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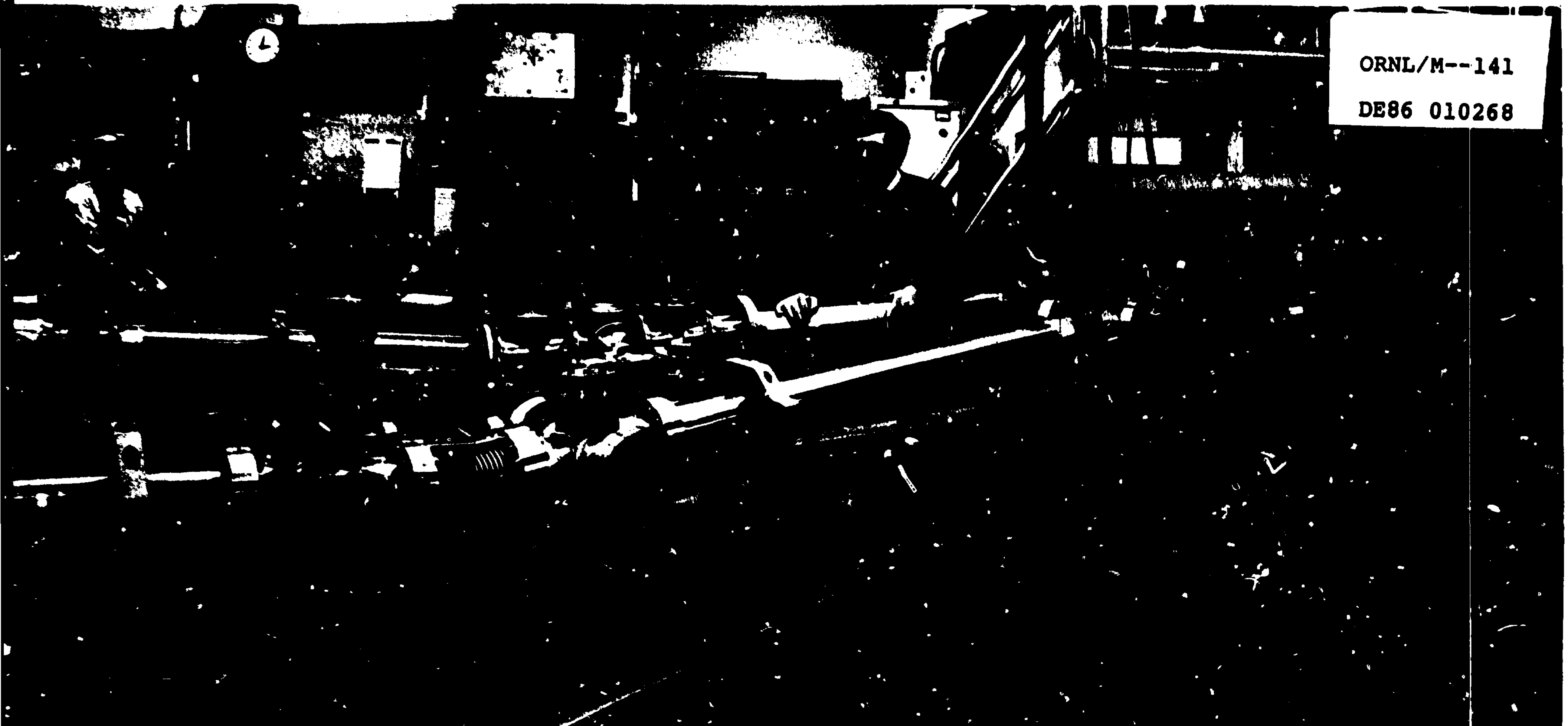
ORNL/M-141

MASTER

Surface Modification and Characterization



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Collaborative Research Center

at Oak Ridge National Laboratory

Cover: The photograph that wraps around the cover is a panorama of the Surface Modification and Characterization facility. Starting to the left on the back cover, the picture shows an edge of the 200 kV implantation accelerator, accompanying beam line, and implantation chamber. At the rear is a conference and computer/data analysis room. The beamline in the right foreground leads from a 2.5 MV Van de Graaff accelerator (not seen) and connects into the ion implantation chamber. The scientist at the rear right is operating electronics used for ion scattering data acquisition. On the front cover rear left is the Van de Graaff control console. To the right is shown a magnet that steers ions from the Van de Graaff accelerator (not seen behind magnet). Four beam lines lead from the magnet. On the inside front cover the laboratory housing a 1.7 MV Tandem accelerator can be seen thru a doorway.

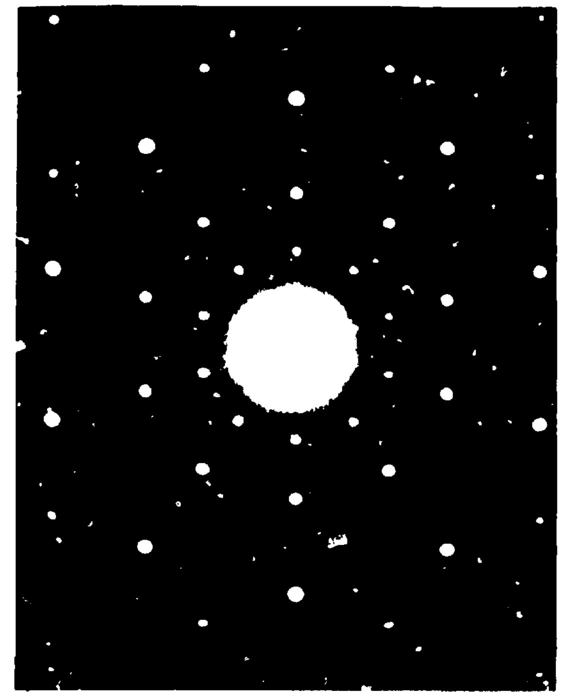
The Surface Modification and Characterization Collaborative Research Center (SMAC/CRC) is a unique facility for the alteration and characterization of the near-surface properties of materials. It is operated by the Solid State Division at Oak Ridge National Laboratory (ORNL) and is open to scientists from universities, industry, government, and other laboratories for basic and applied materials research.

The SMAC/CRC facility is equipped with particle accelerators and high-powered lasers which can be used to improve the physical, electrical, and/or chemical properties of solids and to create unique new materials not possible to obtain with conventional "equilibrium" processing techniques. Surface modification is achieved using such techniques as ion implantation doping, ion beam mixing, laser mixing, ion deposition, and laser annealing. These techniques are suitable for tailoring desired changes in a wide range of metals, semiconductors, ceramics, and insulators.

