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ADVANCED LIGHT SOURCE

Putting Synchrotron Radiation To Work

New Opportunities For Industrial R&D

March 1991

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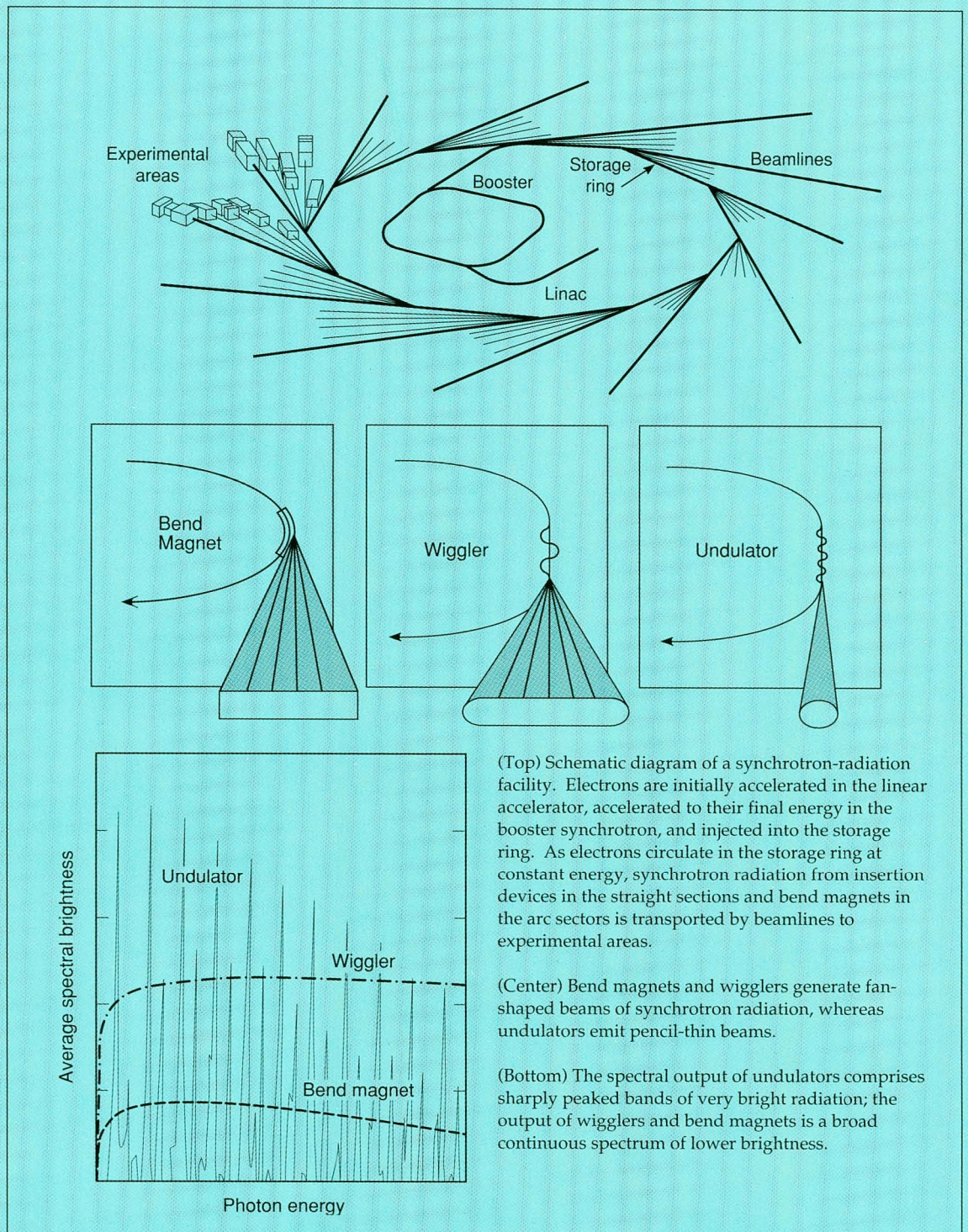

(Top) Schematic diagram of a synchrotron-radiation facility. Electrons are initially accelerated in the linear accelerator, accelerated to their final energy in the booster synchrotron, and injected into the storage ring. As electrons circulate in the storage ring at constant energy, synchrotron radiation from insertion devices in the straight sections and bend magnets in the arc sectors is transported by beamlines to experimental areas.

(Center) Bend magnets and wigglers generate fan-shaped beams of synchrotron radiation, whereas undulators emit pencil-thin beams.

(Bottom) The spectral output of undulators comprises sharply peaked bands of very bright radiation; the output of wigglers and bend magnets is a broad continuous spectrum of lower brightness.

Front Cover: A low concentration of small-diameter particles is often introduced into ceramic materials to improve their strength, which is strongly related to the particle size and spatial distribution. This x-ray microprobe image (see page 4) shows a clumped titanium distribution in a silicon carbide ceramic containing titanium diboride particles. The titanium concentration is lowest in the black and highest in the white regions. The image area is 150 micrometers by 135 micrometers. Data were obtained with the Lawrence Berkeley Laboratory microprobe at the National Synchrotron Light Source.

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WHY SYNCHROTRON RADIATION?

For those working in the ultraviolet or x-ray regions of the spectrum, synchrotron radiation is usually the tool of choice. Although sometimes classified as "big science" because of its connection with large accelerator facilities, research with synchrotron radiation is actually only an extension of the "small science" that the laboratory-based experimentalist does with benchtop spectroscopic, imaging, and diffraction instruments equipped with conventional x-ray, ultraviolet, or electron-beam sources. Anyone using this kind of instrumentation to solve R&D problems is highly likely to find the enhanced research capabilities associated with synchrotron radiation more than worth the modest inconvenience of traveling to a synchrotron light source.

At a synchrotron source, electrons forced to follow a curved trajectory emit light—so-called synchrotron radiation. The characteristics of the radiation depend on the energy of the electrons and the detailed nature of their curved path. The electrons circulate for many hours at constant energy in an electron storage ring. In the places where magnets bend them into curving arc segments, the electrons emit sweeping beams of light—like the headlight of a train on a curving track. The storage ring is, in effect, a marvelous light bulb providing x-ray and ultraviolet radiation with an unrivaled collection of properties in this spectral range.

The quality of synchrotron radiation can be enhanced still further by inserting undulators or wigglers in the straight sections of the storage ring between the arc segments. These periodic magnetic structures, collectively known as insertion devices, bend the electrons along an undulating path. Because the radiation from undulators emerges in a very narrow cone, sharply peaked in narrow wavelength bands that can be tuned by adjusting the magnetic field, undulator radiation is much brighter than that from bend magnets. Wigglers produce a broad spectrum which is similar to that of bend magnets but more intense and shifted to higher photon energies.

Next-generation synchrotron light facilities of the type now under construction emphasize the use of insertion devices and specialize in producing either soft (long-wavelength) x-rays and ultraviolet radiation or hard (short-wavelength) x-rays.

Synchrotron radiation is:

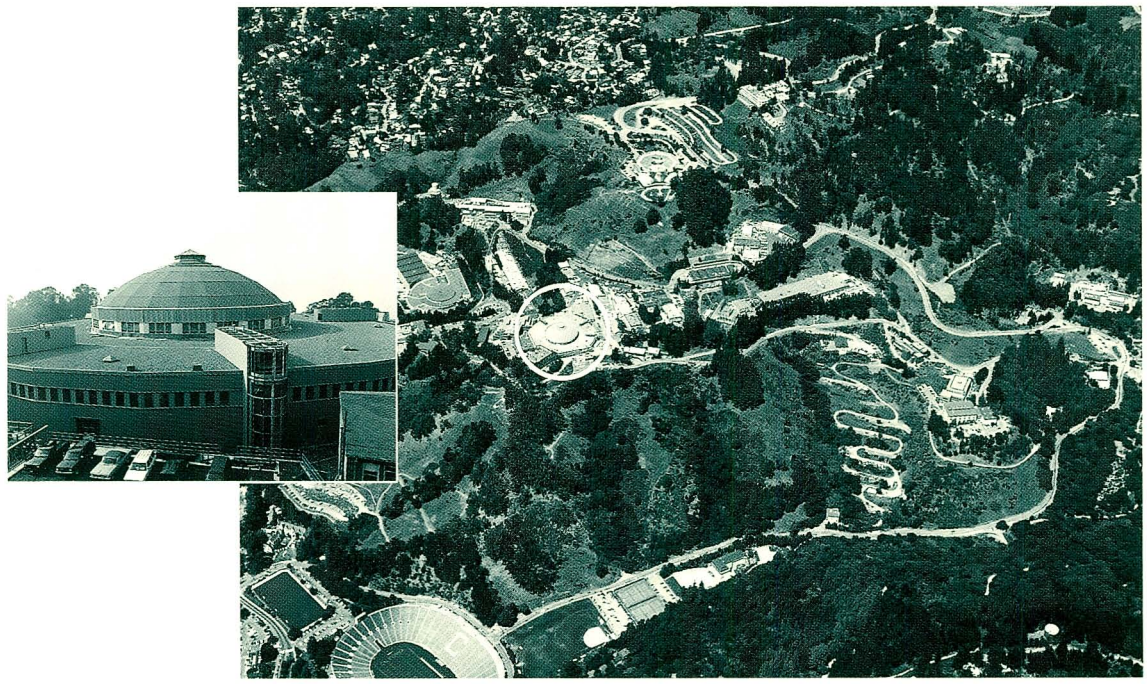
- Intense
- Collimated
- Wavelength tunable
- Polarized
- Pulsed
- Nondestructive

THE ADVANCED LIGHT SOURCE

The Advanced Light Source, a next-generation synchrotron source of ultrabright x-ray and ultraviolet radiation, is under construction in Berkeley, California, at the Lawrence Berkeley Laboratory of the University of California with a planned start-up date of spring 1993. As a U.S. Department of Energy national user facility, the ALS will be available to visiting and in-house researchers in materials, interface, and surface science, in atomic and molecular physics, in chemistry, in the life sciences, in earth science, and in x-ray optics. It will also serve those interested in developing the fabrication technology for micro- and nanostructures, as well as for characterizing them.

