilayer mirrors reveal important features that cannot be captured by standard imaging instruments operating at longer wavelengths. Furthermore, because multilayer mirror surfaces are reflective only within a certain wavelength range, they can be used to isolate a particular region of the spectrum of interest to astronomers (Figure 3).

Barbee and his staff at Stanford designed a set of magnetron sputter deposition systems to produce multilayers based on copper layered with the transition metal niobium, tantalum, molybdenum, and tungsten. From analyzing these early multilayers, they found that the structures might be of x-ray optical quality.

An effort was begun to explore this opportunity with the material pair tungsten and carbon. These elements were selected because only a minimum number of layers were required to achieve significant reflectivity, minimizing the demands on the stability of the mating sputtering process. These materials proved to be very effective and have been a staple of the international community. Multilayer x-ray optics field ever since. In addition, the development effort was aided by the appearance of new tools, namely the scanning transmission electron microscope (STEM) for characterizing multilayer structures and synchrotron x rays for characterizing mirror performance.

When Barbee came to Livermore in 1985, he set out to advance the sputtering process, develop more advanced materials, and find new commercial uses for the technology. One of the most important commercial applications of multilayers is in the coatings industry. Multilayers are commonly used in springs and tools. With their high strength and nonmagnetic nature, and more environmentally friendly materials, multilayers are used to replace beryllium–copper alloys commonly used in springs and tools.

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Multilayers

Extensive Effort Under Way

The Laboratory-wide multilayer development effort consists of more than 15 senior researchers and 25 technicians at work in five laboratories. The results of their work can be seen across Lawrence Livermore’s directorates—Chemistry and Materials Science, Engineering, Defense and Nuclear Technologies—and especially in the Laboratory’s Laser Programs. Barbee’s team produced more than 250 multilayer optics last year for laser applications, particularly for laser-fusion research.

“Using multilayer technology, we’ve been imaging high-energy-density plasma of the Sun and then turning around and imaging the same kinds of phenomena in laser fusion,” Barbee explains.

Multilayer optics make possible x-ray interferometry for characterizing plasmas created by high-power lasers.

Capacitors around a Corner

One research avenue of significant potential is using multilayers as ultra-compact, high-energy storage, and extremely cost-effective capacitors made up of reactive materials such as aluminum and nickel that would act as a highly portable welding tool. A piece of the multilayer could be slipped into a break or crack of metal, for example, and the foil would be lit with a match. The multilayer would quickly reach a temperature of up to 2,000°C to repair the crack. The multilayer materials would be chosen to produce different temperatures and rates of heat release to correspond to the material being welded.

Replacing Loud Compressor

Further away from commercial realization than multilayer capacitors or welding materials, yet with as many potential applications, are multilayer thermo-electrics. The thermo-electric effect uses heat transported by electrons to produce cooling with electrical current. Conversely, thermo-electric materials can also take advantage of diffusion of electrons in a thermal gradient to produce a current. Thermo-electric materials have no moving parts, so they can be miniaturized and may be very reliable. Current applications include temperature-sensing thermocouples, electric power generators for spacecraft, and portable food and beverage coolers.

The application of thermo-electric devices for cooling or heating large equipment is primarily limited by their efficiency, which is lower than that of conventional gas cycle refrigeration. However, the development of multilayers has sparked interest that multilayer thermo-electric materials may be the key to taking these devices into the commercial mainstream.
“Multilayers may have the potential to increase the efficiency of thermo-electric materials by a factor of three or four,” says Livermore material scientist Andrew Wagner. He notes that an efficient multilayer thermo-electric cooling system could replace the conventional large, heavy, and noisy refrigerator compressor that often cycles on and off. A multilayer thermo-electric device would be silent, operate continually, and not require environmentally unacceptable hydrofluorocarbon gases.

Wagner, together with researcher Joseph Farmer and technicians Ronald Foreman and Leslie Summers, has conducted basic research on the feasibility of producing multilayer thermo-electric materials, which, in that application, would require millions of alternating layers of conducting and insulating materials.

Another area of active development is using multilayers as optics for imaging sources of neutrons. This application has important implications for medical imaging. For example, the National Institutes of Health and Argonne National Laboratory are using multilayers to improve the sensitivity of neutron-imaging systems.

The neutron work is another application for multilayers. But multilayers have that way about them: they force new thoughts about making materials—this time on the atomic scale—and finding applications that will benefit society.

—Arnie Heller

**Key Words:** multilayers, nanostructured materials, sputtering, thermo-electrics, x-ray optics, x-ray lasers.

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**About the Scientist**

TROY W. BARBEE, JR., is a materials scientist at the Laboratory, focusing on the science, technology, and application of multilayers. Before arriving at Livermore in 1985, Barbee was at Stanford University, where he was a senior research associate in the Department of Materials Science and Engineering and laboratory director at the Center for Materials Research. Barbee also was a visiting professor in San Jose State University’s Materials Science Department and at the Stanford Research Institute. Barbee received his B.S. in metallurgical engineering and his M.S. and Ph.D. in materials science engineering from Stanford.

**Making Multilayers by Sputtering**

In manufacturing multilayer materials, the Livermore team uses a process called sputtering, a technique created more than a century ago. Livermore materials scientist Troy W. Barbee, Jr., applied an advanced form of sputtering, called magnetron sputtering, to fabricating multilayers in the 1970s. Today, the semiconductor industry, for example, uses magnetron sputtering to deposit thin films on computer parts, and the machine tool industry uses the technique to apply hard coatings to cutting tools. It is even used to tint windows by forming thin, optically active interference coatings of metal upon glass and to coat jewelry with gold-appearing coatings.

Most of the sputtering work at Livermore takes place at the vapor-phase deposition laboratory. Here, technicians secure a substrate to a table that rotates over two magnetron sputter sources of material for the multilayer. The table rotates at a predetermined speed, and the alternating layers are quickly built up as the substrate passes over first one material source and then the other. The sputter sources operate by bombarding plates of the material to be deposited with high-energy argon gas ions. The impact of these ions blasts atoms from the surface of the sources into the vapor and onto the substrate. As the multilayers revolve from magnetron source to magnetron source, the alternating layers, ranging from a few to many thousand, are sequentially formed.

Sputtering gives a constant deposition rate in which the thickness of each layer is precisely determined by the distance of the substrate from the sources and the time the substrate spends over each source. The technique enables layer thickness control of one-hundredth of an atomic diameter for up to one thousand layers. This process can also achieve a layer thickness uniformity of better than 0.7% (approximately one-third of an atomic diameter) over a 10-centimeter-diameter substrate (see photo at left).

To help evaluate the performance of multilayers, researchers use a soft x-ray diffractometer that was designed and built at Livermore. It is contained in a vacuum chamber and scans the surface of a sample under computer control to provide a map of reflectivity uniformity. In addition, samples are sectioned and thinned for electron microscope analysis to inspect interface sharpness, layer-to-layer uniformity, and layer smoothness.