Changes in surface properties as a result of processing by these powerful tools can be probed with ion beams, electron microscopy, and other surface and bulk sensitive techniques. Theoretical modeling and data reduction are possible using the extensive computer analytical support and services that are available to visiting researchers.

The combination of processing and analysis capabilities at the SMAC/CRC is ideal for fundamental materials research. Scientists can study such complex mechanisms as melting and crystal growth, diffusion of atoms in materials, the stability of materials, superconductivity, radiation effects on materials, surface crystallography, etc. In addition, practical applications in friction, wear, corrosion, catalysis, and other fields can be explored. Surface modification research at ORNL has led to important commercial applications.

The collaborative aspect of the SMAC/CRC was established informally in 1982 in response to increasing requests for use of the research facilities. At the same time, a program was initiated to expand and improve the Center to accommodate additional users. Because of the complexity of the facilities only research performed in collaboration with ORNL researchers is supported. The goals of these mutually agreeable collaborations are to utilize the unique capabilities of the SMAC/CRC facilities for fundamental research or to demonstrate the usefulness of surface modification techniques for a particular materials application. Routine service alterations or analyses are discouraged.



Microdiffraction pattern obtained from a quasicrystal produced by implanting Mn ions into Al films held at 150 C and then laser melting. The diffraction peaks show 10-fold symmetry, a condition not allowed by crystallographic principles for periodic lattices, hence the term 'quasicrystal'. It has been found that grains up to 2500 A can be produced by pulsed laser melting of the implanted Al-Mn films. These unusual materials have generated much fundamental interest and facilities like the SMAC/CRC are attempting to unravel the structure.

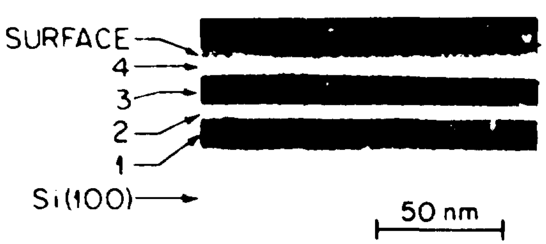
Alteration of the near-surface properties of materials is achieved using energetic ion beams and lasers. These techniques can be grouped into several processing categories:

ION IMPLANTATION DOPING: Ions that have been mass and energy selected in an ion accelerator can be injected into a solid to a desired concentration profile. The implanted ions alter and may even dominate the electrical, chemical, mechanical, or optical properties of the near-surface region of the solid.

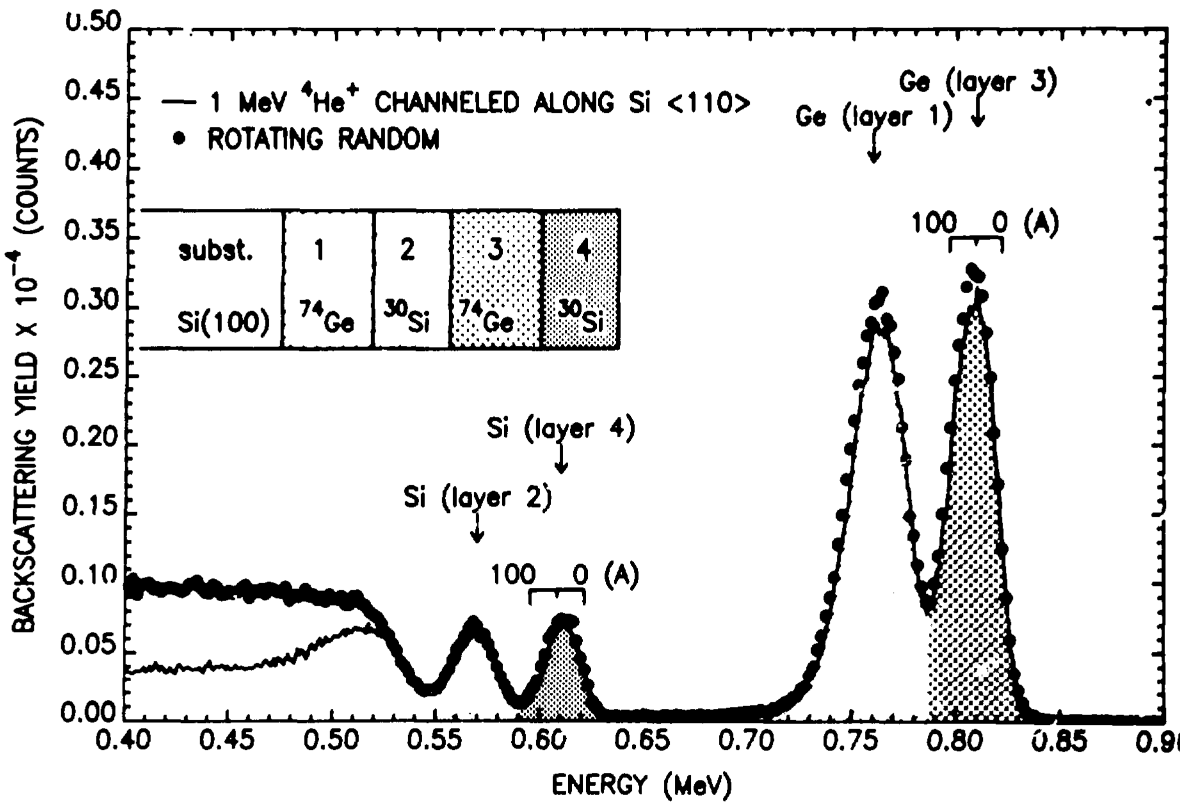
DIRECT ION BEAM DEPOSITION: Isotopically pure thin films can be deposited on selected substrates by decelerating ions extracted from an implantation accelerator to energies below the threshold for sputtering.

ION BEAM MIXING: Ballistic collisions, defect production, and other phenomena initiated when energetic heavy ions bombard a thin film of one material deposited on another can induce the two materials to interact at their interface. This can often lead to new and unique materials properties.

ION BEAM ANNEALING: Intense beams of energetic ions can be used to anneal solids as a result of beam heating and radiation-enhanced diffusion. This process may occur at the same time the dopant atoms are implanted.



Alternate germanium/silicon layers were formed by direct ion beam deposition (IBD) on a Si(100) substrate. A schematic diagram of the superstructure is given in the figure. A Rutherford backscattering spectrum indicates that the interfaces between the four films are sharp with no intermixing between the layers. A cross section TEM micrograph above gives directly the thicknesses of the layers and shows with high resolution the near-atomic sharpness of the interfaces.