The ALS facility consists of an accelerator complex, a complement of insertion devices, beamlines, and associated experimental apparatus, and a building to house this equipment. The state-of-the-art (low-emittance) storage ring has 10 straight sections available for insertion devices (undulators and wigglers). Initially, 24 high-quality bend-magnet ports will also be available. The undulators will generate high-brightness radiation at photon energies from below 10 eV to above 2 keV in the ultraviolet and soft x-ray regions of the spectrum. The wigglers will access the hard x-ray region by generating broad-band radiation up to 20 keV. Bend magnets will be useful below 10 keV. Infrared radiation will also be available from the bend magnets. In the normal operating mode, the time structure of the radiation will comprise pulses with a full-width-half-maximum of about 30 ps and separation of 2 ns. Operation with pulse separations up to 656 ns can be arranged.

These capabilities will support an extensive research program in a broad spectrum of scientific and technological areas in which x-ray and ultraviolet radiation is used to study and manipulate matter in all its varied gaseous, liquid, and solid forms. The high brightness of the ALS will open new areas of research while the facility continues to serve as a reliable source for experimental techniques that have proven their worth in solving problems in basic research and applied technology.



The Lawrence Berkeley Laboratory is located on the hillside above the campus of the University of California at Berkeley. The new ALS building (inset) retains the dome that covered the first large accelerator at LBL, the 184-Inch Cyclotron built by Laboratory founder E.O. Lawrence during World War II.

INDUSTRIAL APPLICATIONS

X-rays and ultraviolet light are tools for learning about the atomic positions, chemical composition, dynamics of structural transitions, electronic quantum states, and magnetic properties of matter. Synchrotron radiation should be considered whenever this information can be advantageously used to address basic research and technological development of solid materials, interfaces, surfaces, liquids, biological molecules, or gases. Examples of industries whose technology benefits from this type of information include:

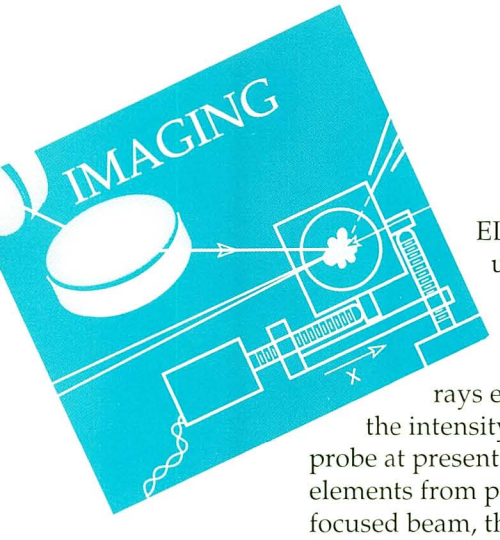
- Aeronautics
- Medical Imaging
- Automobiles
- Oil
- Biotechnology
- Petrochemicals
- Ceramics
- Pharmaceuticals
- Chemicals
- Semiconductors
- Communications
- Space
- Computers
- Superconductors
- Energy Storage
- Steel
- Environmental Protection
- Synthetic Materials
- Holography
- X-ray Lithography
- Magnetics
- Waste Management

Many companies have already demonstrated to themselves the benefits of synchrotron radiation through their research at existing facilities around the world. Firms with recently active programs in the United States include:

- Aerospace Corporation
- Allied Signal Research
- Aracor
- AT&T Bell Laboratories
- Becton Dickinson & Company Research Center
- Boeing Company
- BP America
- Chevron Oil Field Research Company
- Chevron Research Company
- Eastman Kodak Research Laboratory
- E.I. du Pont de Nemours & Company
- Electric Power Research Institute
- Exxon Research & Engineering
- GTE
- Hewlett-Packard Laboratories
- Hoechst-Celanese
- Hoffman-LaRoche Inc.
- IBM Almaden Research Center
- IBM T. J. Watson Research Center
- Intel Corporation
- Lockheed Research Laboratory
- 3M Central Research Laboratory
- Macroatom, Inc.
- Martin Marietta
- Mobile
- Monsanto Company
- Palo Alto Veterans Hospital
- Schlumberger-Doll Research
- Signetics Corporation
- SRI International
- Union Carbide
- University City Science Center
- W.R. Grace & Company
- Xerox

The following pages describe the basic categories of experimental techniques that have been successfully exploited at existing synchrotron facilities or, in some cases, that are expected to join the research armamentarium at the next-generation synchrotron sources now under construction, such as the ALS. In each case, a selection of typical industrial applications is noted. To obtain more specific information about the ALS and its capabilities, please turn to the end of this booklet.

MICROPROBE



ELEMENTAL ANALYSIS BY MEANS OF A HIGH-ENERGY x-ray microprobe using focused x-rays from a synchrotron source is characterized by high sensitivity, spatial resolution approaching 1 micrometer, ease of operation, and the ability to examine samples in a variety of environments. Quantitative, nondestructive detection of elements is by means of the characteristic fluorescent x-rays emitted by the irradiated sample, the photon energy identifying the element and the intensity measuring the quantity of that element. Elemental sensitivity of the microprobe at present reaches the femtogram level with counting times on the order of 30 seconds for elements from potassium to zinc in the periodic table. By scanning a sample through the focused beam, the spatial distribution of many elements can be mapped. With multilayer-coated glancing-incidence mirrors, it is possible to focus an x-ray beam routinely to a diameter of less than 7 micrometers . With additional beam-defining apertures, the focused beam can be further reduced—a diameter of approximately 2 micrometers has been recently demonstrated and 1 micrometer is foreseeable at next-generation synchrotron sources.

A major advantage of the x-ray microprobe is that the specimen does not have to be kept in vacuum or subjected to special contrast-enhancing preparation. Additional detection sensitivity is imparted by the ability to select the x-ray photon energy to avoid excitation of interfering fluorescence from elements other than those being sought. Consequently, applications of the microprobe are extremely diverse, including such examples as size and distribution of small strengthening particles in ceramics, distribution of doping materials in semiconductors, composition of inclusions in geological materials, analysis of ancient documents and artwork, and trace element analysis of biological materials.

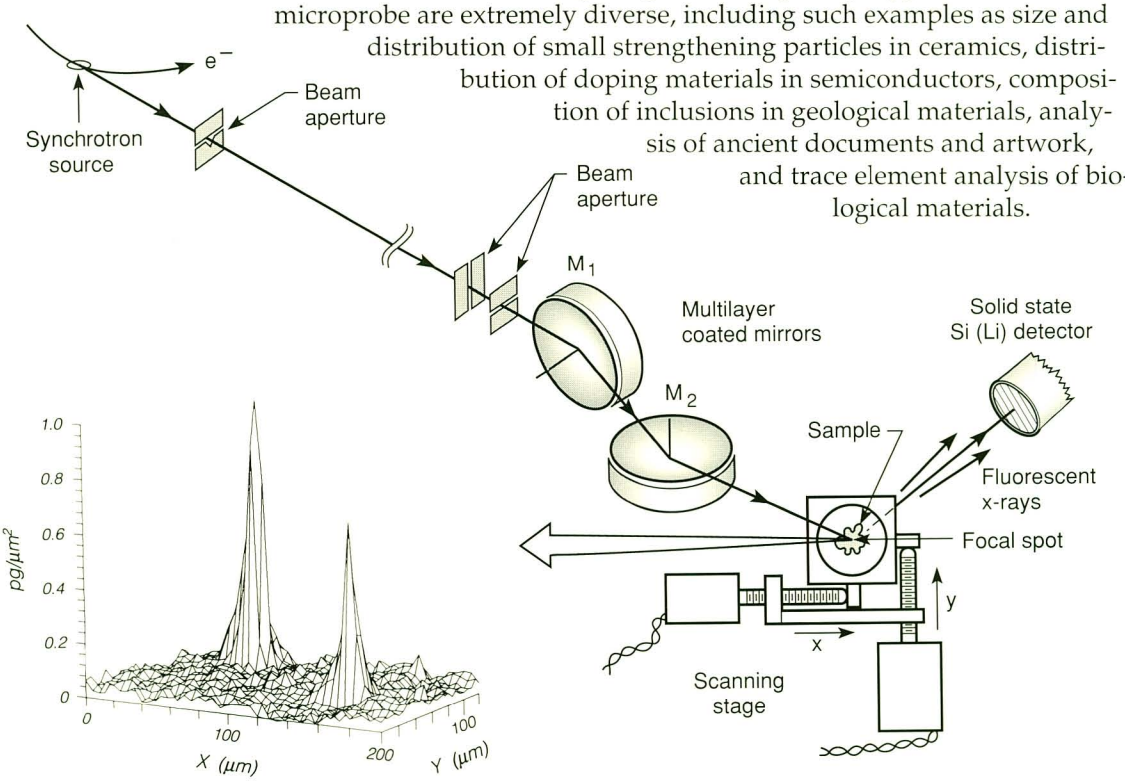
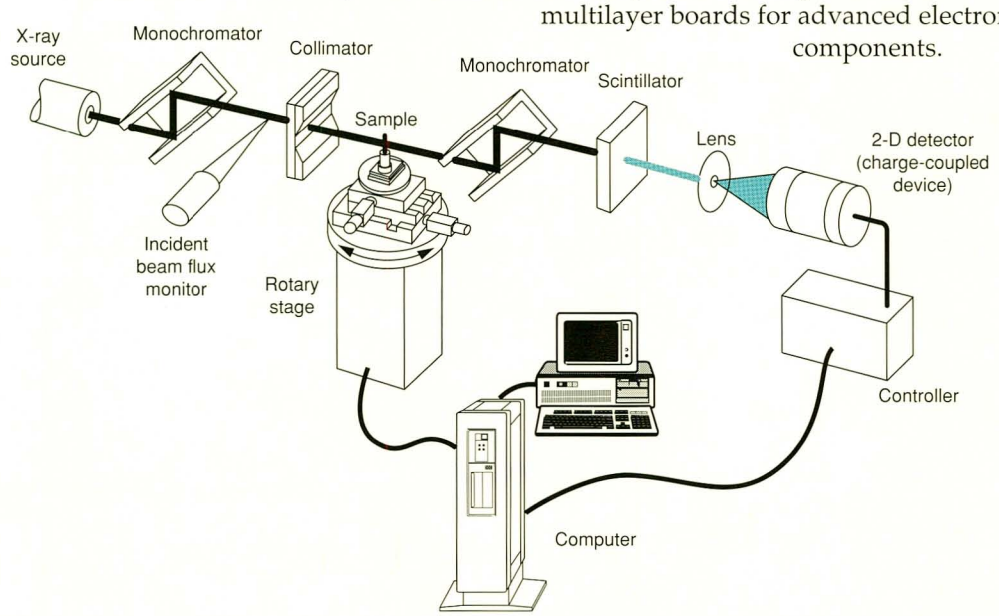


