



*Spectacular advances in the development of artificial materials—now engineered on the nanometer scale—have spurred the parallel development of new tools to characterize surface and interfacial structure at the atomic scale. Our surface physics facility applies ultra-high-vacuum scanning tunneling microscopy to accelerate the development of such advanced materials.*

# Scanning Tunneling Microscopy: Opening a New Era of Materials Engineering

**I**N the last decade, the ability of materials scientists to “nanoengineer” artificial materials—to build materials atom by atom with a predetermined arrangement and goal—has enabled the development of new technologies with applications that range from the spectacular to the mundane.<sup>1,2</sup> For example, x-ray mirrors composed of alternating, thin (less than 20-nanometer) films of molybdenum and silicon constitute the optics that are used to produce high-resolution pictures of the sun. Optoelectronic components composed of alternating atomic layers of different elements are the devices that enable us to extract information from video compact disks and to generate and detect transoceanic telephone signals by fiberoptic cables. The alternating, ultrathin layers of cobalt and iron in new high-density magnetic storage heads, and increasingly miniature microelectronics, are fundamental constituents of powerful desktop computers, portable laptops, and pocket-size wireless telephones.

The smaller these devices become, the more their performance depends on the atomic ordering of their constituent materials. Such details include the arrangement of atoms in crystal structures and the presence, size, and density of grain boundaries, impurities, dislocations, or other imperfections. Enhanced performance of a device—increased reflectivity in the case of x-ray mirrors, efficiency in the case of

optoelectronics, switching speed in the case of transistors for microelectronics, and hardness in the case of high-strength coatings—therefore depends critically on the precise control of the details of atomic ordering during manufacture. This is where LLNL’s surface physics facility in the Chemistry and Material Science Directorate enters the picture with its ultra-high-vacuum scanning tunneling microscopy capabilities.

## Analyzing Atomic Arrangement

To diagnose the effect of atomic arrangement on material performance, materials scientists use a battery of techniques. Traditionally, diffraction-based probes have been the mainstay of structural analysis, and have provided most of our basic knowledge about the atomic arrangement of materials. In diffraction, a beam of light or particles (neutrons, electrons, etc.) is scattered from an object, and the three-dimensional, geometric distribution of the scattered rays is determined by the structure of the object. For example, the pattern of visible light reflected from the surface of an audio compact disc held under bright light indicates the spacing of bits written onto the disc. Similarly, the diffraction of beams of a wavelength that is comparable to the spacing between atoms in a crystal indicates the spacing between the atoms.

X-ray diffraction, the primary tool for analyzing the long-range, atomic ordering of solids, enabled the development of crystallography and provided the experimental data from which the structure of DNA was deduced. Transmission electron microscopy, another diffraction-based tool, is often used to provide images of imperfections in crystals. In both x-ray diffraction and transmission electron microscopy, however, diffraction measurements reveal the internal atomic arrangements of a material only when crystalline order extends over at least several hundred atomic spacings; in this case the material is said to exhibit “long-range” order. In contrast, when crystalline order exists over shorter distances, the material is said to exhibit “short-range” order, which may not be detected by diffraction.

## Analyzing Surface Structure

These two diffraction techniques present the “bulk,” or three-dimensional, atomic arrangement of a material. In nanoengineering, however, we must control how the individual atomic layers of material are deposited. Because the structural integrity of each atomic layer depends critically on the detailed atomic ordering of the surface upon which it is deposited, we must be able to “see” the atomic ordering, or structure, of that surface. To do this, we need a separate class of diagnostics that presents the two-dimensional atomic

arrangement of the outermost layer of atoms in a material, rather than its three-dimensional bulk structure.