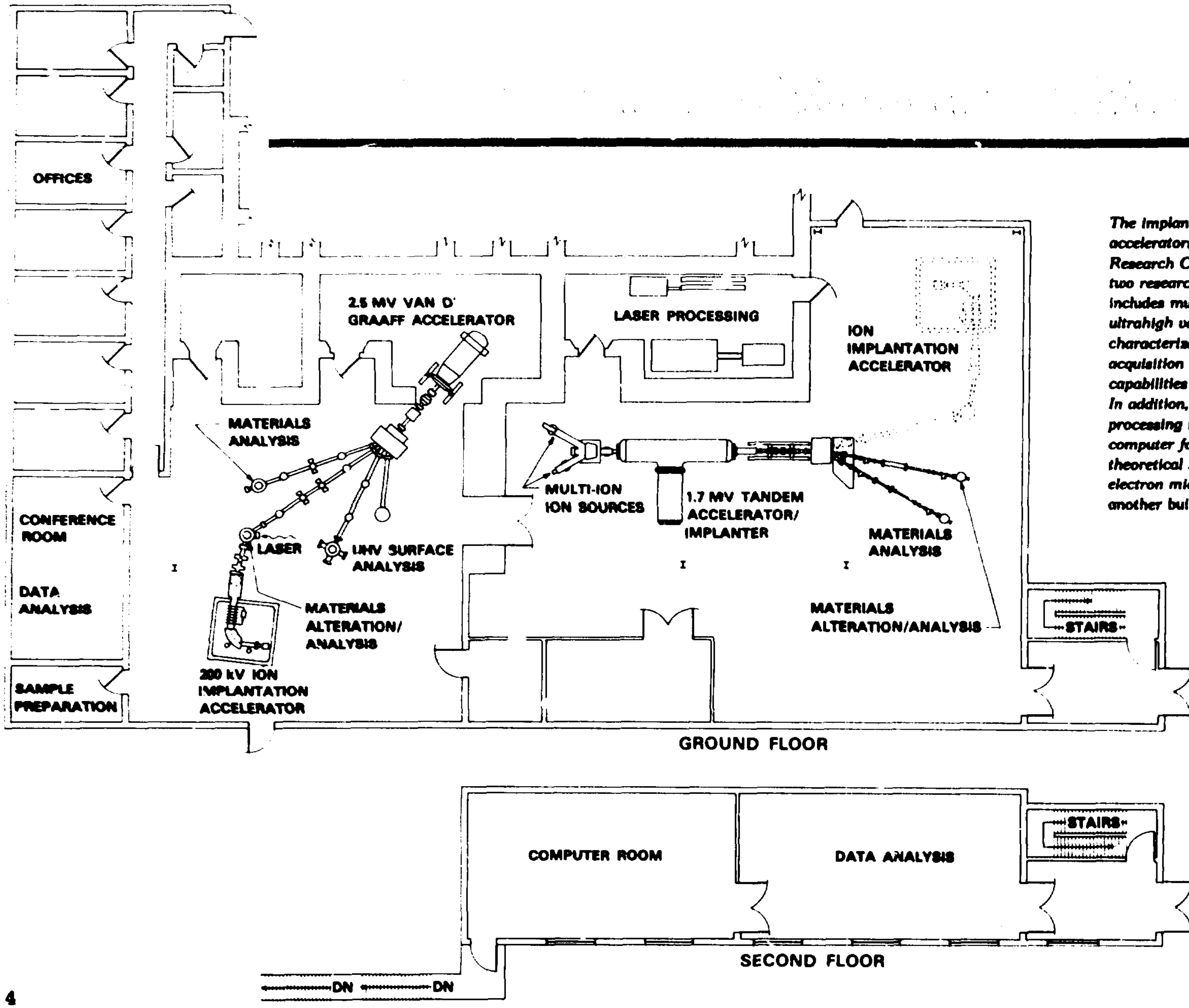


PULSED LASER ANNEALING: The near-surface regions of many solids can be melted on nanosecond time scales to controllable depths up to approximately a micron. The subsequent ultrarapid resolidification (quench rates from 10^6 to 10^{12} °C/s) often leads to nonequilibrium materials properties.

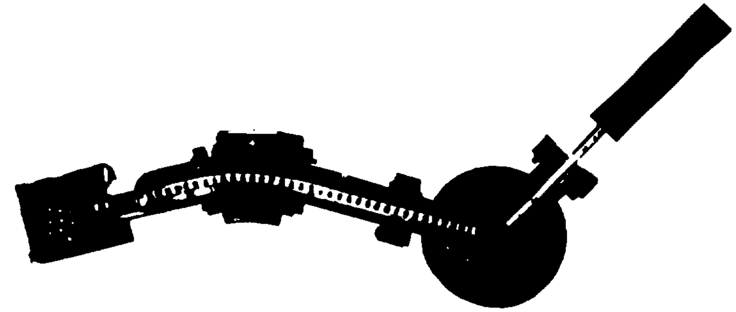
PULSED LASER MIXING: Deposited surface films may be mixed with the underlying layers using a pulsed laser of sufficient energy density to melt through the interface.

Cross section transmission electron micrograph of pulsed laser annealed amorphous silicon. A large grain polycrystalline silicon layer on top of a fine grain polycrystalline layer has regrown at the surface as a result of laser melting. The dark horizontal band is unmelted amorphous silicon and below that is the crystalline substrate.

Excimer laser and laser optics.



The implantation and ion scattering accelerators at the Collaborative Research Center are integrated into two research areas. Each area includes multiple beam lines, several ultrahigh vacuum processing and characterization chambers, and data acquisition electronics, and has the capabilities for in situ laser annealing. In addition, there is a separate laser processing room and a dedicated computer for data analysis and theoretical studies. A scanning electron microscope is located in another building.



EXISTING FACILITIES

ACCELERATORS	SPECIES	ENERGY	CURRENT*	BEAM DIA	PRIMARY USES
2.5 MV Van de Graaff	H^+	0.1–2.5 MeV	0.5 μA	0.5–2 mm	Ion beam analysis,
	$^4He^+$, $^3He^+$	0.1–2.5 MeV	250 nA	0.5–2 mm	channeling,
	Selected gases	0.5–2.5 MeV	10–50 nA	0.5–2 mm	nuclear reaction analysis
1.7 MV Tandem	H^+	0.8–3.4 MeV	6 μA	0.5–2 mm	Ion beam analysis,
	He^+	0.8–5.1 MeV	100 nA	0.5–2 mm	channeling, nuclear reaction analysis
	Most heavy ions	0.8–5.1 MeV		0.5 mm–8 cm	High energy implantation, nuclear reaction analysis
200 kV Ion implanter	Mass <185 amu	35–180 keV	0.01–1 mA	2.5 cm	Singly charged implantation
	Most species	70–360 keV	10–100 μA	2.5 cm	Doubly charged implantation
	Most species	0.02–1 keV	10–50 μA	1.5 cm	Ion beam deposition