Diagram of an x-ray microprobe built at the Lawrence Berkeley Laboratory shows how a pair of grazing-incidence mirrors coated with multilayers can be used to focus a beam of high-energy (hard) x-rays to a spot several micrometers in diameter. The beam apertures further reduce the spot size to about 2 micrometers. The three-dimensional perspective graph illustrates the spatially resolved trace-element capability of the LBL microprobe with a quantitative map of the distribution of iron impurity in a silicon carbide ceramic. The data were taken at the National Synchrotron Light Source.

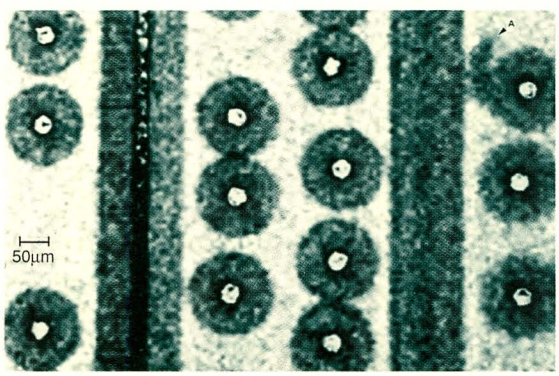
TOMOGRAPHY

High-resolution computed tomography (or microtomography) is a comparatively new technique based on the well-developed concept of reconstruction of cross-sectional images from a sequence of x-ray absorption measurements at several angles around an axis of rotation. Computer-imaging software uses a series of reconstructions to create a three-dimensional image. With a high-intensity, synchrotron x-ray source, advanced detectors, and already demonstrated x-ray optics, the spatial resolution can approach 1 micrometer. With wavelength tunability, chemical sensitivity is achieved by making images just above and just below an absorption edge characteristic of the element of interest in its particular chemical state (dual-wavelength imaging).

It is convenient to divide the many industrial applications of high-resolution computed tomography according to x-ray photon energy. Applications particularly suited to the ALS are those requiring the high spatial resolution that is easiest to achieve with low-energy x-rays. Other applications requiring high-energy, short-wavelength x-rays in order to penetrate the samples are best done elsewhere. Typical applications include: formation of microcracks and microleakage in the region behind HAP (hydroxyapatite)-coated implants in mineralized tissues (bone or dentin), in vitro bioassay, the effect of pore-size distribution on secondary oil recovery in sandstones, low-temperature combustion of coal, effects of caustic atmospheres on catalysts, time and spatial evolution of fatigue crack growth and fracture in advanced fiber composites, pore formation during sintering of ceramics, catalyst pore structure under operational conditions, and nondestructive inspection of integrated circuits and multilayer boards for advanced electronic components.



(Above) Diagram of the computed-tomography apparatus developed at the Lawrence Livermore National Laboratory shows how images of transmitted x-ray intensities are accumulated at several viewing angles around a sample. From these data the computer reconstructs quantitative cross-sectional maps of density variations or of elemental distributions.

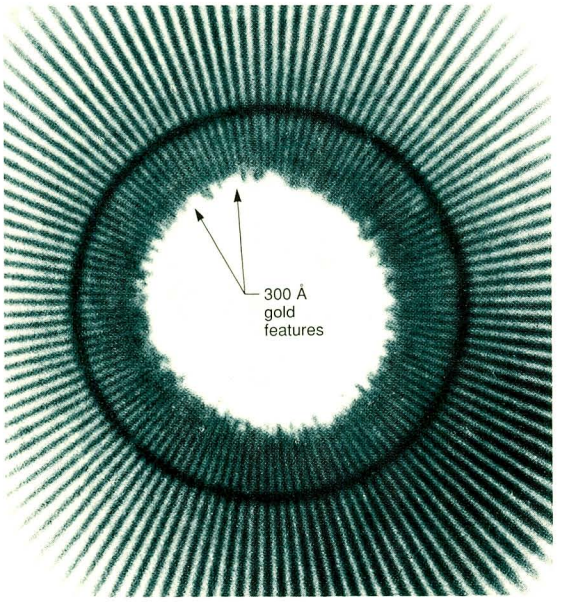


(Right) Cross-sectional density map of a two-dimensional fiber composite material (silicon carbide fibers in a calcium alumino-silicate matrix) clearly shows defects introduced during processing, such as the fiber fragment (A) lodged between two fiber plies, a potential nucleation site for cracks during service. Data were taken with the LLNL instrument at the Cornell High Energy Synchrotron Source.

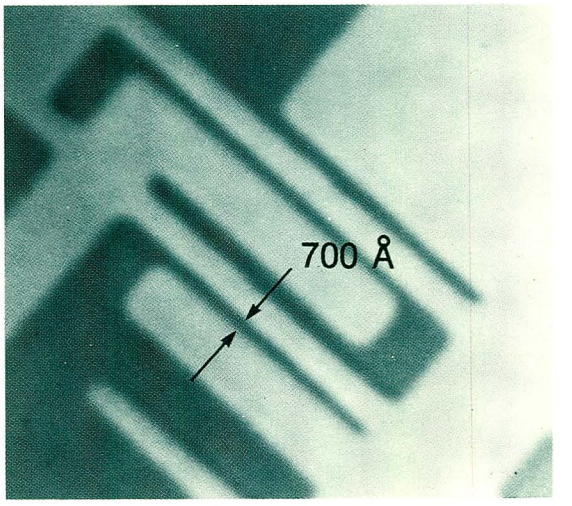
X-RAY MICROSCOPY

X-ray microscopy is an old idea that has been made practical by the advancing technologies of x-ray sources, x-ray optical components (lenses and mirrors), and x-ray detectors. In contrast to optical microscopy based on reflected light, the contrast in x-ray images is usually due to the absorption of radiation, as in radiography. However, it is also possible to use the photoelectrons emitted from the irradiated material to generate contrast. X-ray images may be recorded on film or by electronic detectors, whereas photoelectron images require electronic detectors in vacuum. Images may be generated in a parallel (imaging) mode with appropriate x-ray or electron optics imaging the photons or electrons emerging from a broadly illuminated sample. Alternatively, images may be generated in a serial (scanning) mode by focusing the incident x-ray beam to a small spot on the sample. The spatial resolution of soft x-ray microscopes based on absorption contrast is routinely better than 1000 angstroms and has reached the 300-angstrom range in some cases.

As an emerging technique, x-ray microscopy has not had time to accumulate a portfolio of successful applications. Demonstration experiments have shown that the technique is capable of imaging patterns such as the submicrometer features of an integrated circuit. By tuning the photon energy to match the absorption edge of specific elements, it is possible to generate quantitative elemental maps, as described in the section on tomography. In the life sciences, x-ray microscopy is expected to fill an important niche between optical and electron microscopy by providing images of subcellular components in near-natural environments. With high-brightness undulator sources, successive images of the same object in real time may make it feasible to study the dynamics of biological or other processes.



X-ray micrograph of a test pattern with 128 radial spokes shows a spatial resolution approaching 300 angstroms. The micrograph was made with the use of an x-ray lens (Fresnel zone plate), made by the Lawrence Berkeley Laboratory and the IBM T.J. Watson Research Center, in an imaging x-ray microscope built by the University of Göttingen at the Berlin Electron Synchrotron Corporation for Synchrotron Radiation (BESSY) .

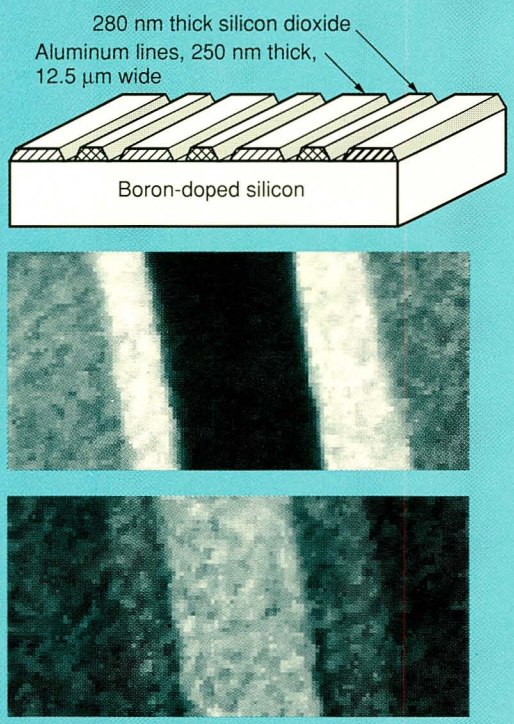


X-ray microscopy could be an attractive analytical tool for the study of future deep-submicrometer devices and circuits, as illustrated by the x-ray micrograph of a test object made of gold on a silicon nitride substrate showing a pattern detail typical of an advanced 0.1-micrometer MOSFET circuit. The micrograph was made at BESSY.