## Low-Energy Electron Diffraction

For many years, the characterization of surface structure has relied on the diffraction of electrons of low energy (fewer than 200 V). Because such low-energy electrons do not penetrate beyond a few atomic layers into a crystal, their diffraction from a crystal yields the long-range atomic order on a surface. Although low-energy electron diffraction is responsible for most of our current knowledge of surface crystallography, it cannot reveal the short-range crystalline order of nanometer-scale dimensions. Yet it is on this very scale that clusters of deposited atoms initially aggregate, or nucleate, and influence the atomic arrangement of subsequently grown material. In this regime, true atomic resolution is necessary, and the scanning tunneling microscope is indispensable.

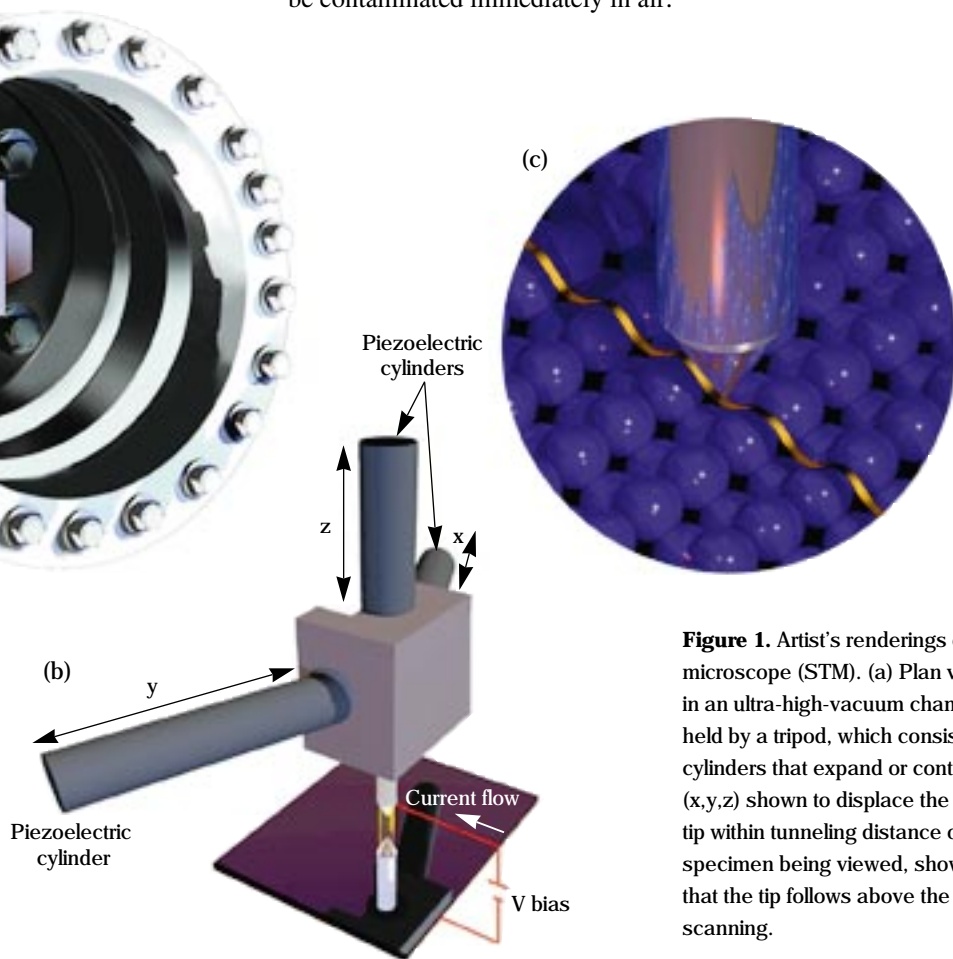
## Scanning Tunneling Microscopy

The scanning tunneling microscope<sup>3</sup> (STM) provides a picture of the atomic arrangement of a surface by sensing corrugations in the electron density of the surface that arise from the positions of surface atoms (see [Figure 1](#)). A finely sharpened tungsten wire (or “tip”) is first positioned within 2 nanometers of the specimen by a piezoelectric transducer, a ceramic positioning device that expands or contracts in response to a change in applied voltage. This arrangement

enables us to control the motion of the tip with subnanometer precision. At this small separation, as explained by the principles of quantum mechanics, electrons “tunnel” through the gap, the region of vacuum between the tip and the sample. If a small voltage (bias) is applied between the tip and the sample, then a net current of electrons (the “tunneling current”) flows through the vacuum gap in the direction of the bias. For a suitably sharpened tip—one that terminates ideally in a single atom—the tunneling current is confined laterally to a radius of a few tenths of a nanometer. The remarkable spatial resolution of the STM derives from this lateral confinement of the current.