*Current at maximum energy and beam diameter

LASERS	WAVELENGTH	PULSE LENGTH	POWER	SPOT SIZE	PRIMARY USES
Pulsed ruby	694 nm	15–30 nsec	3 J TEM_{00}	2 cm	Laser annealing, laser mixing, rapid solidification
Pulsed excimer	248 nm	25 nsec	0.5 J	0.5 cm	

SEM	VOLTAGE	RESOLUTION	ATTACHMENTS	PRIMARY USES
JEOL JSM 840	0.2–40 kV	3–4 nm	X-ray detector, EBIC imaging system	Surface topography, elemental analysis

COMPUTER	OPERATING SYSTEM	PRIMARY USES
PDP11/44	RSX 11M+	Data reduction, theoretical modeling, plotting

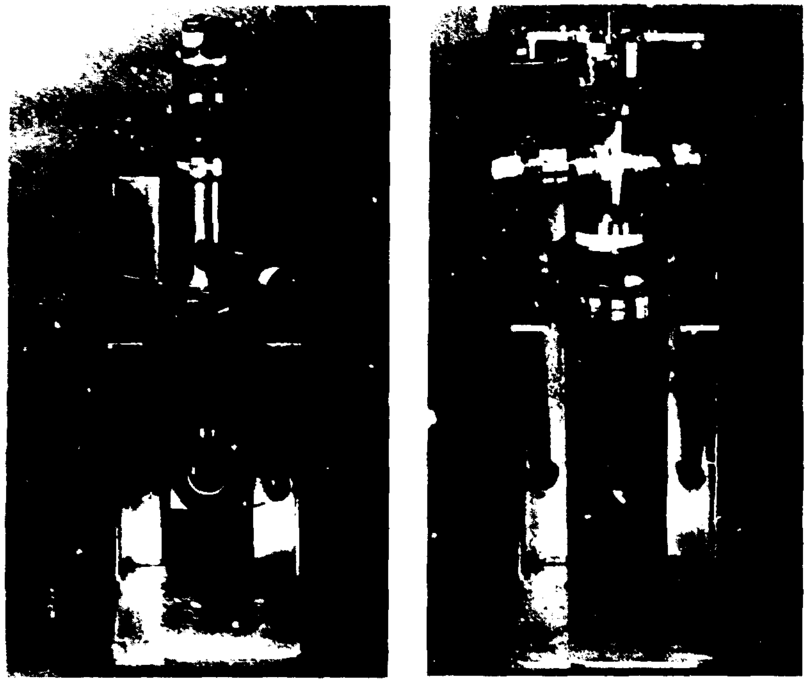
PROPOSED FACILITIES

ACCELERATOR	CAPABILITIES	USES	AVAILABILITY
Ion implanter	200 keV, 1–10 mA, all species	Ion implantation, ion beam deposition	1987

LASER	PULSE LENGTH, POWER	USES	AVAILABILITY
Short pulsed excimer	03–20 nsec pulse length, 1 J total energy	Ultrarapid solidification	1988

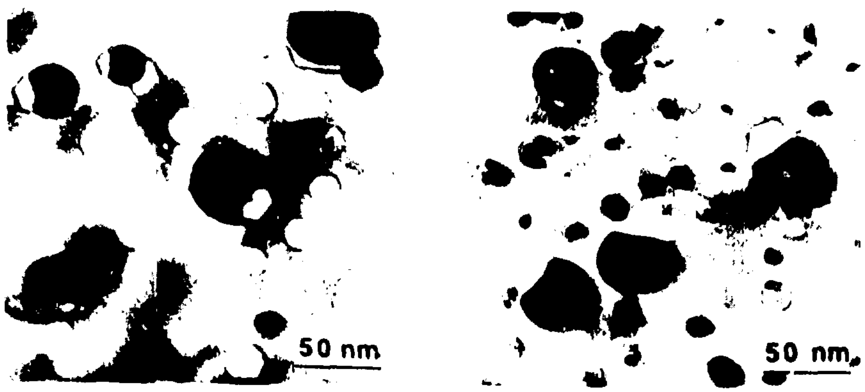
COMPUTER	USES	AVAILABILITY
Super mini	Data reduction, theoretical simulation, graphics modeling	1987

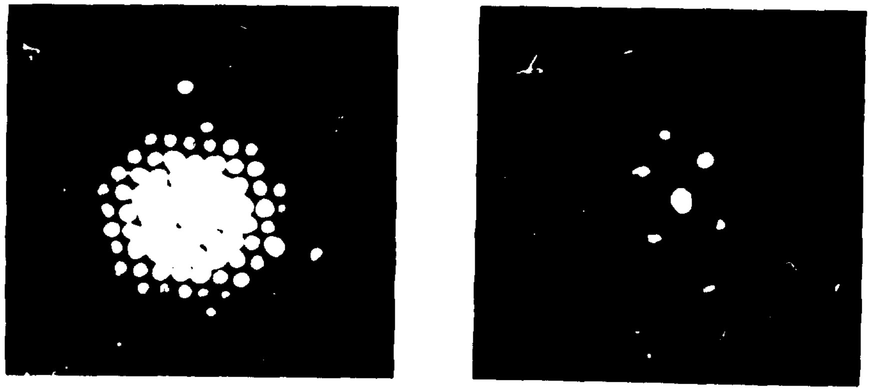
Cross section, z-contrast, scanning transmission electron micrograph from a silicon sample implanted at 80 keV with antimony. The light areas are due to enhanced electron scattering from the near-Gaussian antimony implantation distribution.



Sample manipulators used for ion implantation or analysis.

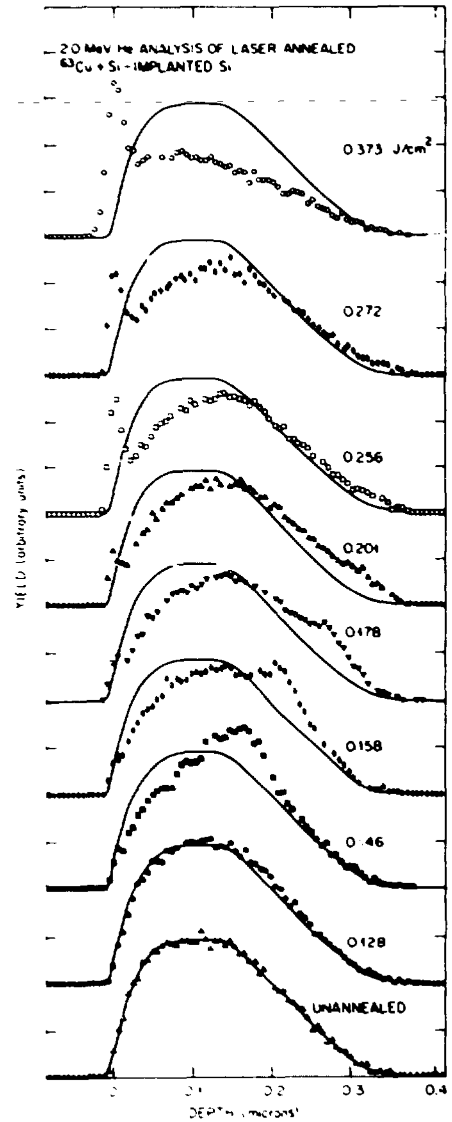
ELECTRON MICROSCOPY OF ^{56}Fe (160 keV, 4 X $10^{16}/cm^2$) IMPLANTED IN Al_2O_3