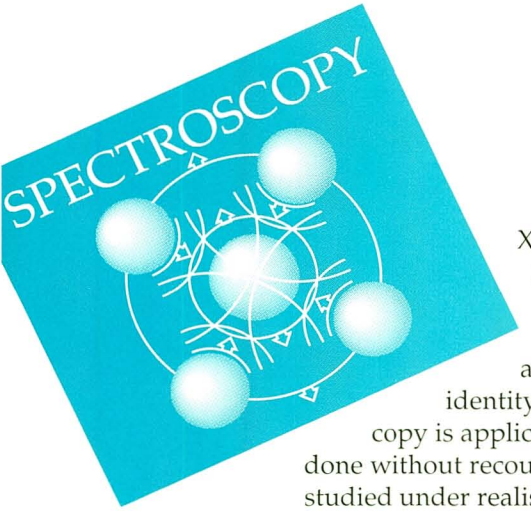
On the Horizon: Spectromicroscopy

An exciting prospect now being tested that will be greatly enhanced by the high brightness of next-generation synchrotron sources is the combination of x-ray microscopy and spectroscopy. In brief, a focused x-ray beam from a bright synchrotron source illuminates a small spot on a specimen with enough photons to generate an absorption, photoelectron, or other type of spectrum without loss of spectral resolution. As in x-ray microscopy (previous page), either imaging or scanning modes can be used for spatially resolved spectroscopy, or spectromicroscopy.

The scientific and technological impact of spectromicroscopy is expected to be extremely wide owing to the pervasive importance of the relentlessly decreasing size of the physical, chemical, and biological systems to be analyzed or fabricated. With shrinking dimensions comes an increased emphasis on surfaces and interfaces, which are often inhomogeneous. Moreover, processes at surfaces and interfaces may be dependent on local structures, such as defects, grain boundaries, edges, and corners. Such processes will be susceptible to study by soft x-ray spectroscopy, which retains its unobtrusive and highly chemically specific character (see the section on spectroscopy) but now has the high spatial resolution of electron microscopy. An important example occurs in photoelectron spectromicroscopy, where, by use of an electron-energy spectrometer to select the photoelectron energy detected, one can map particular elements and distinguish different chemical bonding states of the same element. Spatial resolutions in the range from 0.1 to 0.5 micrometer have already been achieved for this technique. More generally, electronic properties of mesoscopic artificial structures, spatially resolved surface chemical reactions, epitaxial growth mechanisms, inhomogeneities at semiconductor interfaces, proximity effects in ceramic superconductors, composite materials, interface formation in fragile materials, and the chemical role of trace elements in biological systems represent some of the general topic areas that spectromicroscopy can fruitfully address.



Photoelectron spectromicroscopy images demonstrate the ability to make spatial distribution maps that distinguish between different chemical bonding states of the same element. (Top) Diagram of a test sample comprising a boron-doped silicon substrate with alternating stripes of aluminum and silicon dioxide. (Middle) Selecting photoelectrons with energies characteristic of elemental silicon images the silicon in the areas between the stripes. (Bottom) Selecting photoelectrons with chemically shifted energies images the silicon in the silicon dioxide stripes. Data were taken by researchers from the State University of New York at Stony Brook who built and now operate a scanning photoelectron microscope at the National Synchrotron Light Source.

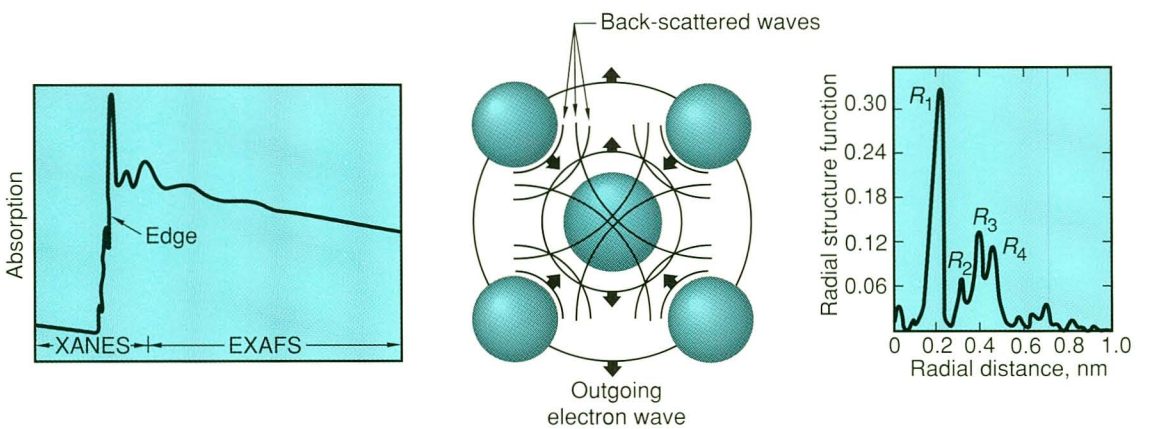


X-RAY ABSORPTION SPECTROSCOPY

X-RAY ABSORPTION SPECTROSCOPY MEASURES the response of a sample to x-rays over a range of photon energies at or above an absorption edge. There are many x-ray spectroscopic techniques that, taken together, reveal the identity, electronic structure. and chemical bonding state of the atomic species absorbing the x-rays and provide information about the identity, number, and arrangement of atoms around the absorbing atom. Spectroscopy is applicable to both crystalline and noncrystalline materials and can frequently be done without recourse to high-vacuum environments, so that systems, such as catalysts, can be studied under realistic conditions.

Extended x-ray absorption fine structure (EXAFS) is a widely practiced form of x-ray absorption spectroscopy that owes its popularity to the tunability and high intensity of synchrotron radiation. Fine structure refers to the details of the absorption spectrum above an absorption edge. These features make it possible to pick out and probe specific elements, often at very low concentrations. EXAFS is particularly valuable for the determination of atomic positions in poorly crystallized or amorphous materials containing more than one atomic species. Moreover, because of the penetrating power of x-rays, in-situ EXAFS studies can be carried out under high-temperature and high-pressure conditions that are relevant to the energy industry.

Typical examples of the use of EXAFS to examine industrially important problems include the physical and chemical structure of coal, shale, tars, and asphaltene materials; the properties of dilute impurities in heavy hydrocarbons (such as iron and sulfur in coal, arsenic in shale, and metal impurities in cokes and combustion deposits); and the mechanism by which a network modifier alters the structure of a glass or an amorphous thin film.

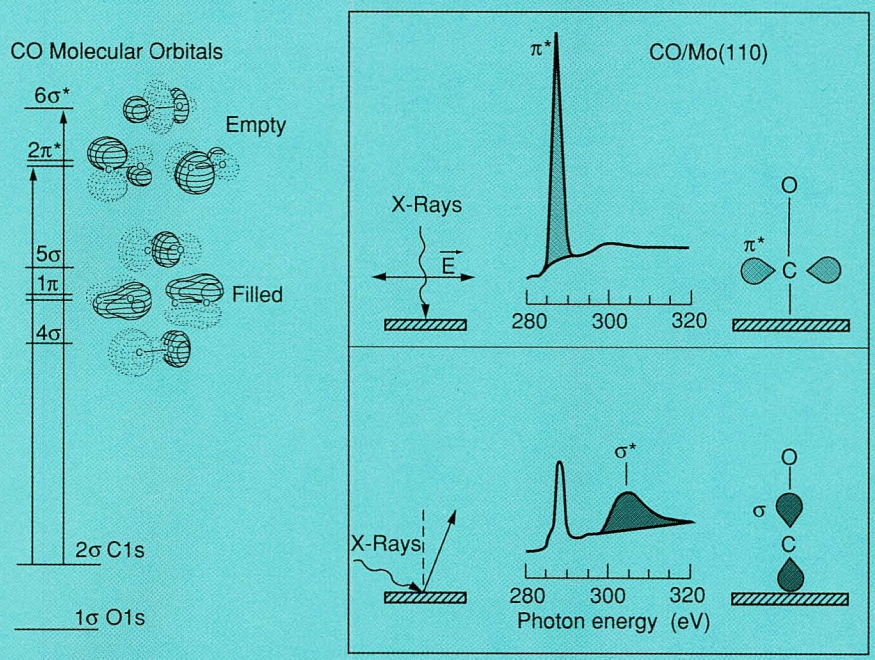


(Left) Diagram shows the EXAFS region above an x-ray absorption edge and the XANES region near the edge (see next page). (Center) Creation of a photoelectron by absorption of an x-ray photon is represented by a photoelectron wave emanating from the absorber. The EXAFS oscillations in the absorption spectrum arise from interference of electron waves back-scattered by atoms near the absorber with the outgoing photoelectron wave. (Right) The radial structure function derived from an EXAFS structure gives information about the distance of successive shells of neighbor atoms from the absorber.

Focus on Surfaces

Extreme sensitivity for determining short-range order on surfaces is offered by the technique of surface EXAFS or SEXAFS. By tuning the photon energy to the absorption edge of an adsorbate atom on the surface of a material and using fluorescence or electron-yield detection, one may determine the local bonding geometry, such as the numbers and distances of atoms that are adjacent to oxygen atoms on the surface of a partially oxidized metal or semiconductor.

SEXAFS and the related technique of x-ray absorption near-edge structure (XANES), also known as near-edge x-ray absorption fine structure (NEXAFS), are a powerful combination for the investigation of molecular orientations and bonding sites on surfaces. XANES is sensitive to bond energy and shape. Systems that can be studied range from diatomic molecules to thin polymer films bonded to surfaces. Molecular chemisorption systems are of fundamental importance in various technological processes, such as heterogeneous catalysis, reactive etching of semiconductor surfaces, or the packaging of electronic devices. With the use of fluorescence detection, samples may be studied in non-vacuum environments similar to those in real catalytic reactions.