Next, additional piezoelectric transducers are used to raster the tip across a small region of the sample. As the tip scans the surface, corrugations in the electron density at the surface of the sample cause corresponding variations in the tunneling current. By detecting the very fine changes in tunneling current as the tip is swept across the surface, we can derive a two-dimensional map of the corrugations in electron density at the surface.<sup>4</sup> Procedures for synthesizing various nanoengineered materials often involve depositing the atoms onto a surface in such a way that the surfaces remain free of contamination. The use of ultra-high vacuum enables the preparation and atomic-resolution imaging of atomically clean surfaces, which would otherwise be contaminated immediately in air.

That is why we integrated a scanning tunneling microscope into an ultra-high-vacuum environment that includes facilities for the preparation and maintenance of atomically clean surfaces, as well as sources of the material to be deposited. We also integrated complementary, conventional surface diagnostics equipment, such as a low-energy electron diffraction probe, into this environment. The latter measures the long-range order on a surface, and STM presents the short-range order that otherwise might not be detected. In this environment, the STM offers a new opportunity for direct diagnosis of how the processing conditions affect the atomic details of surfaces.



**Figure 1.** Artist's renderings of a scanning tunneling microscope (STM). (a) Plan view of the STM mounted in an ultra-high-vacuum chamber. (b) The probe tip as held by a tripod, which consists of three piezoelectric cylinders that expand or contract in the directions (x,y,z) shown to displace the tip. (c) A close-up of the tip within tunneling distance of the surface of the specimen being viewed, showing the ribbon-like path that the tip follows above the surface atoms during scanning.

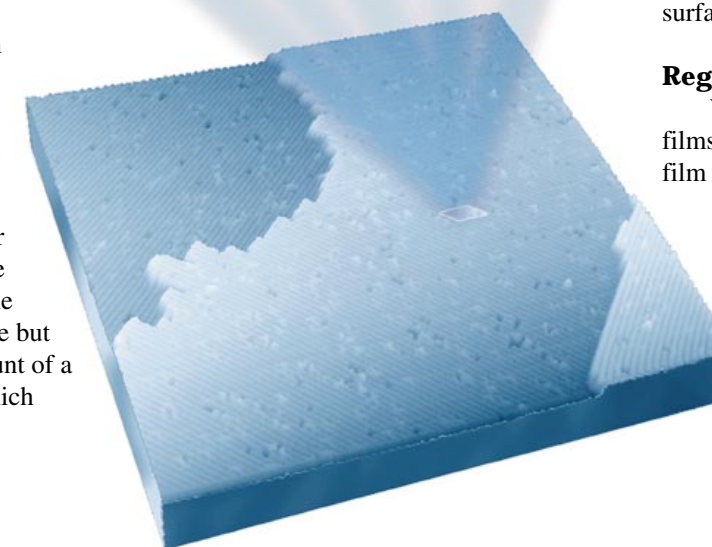
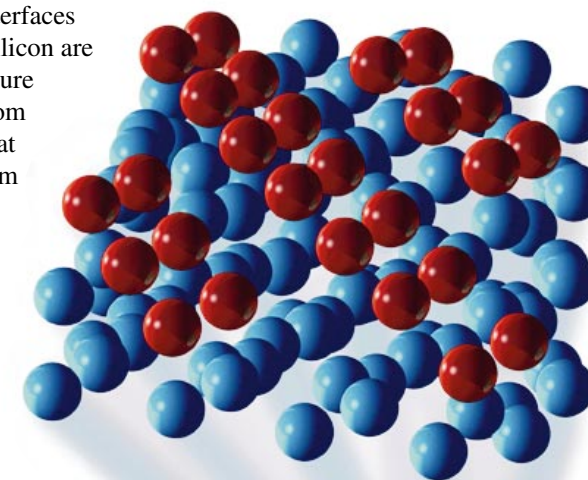
## How the Molybdenum-Silicon Interface Forms