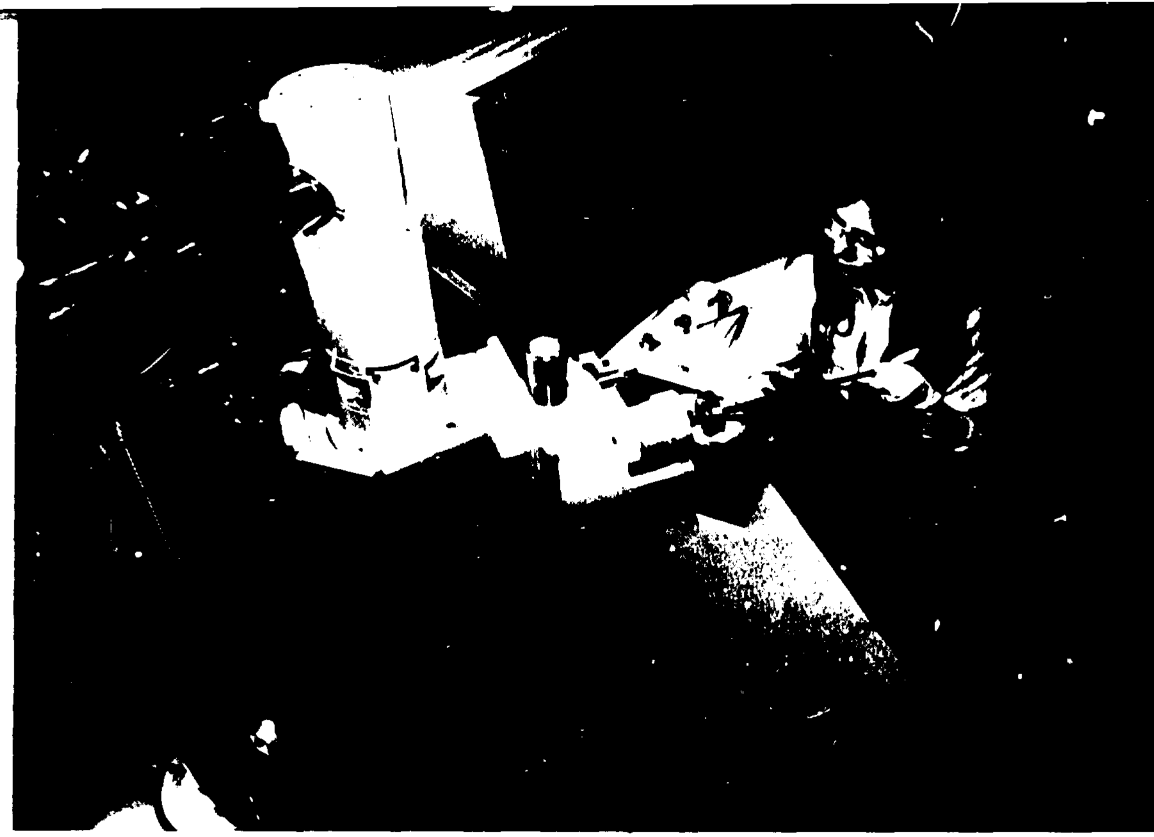


PRECIPITATES Fe_3O_4 PRECIPITATES α Fe

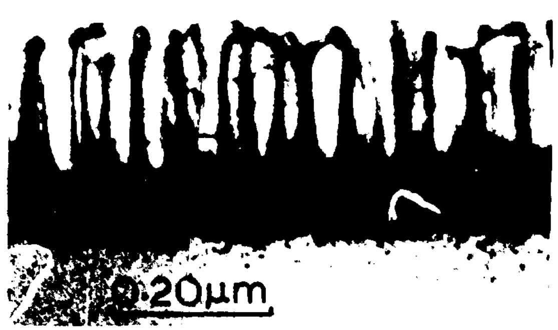
Surface modification is used to alter mechanical properties such as surface hardness or fracture toughness in ceramics. The transmission electron micrographs shown here are from alpha-Al_2O_3 implanted with 160 keV Fe to a dose of 4 × $10^{16}/cm^2$ and annealed for 1 hour in oxygen (upper left) or hydrogen (upper right). The dark regions are surface precipitates, the light regions are voids, both produced as a result of surface processing. Convergent beam electron diffraction patterns obtained from the precipitates and shown below the micrographs indicate the precipitates are Fe_3O_4 (lower left) and α-Fe (lower right). These samples exhibited increased surface hardness as a result of processing.



The use of ion implantation and laser annealing to study melting and resolidification in solids is illustrated by these Rutherford backscattering spectra of depth distributions of Cu in amorphous Si following laser annealing. The solid line is the as-implanted Cu distribution. Since Cu preferentially segregates into the melt, movement of Cu deeper into the Si, which occurs at the lower laser energy densities, is expected for a buried molten layer that propagates into the solid. At higher energies Cu is transported to the surface and some evaporates as the melt front moves to the surface.



Scanning electron microscope at the Collaborative Research Center.