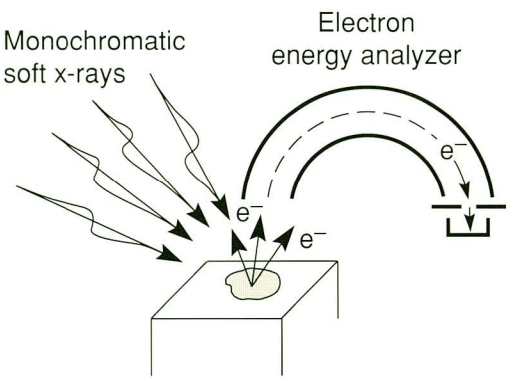


Linearly polarized synchrotron radiation can be exploited to determine the orientation of adsorbed molecules on a surface because x-ray absorption is maximized when the electric field vector $\vec{E}$ of the radiation points in the same direction as the molecular orbital (above left) responsible for the absorption, which in turn depends on the molecular orientation. In the figure, based on data obtained by scientists from the IBM Almaden Research Center, the vertical orientation of a carbon monoxide molecule on a molybdenum surface is verified by the strong absorption due to the π^* orbital when the electric vector is parallel to the surface (top right) and by absorption due to the σ^* orbital when the electric vector is nearly normal to the surface (bottom right).

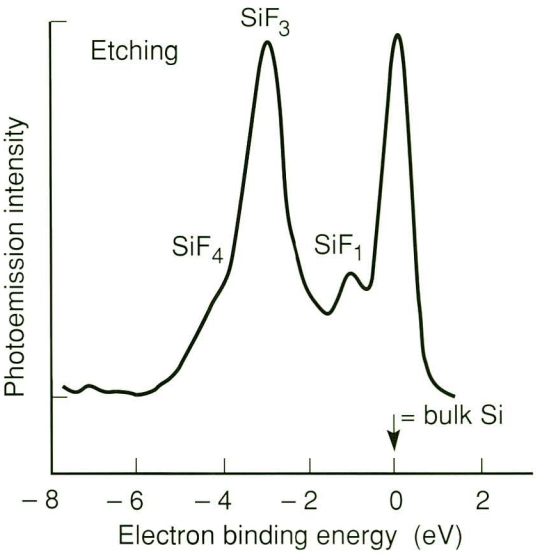
PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy, which is based on analysis of the kinetic energy of electrons emitted from a material after the absorption of x-rays, is the most direct spectroscopic tool for investigating in detail the electronic structure of solid, liquid, and gaseous matter and, in particular, for probing the chemical state of atoms in different environments. It has been a particularly useful tool for probing surfaces, whether clean, covered with adsorbed species, or coated with thin films. The tunability of synchrotron radiation provides the means for making photoelectron spectroscopy surface sensitive because the depth below the surface from which photoelectrons can escape the sample and be detected depends strongly on their energy, which in turn is controlled by the energy of the exciting photons.

It is convenient to distinguish between x-ray photoelectron spectroscopy (sometimes also known as ESCA) and ultraviolet photoelectron spectroscopy. X-rays are absorbed by tightly bound inner (core) electrons, whereas ultraviolet photons are absorbed by the more loosely bound outer (valence) electrons. Applications of photoelectron spectroscopy in the microelectronics industry include growth processes of films and layers on semiconductor surfaces and the pathways by which reactive ion etching proceeds. In catalysis, photoelectron spectroscopy gives direct insight into the formation of the chemical bonds, such as the effect of alkali promoters on C-O bond weakening in Fischer-Tropsch reaction chemistry, and the interaction between metallic elements in bimetallic catalysts and between metal particles and their support. Measurement of photoemission peak intensities from core levels as a function of the electron-emission direction from the surface and/or as a function of photon energy, a technique called photoelectron diffraction, gives structural information similar to that derived from SEXAFS. With the use of circularly polarized radiation or detectors sensitive to the spin of the photoelectrons, it is possible to investigate the magnetic structure of surfaces and thin films, a subject of interest for the magnetic recording industry.



In photoelectron spectroscopy, electrons ejected from a sample after absorption of x-ray or ultraviolet radiation are analyzed for their kinetic energies, which can be related to the binding energies of the electrons in the sample.

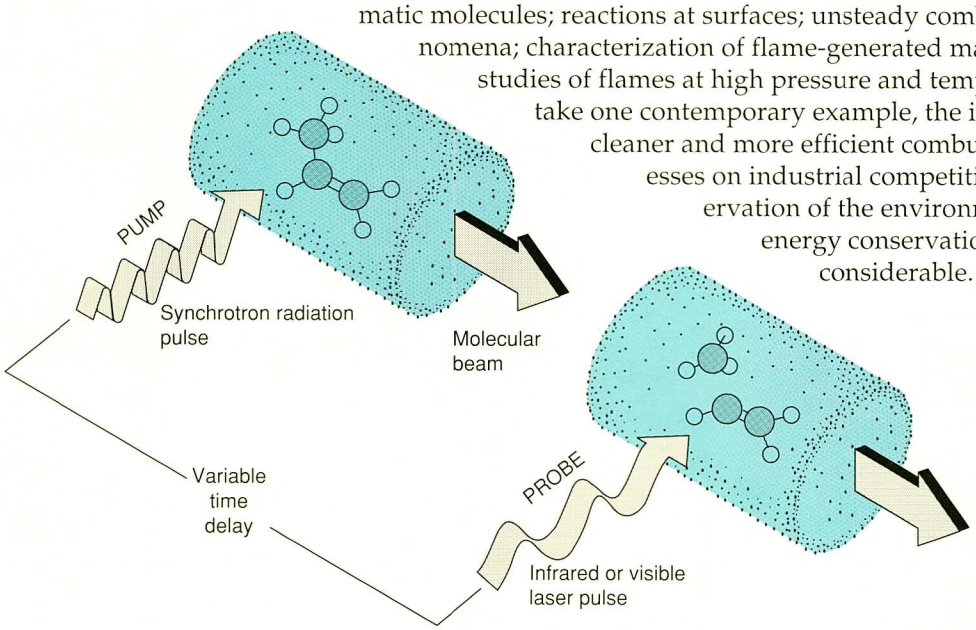


Data taken at the National Synchrotron Light Source by a group from the IBM T.J. Watson Research Center show the predominance of silicon trifluoride on a silicon surface during an ion-etching experiment, suggesting that removal of this species is a rate-limiting step during the etching process.

TIME-RESOLVED SPECTROSCOPY

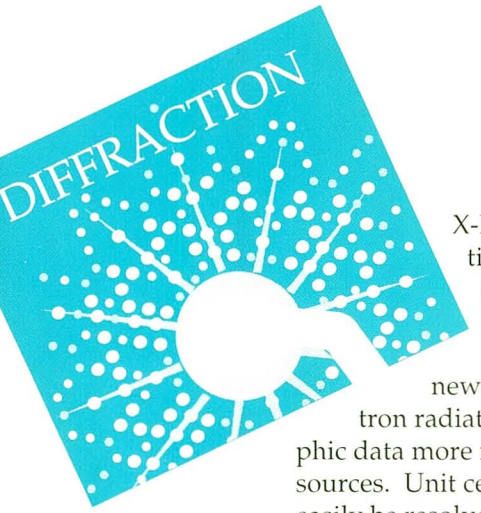
The high flux and the variable time structure of ALS radiation open the way to a variety of time-resolved measurements not generally feasible in the past. The simplest time-resolved experiment is to measure the response of a specimen to excitation by the synchrotron-radiation pulse. High flux guarantees that there are enough photons in a single pulse to generate a measurable signal, such as photons or photoelectrons, at various times after the excitation. The ability to control the interval between pulses makes it possible to examine processes with long or short lifetimes. A more demanding type of time-resolved experiment requires two photon pulses, one to excite the specimen and the other to probe the excited state by stimulating it to respond in some way. The two photons in a so-called pump-probe experiment may both come from the synchrotron source, but more often either the pump or the probe pulse will come from a second source, such as a short-pulse laser, that can be synchronized with the synchrotron. The time response of the process under study is mapped by recording the outcome of a sequence of pump-probe events with the probe pulse arriving at increasing time intervals.

Chemical reaction dynamics is a particularly prominent beneficiary of time-resolved spectroscopy. Several important and challenging areas ripe for investigation by this means are the chemical reactivity, structure, and spectroscopy of polyatomic radicals, reaction intermediates, clusters, and unusual transient species; the mechanisms of soot formation and destruction; ignition processes; nitrogen chemistry; the dynamics and mechanics of the decomposition of aromatic molecules; reactions at surfaces; unsteady combustion phenomena; characterization of flame-generated materials; and studies of flames at high pressure and temperature. To take one contemporary example, the impact of cleaner and more efficient combustion processes on industrial competitiveness, preservation of the environment, and energy conservation would be considerable.



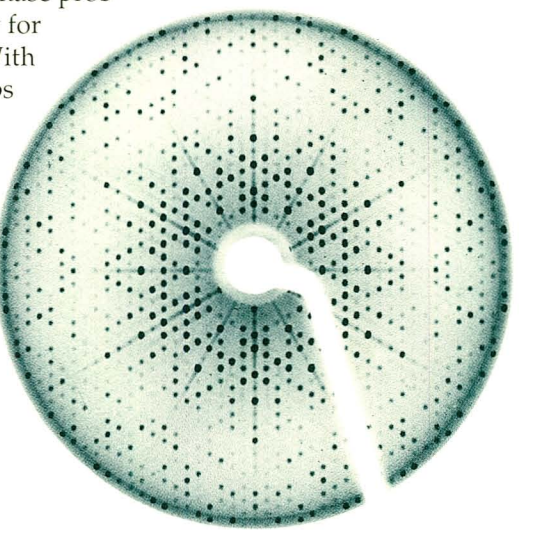
The kinetics of chemical reactions can be investigated with pulsed light from two sources (pump-probe or two-color experiments). In the diagram, a "pump" pulse from the synchrotron source initiates a chemical reaction that is interrogated by a "probe" pulse from a laser. The ALS will provide pulses about 30 ps in duration at intervals of 2 ns or longer.