Recently, we used this combination of surface diagnostics to study the structural development of thin films (films from one atom to several tens of nanometers thick) resulting from depositing molybdenum atoms on atomically clean silicon substrates. The data from this study can be used to develop new processes for synthesizing films that can achieve higher performance for particular applications.

For example, multilayer x-ray mirrors composed of alternating, 5- to 20-nanometer-thick layers of molybdenum and silicon achieve the best reflectivity when the interfaces between molybdenum and silicon are most abrupt—that is, when pure molybdenum is separated from pure silicon by a perfectly flat plane. However, molybdenum and silicon tend to react to form crystalline compounds, or interfacial silicides, which may adopt a variety of distinct crystal structures called phases. Because these silicides degrade this interfacial abruptness, we are trying to define processing conditions that minimize the amount of interfacial silicide.

However, molybdenum silicides also appear in other applications, such as high-temperature coatings and diffusion barriers for interconnects in very large-scale integrated circuits. For these applications, it may be desirable *not* to minimize the amount of interfacial silicide but rather to *maximize* the amount of a particular silicide phase, which

may lead to enhanced performance. Our analysis is therefore intended to provide a broad correlation between the processing conditions (for example, substrate temperature and deposition rate) and the microstructural details of the resulting films, which ultimately determine how well the device will perform for a specific application. We have found that film morphology—characteristics such as roughness, crystalline structure, and grain size and orientation—depends strongly on small structures called precursors. These structures form during the initial stages of film growth and can only be detected with scanning tunneling microscopy.<sup>5</sup>



## Phases and Atomic Compositions

This reaction between molybdenum and silicon exhibits a particularly rich variety of phases and relative compositions of molybdenum and silicon, such as  $\text{MoSi}_2$  and  $\text{Mo}_3\text{Si}$ . The structure of disilicide thin films, as opposed to bulk crystals, is further complicated by interfaces—both the silicide/substrate interface and the silicide surface itself. For example, there is a thin disilicide film phase that exhibits hexagonal symmetry that does not even appear in the bulk phase. Furthermore, the precise temperature at which this phase transforms to the equilibrium phase of tetragonal symmetry appears to be highly process dependent. The STM can help us understand these phases and transformations.

For example, we used the surface of crystalline silicon—designated  $\text{Si}(100)$ —as the starting substrate for film deposition. When clean  $\text{Si}(100)$  is exposed, the atoms of the surface are rearranged—as is the case with most semiconductor materials. In fact, bonds are formed between adjacent atoms, each pair of which is called a “dimer.” The dimers then align themselves into rows on the surface, as shown in **Figure 2**. These surface structures are important to STM studies that seek to extract chemical information about a particular surface (see **box on page 8**).