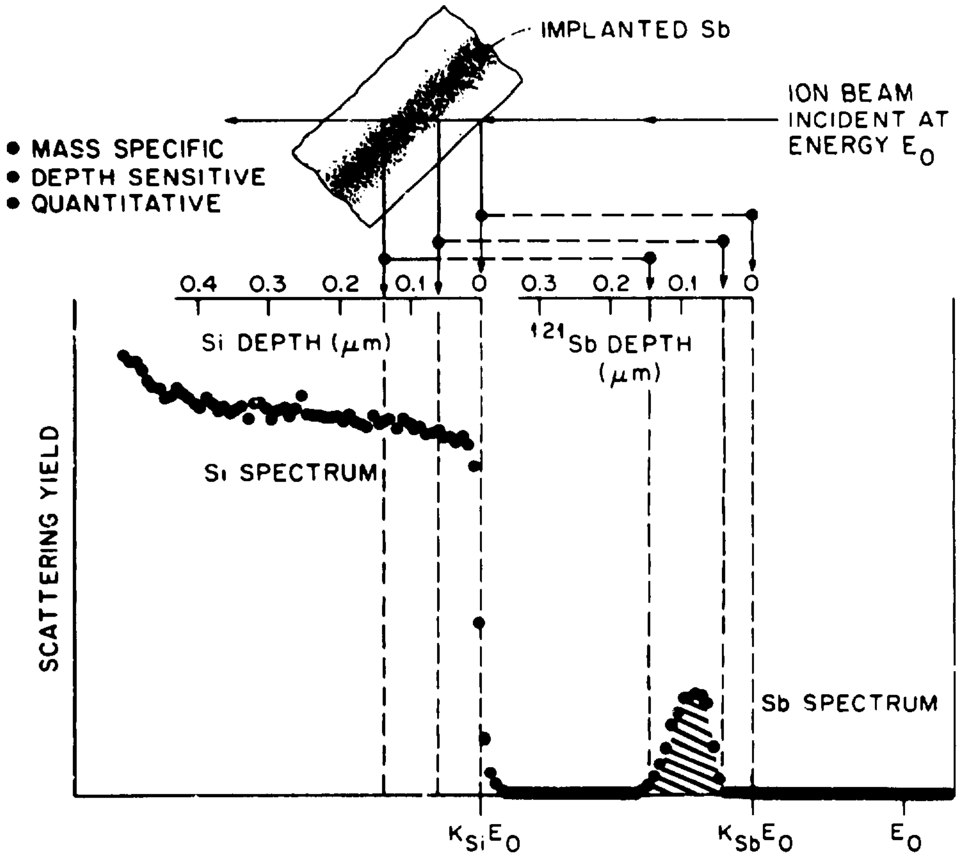
Cross section transmission electron micrograph of Ge(111) after room temperature implantation of 5×10^{15} In/cm² at 120 keV. The heavy ion irradiation initially amorphizes the near-surface region. Additional implantation initiates a morphological instability in the amorphous Ge which erupts to form surface craters.

Computer facility at the Collaborative Research Center.

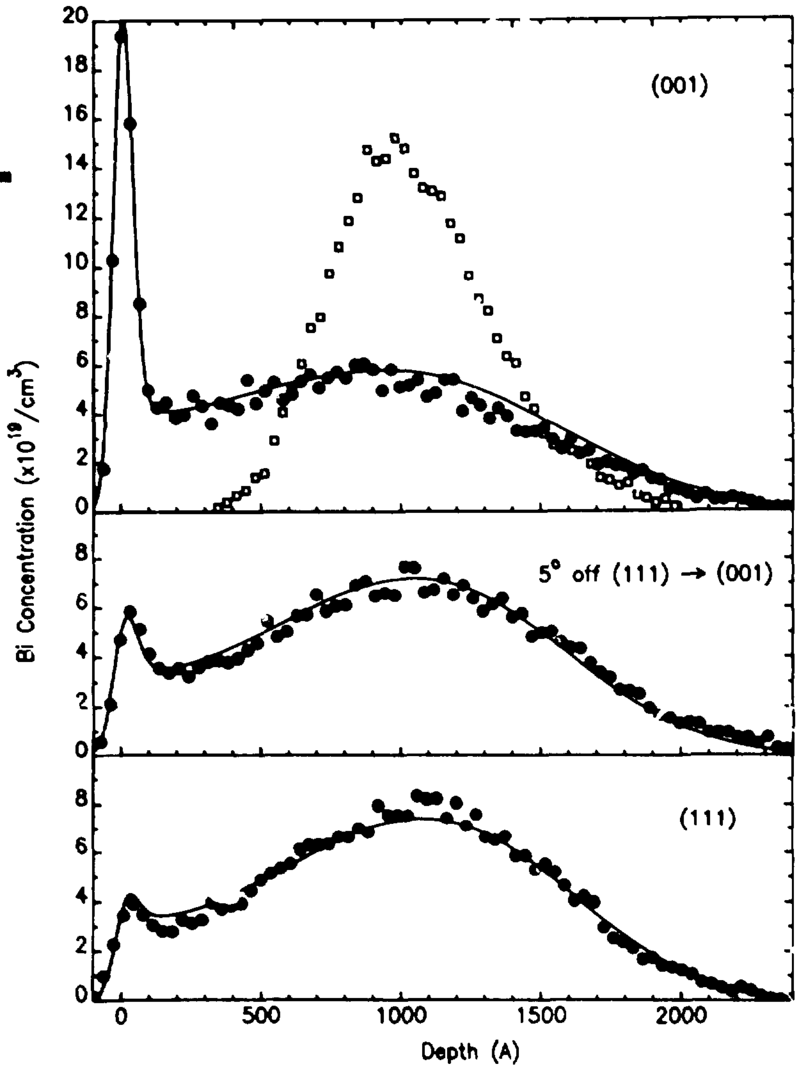
In situ characterization of the near-surface region of samples processed at the SMAC/CRC is possible using ion beam and surface analytical techniques.

ION SCATTERING: Positive ion scattering provides a nondestructive, mass specific, quantitative, and depth sensitive profile of the near-surface stoichiometry of virtually any solid. Specific techniques include Rutherford backscattering, enhanced elastic backscattering, elastic recoil detection, and others.

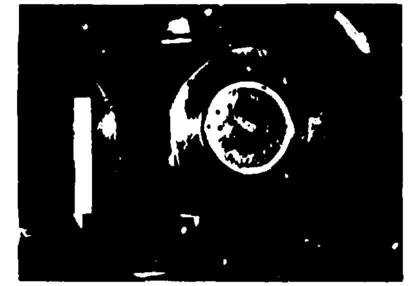
POSITIVE ION CHANNELING: The channeling phenomenon of positive ions in single crystals can be used to monitor lattice perfection and/or ion damage, locate positions of impurity atoms in the lattice, deduce annealing behavior, determine impurity diffusion and interactions, investigate stopping powers and atomic interaction potentials, and analyze other induced materials interactions and fundamental materials properties.



Rutherford elastic scattering spectrum for helium scattered from silicon implanted with antimony.



Si samples of various orientations were given identical Bi implants of $5 \times 10^{14}/cm^2$ at 100 keV and annealed using a pulsed excimer laser with a wavelength of 248 nm, pulse duration 24 ns FWHM. Following this treatment, redistribution of the Bi was measured using ion scattering. The depth profiles were fit using computer codes that model the nonequilibrium atomic diffusion and trapping processes occurring. The agreement between experiment and computer simulation indicates the melt and regrowth model adequately explains the physics and provides quantitative predictions of physical parameters in the model.