PROTEIN CRYSTALLOGRAPHY

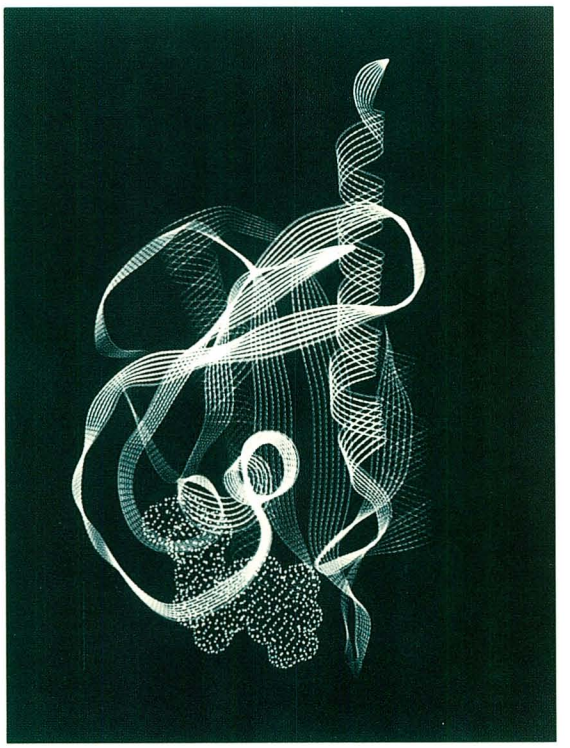


X-RAY DIFFRACTION IS THE STANDARD TECHNIQUE for locating the positions of atoms in crystalline materials and has been particularly valuable to life scientists for the structural analysis of proteins, nucleic acids, and viruses. Use of synchrotron radiation has both enormously improved the quality of data collected using conventional techniques and led to the development of several new structural techniques. Because of the extraordinarily high intensity of synchrotron radiation, it is now possible to collect high-quality, single-crystal x-ray crystallographic data more rapidly and generally to a higher resolution than with conventional x-ray sources. Unit cell dimensions of 600 angstroms or more—typical in virus crystallography—can easily be resolved. A rapidly developing use of protein crystallography is in the pharmaceutical industry where knowledge of the three-dimensional structures of biological macromolecules will aid in the investigation of the mechanisms by which disease-causing agents work and hence lead to the rational design of new drugs.

The tunability and pulsed time structure of synchrotron radiation are equally important features for protein crystallography. With a low-bandwidth x-ray beam whose wavelength can be tuned, anomalous scattering intensities (the intensity just above and below an absorption edge) can be obtained for suitable atoms in the sample protein. These multi-wavelength data from a single sample can then be used to solve the "phase problem" in protein crystallography without the necessity for additional samples called heavy-atom derivatives. With fast electronic detectors, the data-collection time drops to a small fraction of a second, making it possible to use the white-light Laue technique to investigate structural changes, such as those in enzymes as they undergo catalysis. As an x-ray source for crystallography, the ALS will match today's best facilities.



X-ray diffraction pattern of the c-H-*ras* oncogene protein obtained by a group led by Lawrence Berkeley Laboratory scientists at the Stanford Synchrotron Radiation Laboratory.



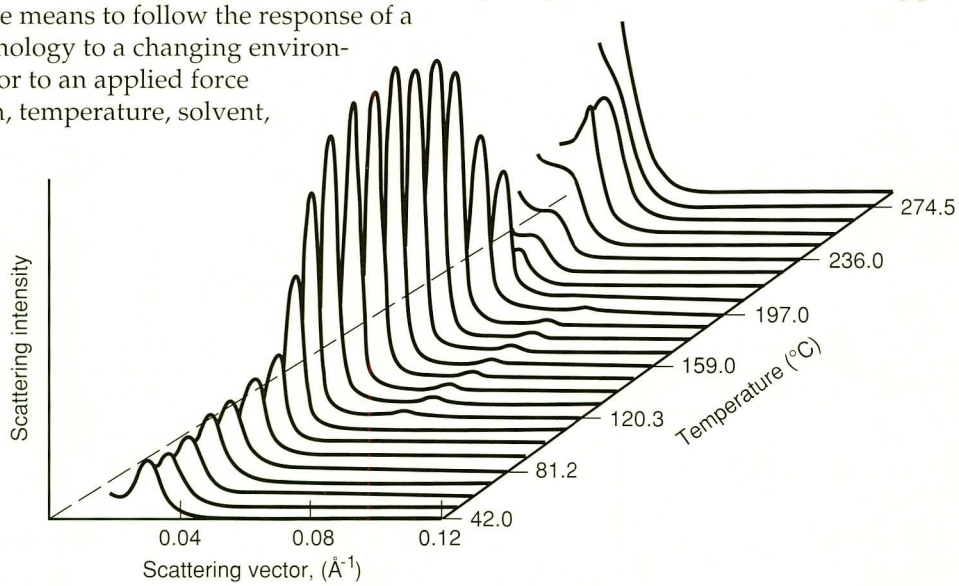
A computer-generated image of the structural backbone of the c-H-*ras* oncogene protein, together with a molecule of guanosine diphosphate, as determined by x-ray diffraction. In its normal form, this protein plays the role of an on-off switch for normal cell growth. Shown here in the "off state," the protein is about 35 angstroms by 40 angstroms by 49 angstroms in volume. A mutant form of the protein has been associated with two of the deadliest cancers in humans, pancreatic and colorectal cancers, and implicated in several others.

SMALL-/WIDE-ANGLE SCATTERING

Disordered materials, polymers, liquids, and the like do not give precise diffraction patterns that reveal atomic positions, but the distribution of scattered x-rays nonetheless gives considerable information about structural units in non-crystalline specimens . In general, the smaller the scattering angle, the larger the structural unit that can be investigated.

Small-angle x-ray scattering applies to structures on a size scale ranging from the tens to thousands of angstroms. For example, it can measure catalyst pore structure under operational conditions, provide information on the morphology of polymers, determine the physical structure of heavy hydrocarbons. such as asphaltenes in petroleum-based heavy feed stocks, probe the internal structure of rocks and porous media, and detect phase separation and defects in surface layers. Scattering of x-rays at higher angles (wide-angle scattering) provides information on a smaller size scale ranging from the tenths to tens of angstroms and is relevant to phenomena such as the local ordering of polymer molecules. High-resolution wide-angle x-ray scattering overlaps small- and wide-angle scattering. It yields precise structural information when only small single crystals are available, as with zeolite crystals, and in materials with separations between repeating structural units up to a few hundred angstroms.

The intense flux from synchrotron x-ray sources makes it possible to collect data of much higher quality and with a significantly better signal-to-noise ratio from weakly diffracting samples, such as fibres, membranes, and solutions. The high flux also generates scattering patterns at least 100 times faster than laboratory x-ray sources. Real-time scattering provides a unique means to follow the response of a morphology to a changing environment or to an applied force (strain, temperature, solvent, etc.).

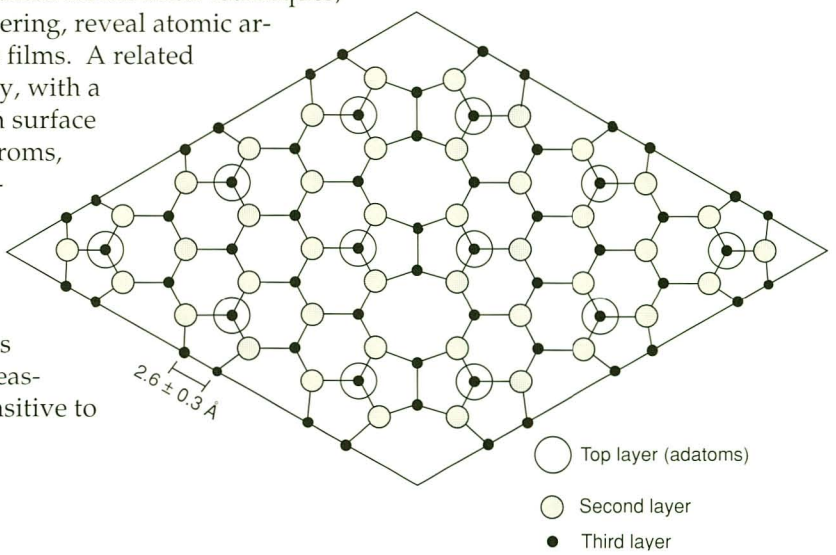


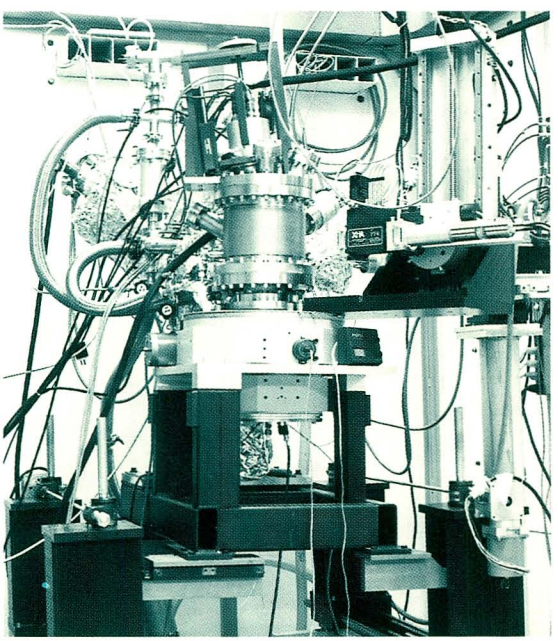
The changing distribution of scattered x-rays for a block copolymer with the constituents α,ω-bis-(dimethylamino)-polyisoprene of molecular weight 18,000 and α,ω-disulfonic acid poly(α-methylstyrene) of molecular weight 14,000 with increasing temperature shows that the system is undergoing a phase separation, often associated with a deterioration of properties. Proportional to the scattering angle at small angles, the scattering vector at which a peak occurs is the inverse of the repeat distance of the structure responsible for the scattering. The data were obtained at the Stanford Synchrotron Radiation Laboratory by scientists from the IBM Almaden Research Center and the University of Liège (Belgium) with a temperature-scanning rate of 10°C/minute, demonstrating the ability to follow structural changes in real time with the use of synchrotron radiation.