## Regimes of Silicide Film Growth

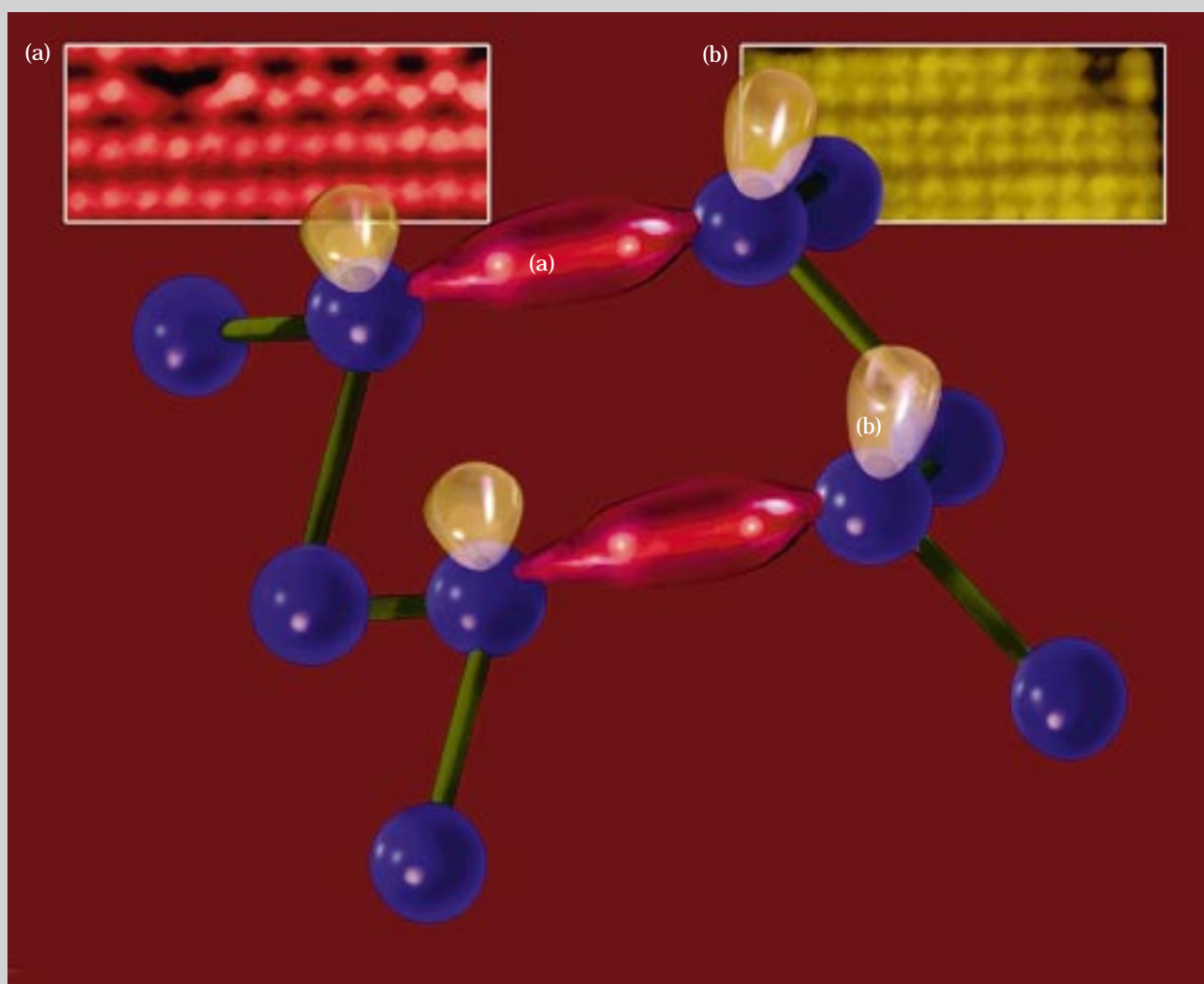
When we use STM to examine these films, we find several regimes of silicide film growth. When molybdenum is

**Figure 2.** (Below) A 650-angstrom (Å) STM image of the surface  $\text{Si}(100)$ , in which each stripe represents a row of dimers. (Above) Illustration of the atomic structure of the  $\text{Si}(100)$  surface. The outermost, dimerized atoms that contribute to the STM image below are shown in red in the illustration above.