NUCLEAR REACTION ANALYSIS: Ion-induced nuclear reactions can be used for quantitative and depth sensitive profiling in specific cases, for example, to improve detection sensitivity for many low-mass species.

SURFACE ANALYSIS TECHNIQUES: Experimental ultrahigh vacuum chambers are available that combine ion beam techniques with the surface sensitive techniques of low energy electron diffraction and Auger electron spectroscopy. This facility is used for studying reordered and relaxed clean surfaces, crystal growth, and other surface phenomena.

COMPUTER ANALYSIS: Computing facilities are available for analyzing spectra obtained at the SMAC/CRC. Extensive software allows convenient viewing and reduction of data, plotting, and manuscript preparation. Theoretical modeling of ion and laser beam interactions with materials is possible using codes that predict deposition profiles, describe laser annealing, and simulate ion scattering from surfaces and other particle-solid interaction phenomena.

Fundamental Materials Interactions

Ion implantation doping, ion beam deposition, pulsed laser annealing, and ion beam and pulsed laser mixing are nonequilibrium processing methods which can lead to ne... ...als properties. Conseque... ... are ideal fundamental researc... ... Some examples of applicabl... ...arch topics include the following

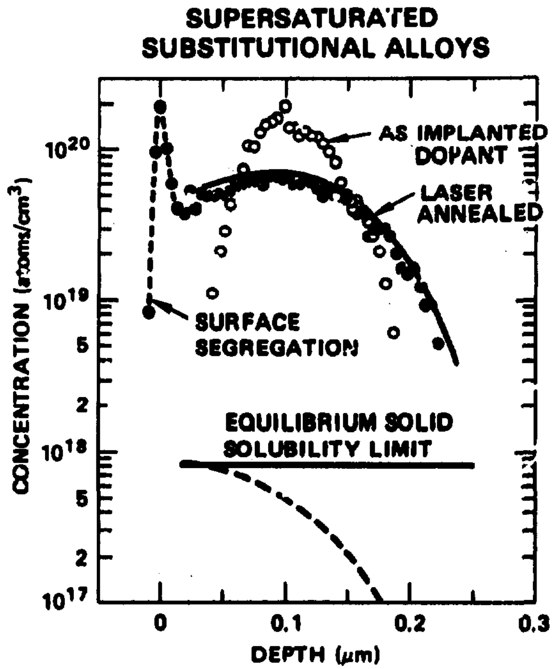
ION-INDUCED INT... ...TIONS: The complex nature of defect production and interactions in ion-irradiated solids offers a new dimension for inducing materials interactions which can lead to unique properties.

ULTRARAPID SOLIDIFICATION: Pulsed laser annealing can be controlled to give surface quenching rates that vary from 10^6 to 10^{12}°K/s. Ion-induced collision cascades in solids provide energy pulses to several thousand atoms within the cascade with simulated quenching rates of 10^{11}–10^{13}°K/s.

RAPID CRYSTAL GROWTH: Crystal growth phenomena ranging from solid to liquid phase epitaxy can be studied at growth rates from 10^{-10} to 10^2m/s by coupling conventional furnace annealing techniques with pulsed laser annealing. Related phenomena include solubility limits, solute trapping, constitutional supercooling, and a host of others.

NUCLEATION KINETICS, PRECIPITATION, AND SEGREGATION: Utilizing the tremendous span of growth rates available, it is possible to study in detail the kinetics of nucleation, precipitate nucleation and dissolution, segregation phenomena, and interfacial instabilities.

NEW MATERIALS PROPERTIES: Ion beam and laser processing techniques have been used to fabricate new metastable alloys, supersaturated substitutional semiconductors, extended solid solutions, new metastable surface structures, unique lattice alterations including layered crystals, and amorphous metaglasses and metals.



Concentration versus depth profiles obtained by ion scattering from a silicon single crystal implanted with bismuth and laser annealed.

Areas of Applied Research

TAILORED MICROSTRUCTURES: Ion bombardment and laser melting can be used to induce grain refinement, nucleation, precipitate formation, amorphous phases and a variety of other microstructural alterations.

CORROSION, FRICTION, WEAR: Most mechanical, chemical, electrical, and optical effects which are surface related can be altered, often quite dramatically, by ion beam and laser processing.

SEMICONDUCTOR AND OPTO-ELECTRONIC DEVICES: Device fabrication problems can be addressed, ranging from the formation of new supersaturated substitutional alloys to adherent metal electrical contacts to improved optical waveguides.

ADHESION: The adhesion of metal films on metals, insulators, and semiconductors has been greatly enhanced by ion beam processing.

AMORPHOUS MIXTURES: Amorphous mixtures and metaglasses of a wide variety of materials can be made over greatly extended compositions because of the extremely rapid quenching rates of ion beam and laser processing.

CERAMIC PROCESSING: The hardness and fracture toughness of high temperature ceramics, the electrical properties of insulators and polymers, and the optical properties of waveguide materials have been beneficially altered using ion implantation.

Titanium alloy (Ti-6A1-4V) samples, unimplanted (left) and ion implanted with N to a dose of 20 atomic percent (right), were wear tested under chemical and mechanical conditions that approximate those existing in hip and knee joints. Dramatic improvement is seen in corrosive wear performance. Artificial joints made using an ion implant treatment on this alloy are presently available.

Researchers interested in more information about the SMAC/CRC should contact the Facility Liaison Scientist.* Those desiring to use the Center will be asked to submit a short proposal detailing the scientific problem to be addressed and an estimate of the support needed and time required.

Acceptance of proposals depends on their scientific merit, the suitability of the Center for the research, the appropriateness of the research to DOE objectives, and selecting an ORNL researcher interested in the collaboration.

There is no charge for use of the SMAC/CRC. Collaborators, however, are responsible for transportation, lodging, and all other costs they incur. In most cases, collaborators will be expected to take part in the research at the Center.

A brief technical report highlighting significant results will be required of SMAC/CRC users. Presentations and publications resulting from collaborations should acknowledge the SMAC/CRC and reprints of published articles need to be available at the Center.