Surfaces, Interfaces, And Thin Films

Considerable information about the structure of surfaces and thin films can be obtained with the technique of grazing-incidence x-ray scattering. Changing the angle of grazing incidence varies the depth of penetration of the highly collimated x-rays from tens of angstroms to tens of thousands of angstroms (i.e., many micrometers). Scattering is confined to within this penetration depth, thereby providing a means of distinguishing the surface atoms from those in the interior. Because of the high flux of synchrotron sources, x-ray scattering by the comparatively small number of surface atoms is large enough to be detected. Furthermore, scattering experiments can be performed in reactive environments because the penetrating x-rays do not require a high-vacuum environment.

Almost all of the diffraction techniques applied to bulk materials may be applied to surfaces and thin films. The structure of reconstructed surfaces and adsorbed layers on metals and semiconductors can be examined. Interactions between surface atoms and chemisorbed molecules can be directly monitored. The lattice parameters, the identification of different crystalline components, crystallite sizes, and strain can be determined in polycrystalline films. Radial distribution techniques, including anomalous scattering, reveal atomic arrangements in amorphous films. A related technique, x-ray reflectivity, with a resolution normal to a film surface of approximately 10 angstroms, can easily detect the segregation of specific components to a surface or an interface in a multicomponent system, such as a polymer. Reflectivity measurements are also very sensitive to surface roughness.





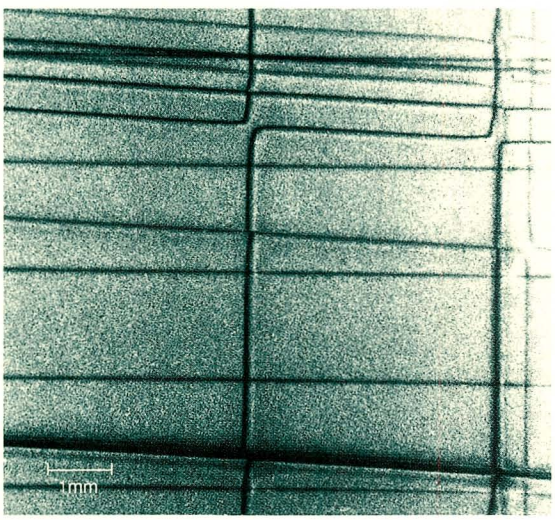
(Above) Grazing-incidence x-ray diffraction measurements by AT&T Bell Laboratories scientists working at the National Synchrotron Light Source played a significant role in unraveling the complex structure of the silicon (111)-7×7 reconstructed surface, which has more than 100 atoms in its unit cell.

(Left) This ultrahigh-vacuum diffractometer, developed by scientists from AT&T Bell Laboratories and the Stanford Synchrotron Radiation Laboratory, is used on an undulator beamline at Stanford to investigate fundamental aspects of surfaces and growth, such as the "premelting" of aluminum surfaces, a phenomenon where a liquid layer a few monolayers thick is in equilibrium with the underlying crystal at temperatures significantly below the melting point of the crystal.

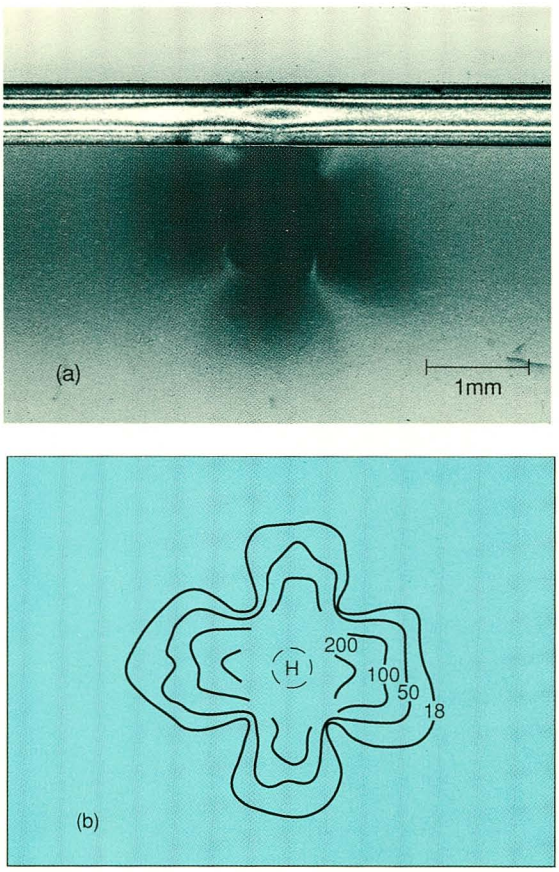
TOPOGRAPHY

X-ray diffraction imaging (normally called x-ray diffraction topography) has been and continues to be a powerful tool for the characterization of industrial materials. Contrast in x-ray topographs arises from local changes in diffracting power due to the presence of defects or to changes in the orientation of the diffraction planes. Features include: (1) extremely high strain sensitivity together with spatial resolution equivalent to that of optical microscopy, (2) the ability to characterize defects such as dislocations and stacking faults nondestructively in the interior of samples, and (3) the ability to map continuous strain distributions or discrete defect densities over fields of view exceeding several square centimeters.

Advantages associated with a synchrotron x-ray source include the ability to tune the x-ray photon energy to that most appropriate for a particular sample and short exposure times. The wealth of results produced in two or three exposures (each of about 1 second to 1 minute duration) would require several weeks or longer with a laboratory x-ray source. The short exposure time also means that processing or growth can be followed in real time. Examples of x-ray topography studies of semiconductor materials include the microstructure of interface breakdown in gallium arsenide, the distribution of oxide precipitates through the thickness of thermally-processed silicon wafers, and the distribution of strain around devices on silicon wafers.

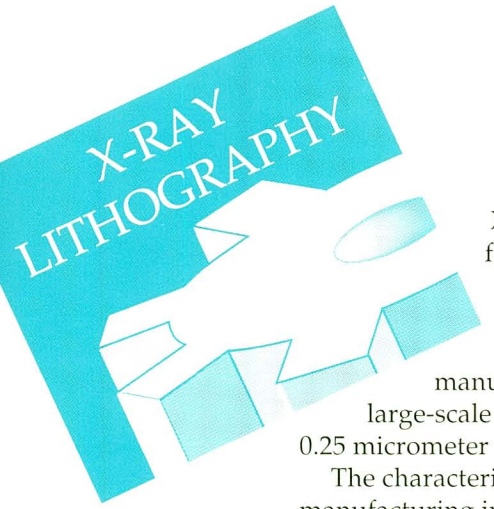


X-ray topograph obtained at the Stanford Synchrotron Radiation Laboratory shows a silicon wafer with misfit dislocations generated in the plane of the interface during processing with deposited thin films of silicon dioxide and silicon nitride. The exposure time for this transmission topograph was 1 second.



The number of diffraction fringes in a section topograph (a-top) is a measure of strain, which is also qualitatively imaged in a projection topograph (a-bottom). The strain map (b) in a laser-drilled silicon substrate was made by step-scanning across the deformed area and making a section topograph at each step. The strain values on the contours are in units of 10^{-6}. Measurements were made by scientists from the Georgia Institute of Technology and the Stanford Synchrotron Radiation Laboratory at Stanford.

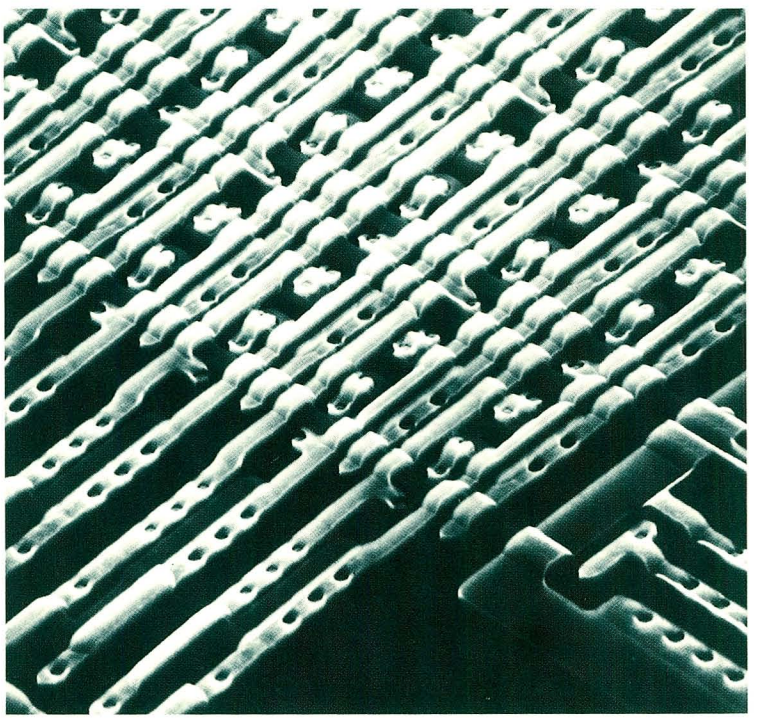
X-RAY LITHOGRAPHY



X-RAY LITHOGRAPHY IS RAPIDLY EMERGING as a viable technique for the fabrication of sub-0.5-micrometer features in integrated circuits. It is expected that the critical dimensions of integrated circuits will go below 0.4 micrometer by the mid-1990s, and it is generally believed that below 0.4 micrometer, optical lithography will become either too difficult or expensive for large-scale manufacturing. If this judgement is true, then x-ray lithography will serve as a large-scale manufacturing tool for integrated circuits with minimum feature sizes down to 0.25 micrometer with proximity printing and even lower with projection printing.

The characteristics of x-ray lithography that make it very attractive for semiconductor manufacturing include high resolution, process latitude, good depth of focus, defect tolerance, and high throughput. The only currently available source that produces x-rays sufficiently intense to make x-ray lithography practical is the synchrotron source, which can be tailored to produce the ideal spectrum and fluence of x-rays. Although they are now large and relatively expensive, synchrotron sources that are smaller, more compact, and dedicated to x-ray lithography are being developed.

In the meantime and before x-ray lithography reaches the production stage, there remains a significant amount of research to be done in several areas, such as mask fabrication, resist characterization, and general process development. In all of these areas, it is very important to have access to a synchrotron-radiation source to test the various elements of the technology under realistic conditions.



Scientists from the IBM T.J. Watson Research Center working at the National Synchrotron Light Source have assembled all the elements of an integrated-circuit fabrication system based on x-ray lithography. The photo above shows an experimental NMOS chip made with this system. The blow-up on the opposite page illustrates the 0.5-micrometer line width achieved in this demonstration experiment.

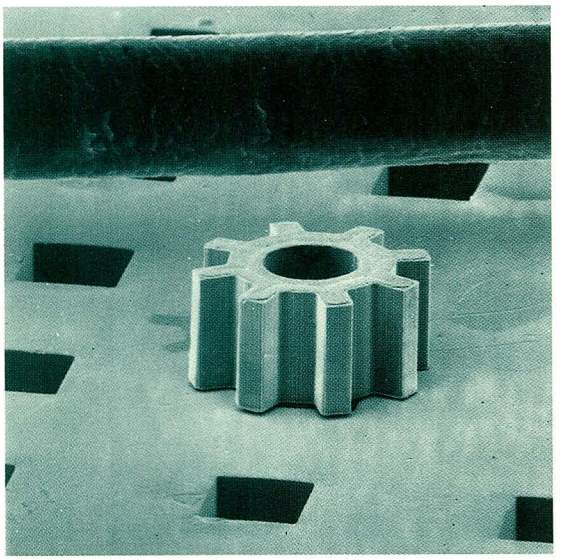
0.5µ

MICROMECHANICS

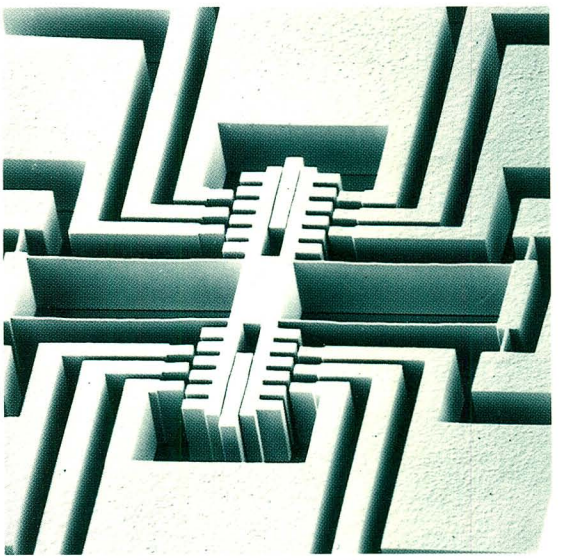
Micromechanics deals with sensors and actuators with dimensions measured in micrometers. These tiny devices are primarily made by extensions and modifications of integrated-circuit processing techniques. The major difference is that integrated circuits are essentially two-dimensional, whereas sensors and actuators are three-dimensional structures.

With x-ray lithography, submicrometer mask features can be converted to photoresist patterns with essentially vertical flanks. The resulting template can be converted to a metal structure by electroplating. Metals and alloys that can be electroplated and are compatible with this microfabrication technology include nickel, copper, gold, platinum, nickel-cobalt, and nickel-phosphorous. It is also possible to make mechanical devices that move, such as gears or turbines. Use of several masks with alignment capability and further extensions of the process now under development are expected to lead to truly three-dimensional devices.

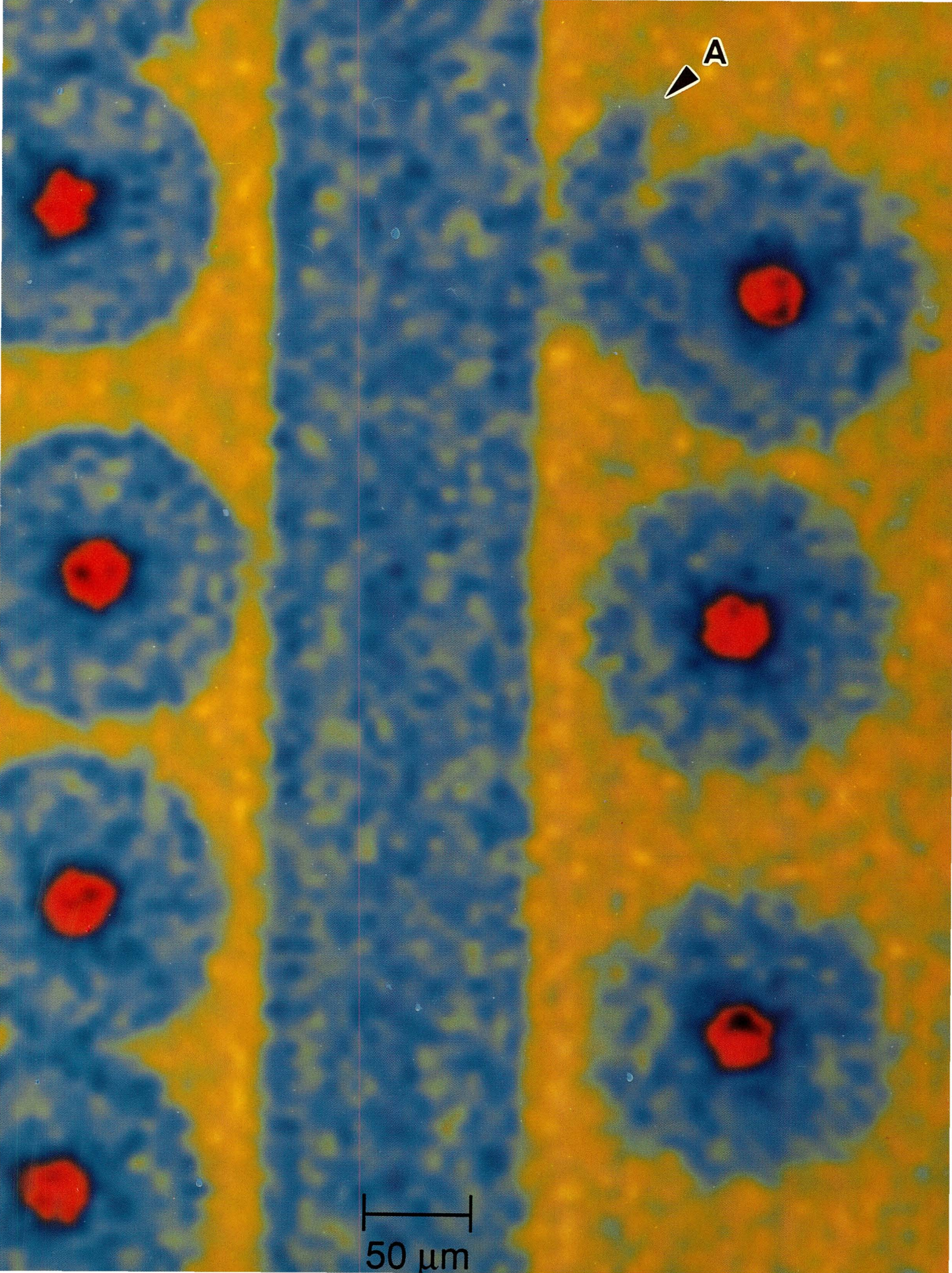
The x-ray lithography systems best suited for micromechanics are quite different from those developed for integrated-circuit applications. Typically, the structures are relatively coarse laterally (from a few to hundreds of micrometers) but may extend several tens of micrometers vertically. Exposure systems are simpler than the corresponding integrated-circuit lithography systems because the coarser lateral dimensions reduce the requirements on the alignment system. The very thick resist needed for these systems makes the use of highly penetrating hard x-rays preferable in order to produce a uniform exposure throughout the material.



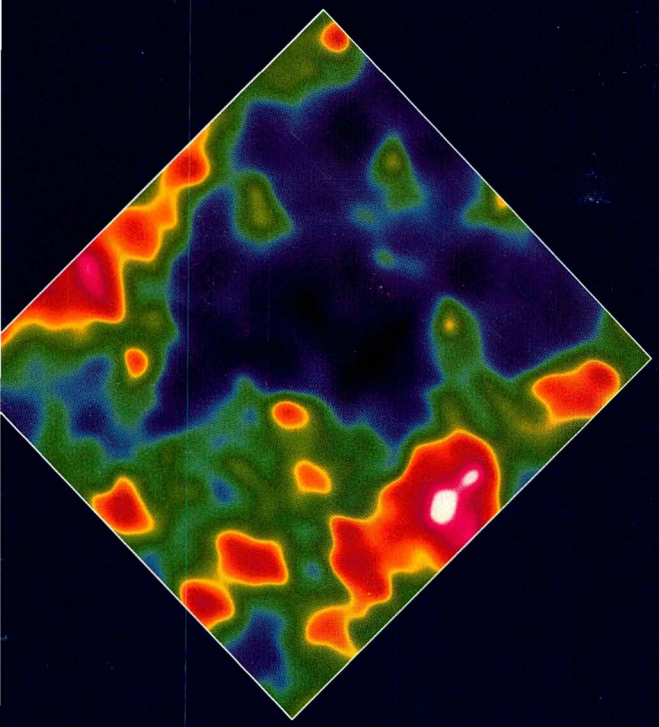
Gear fabricated by electroplating nickel onto a pattern generated in an x-ray resist at the University of Wisconsin Synchrotron Radiation Center by scientists from Wisconsin's Center for X-ray Lithography. The height of the gear is 50 micrometers. The human hair above the gear gives an additional sense of scale.



Linear actuator made of electroplated nickel 100 micrometers in thickness. Motion of the center part (rotor) is driven electrostatically. The gap between the rotor and stator is 3 micrometers. The actuator was made at the University of Wisconsin Synchrotron Radiation Center by scientists from Wisconsin's Center for X-ray Lithography.


A
50 µm

Lawrence Berkeley Laboratory
Advanced Light Source
University of California
Berkeley, California 94720



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