Send requests for information and proposals for use to:

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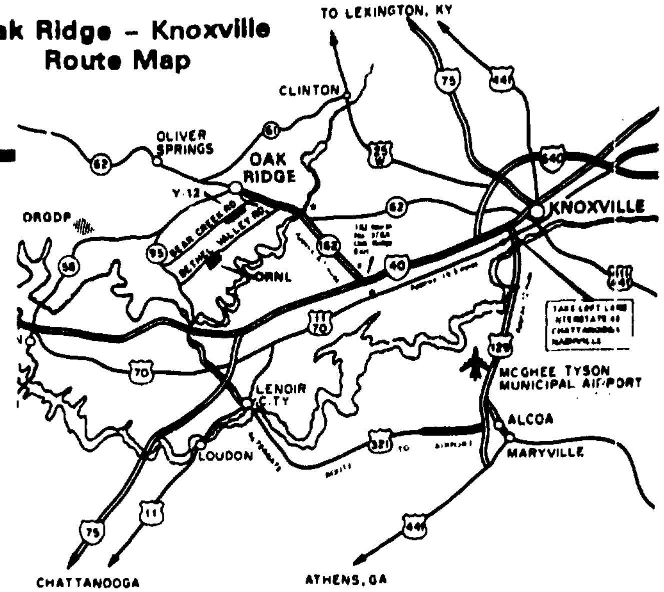
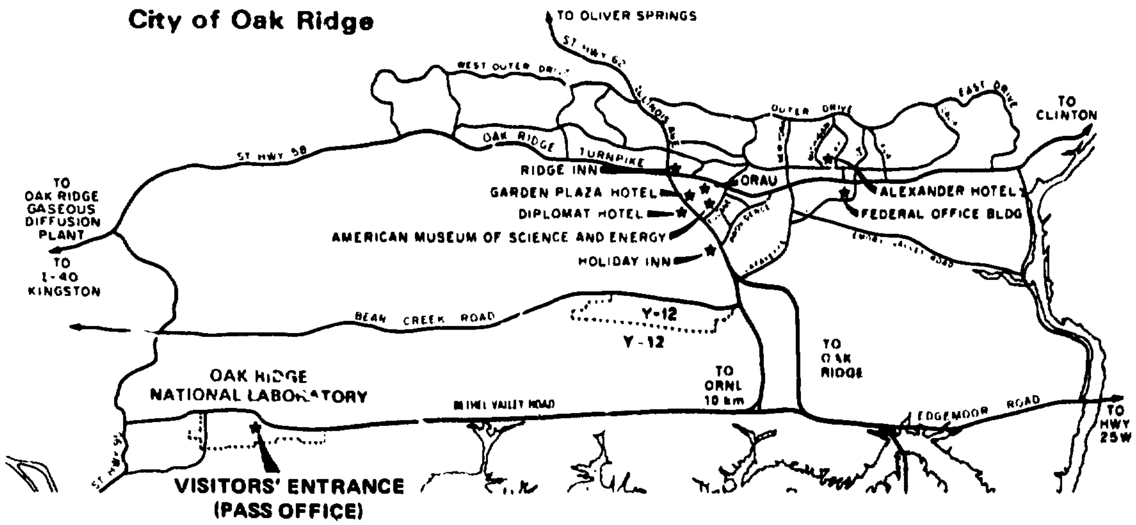
Oak Ridge - Knoxville Route Map



City of Oak Ridge



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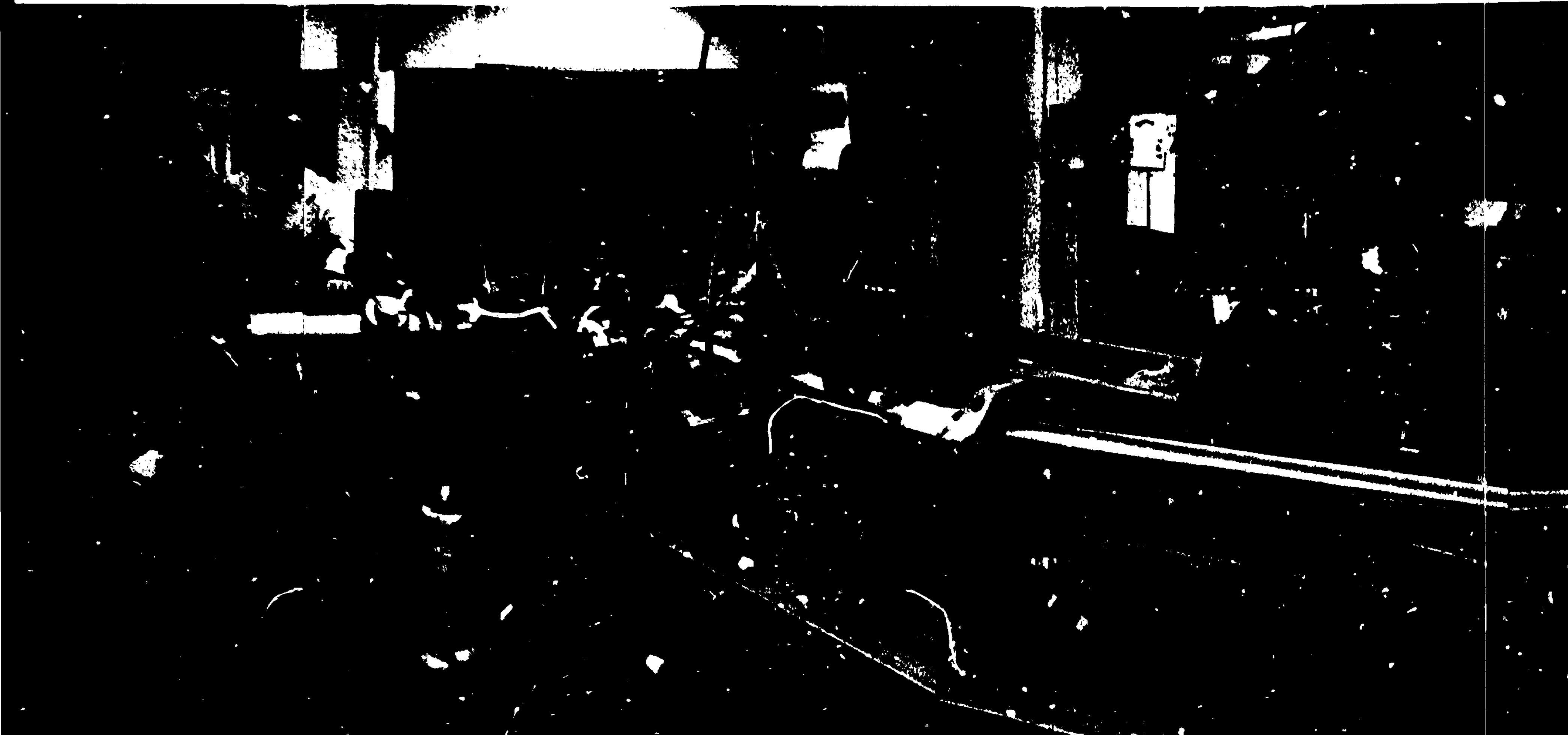
Photograph of the 1.7 MV Tandem accelerator facility. The beamline and experimental vacuum chamber to the left is designed for conventional ion backscattering analysis. The beamline to the right includes a rastor scan for the beam so that high energy implantations are possible for many elements.



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