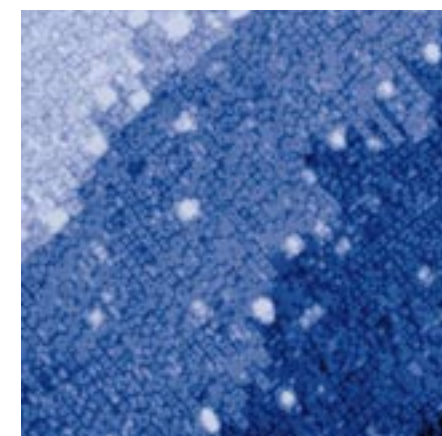
### Imaging Surface Electronic Structure with STM

Because the trajectory executed by an STM tip is determined by the overlap of the electronic-state density of the tip with the local electronic-state density of the surface, the STM can be used to extract chemical information associated with a particular surface structure. On the Si(100) surface, for example, dimerization results in a concentration of valence electron density between dimerized atoms (bonding orbitals) and a depletion of valence electron density in "anti-bonding" orbitals, of which there is one for each surface atom. In the model below, which presents the bonding geometry of a pair of dimers on the surface of Si(100), the bonding orbitals are represented in red, and the antibonding orbitals in gold.

If the STM is operated with a positive tip-to-sample junction, so that electrons must tunnel from the surface to the tip, the concentration of surface valence electron density within dimers causes the STM image to display rows of dimers, as in image (a) below. The individual dimers, displayed in red in image (a) correspond to the dimer bonds shown in red in the model. If the polarity is reversed, and electrons tunnel from the tip to the antibonding orbitals of the surface, then the resulting image (b) will enhance individual atoms. Each gold spot in image (b) then corresponds to one antibonding orbital, which in turn is associated with a single surface atom, as shown in the model.



deposited on Si(100) at 475°C, a novel ordering of atoms occurs only within the outermost layer of the surface (Figures 3 and 4). Because this ordering



**Figure 3.** A 500-Å atomic-resolution STM image of Si(100) following deposition of one-half monolayer of molybdenum at 475°C. The surface atoms form ordered arrangements over short ranges.

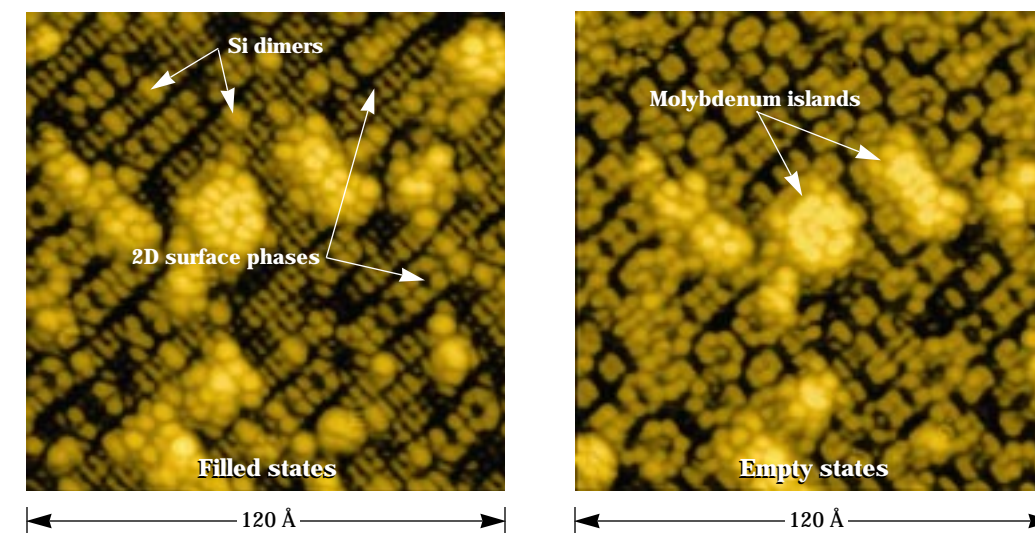
cannot be detected by conventional x-ray crystallography and is not readily detectable by electron diffraction, the resulting surface previously was thought to be amorphous. With STM, it is now possible to identify the presence and locally ordered character of this new interfacial material.

At higher temperatures (between 650 and 750°C) in this process, some of the material nucleates into the hexagonal phase of disilicide MoSi<sub>2</sub> (Figure 5). This nucleation acts as a precursor for disilicide grains that grow when additional molybdenum is deposited on the surface.

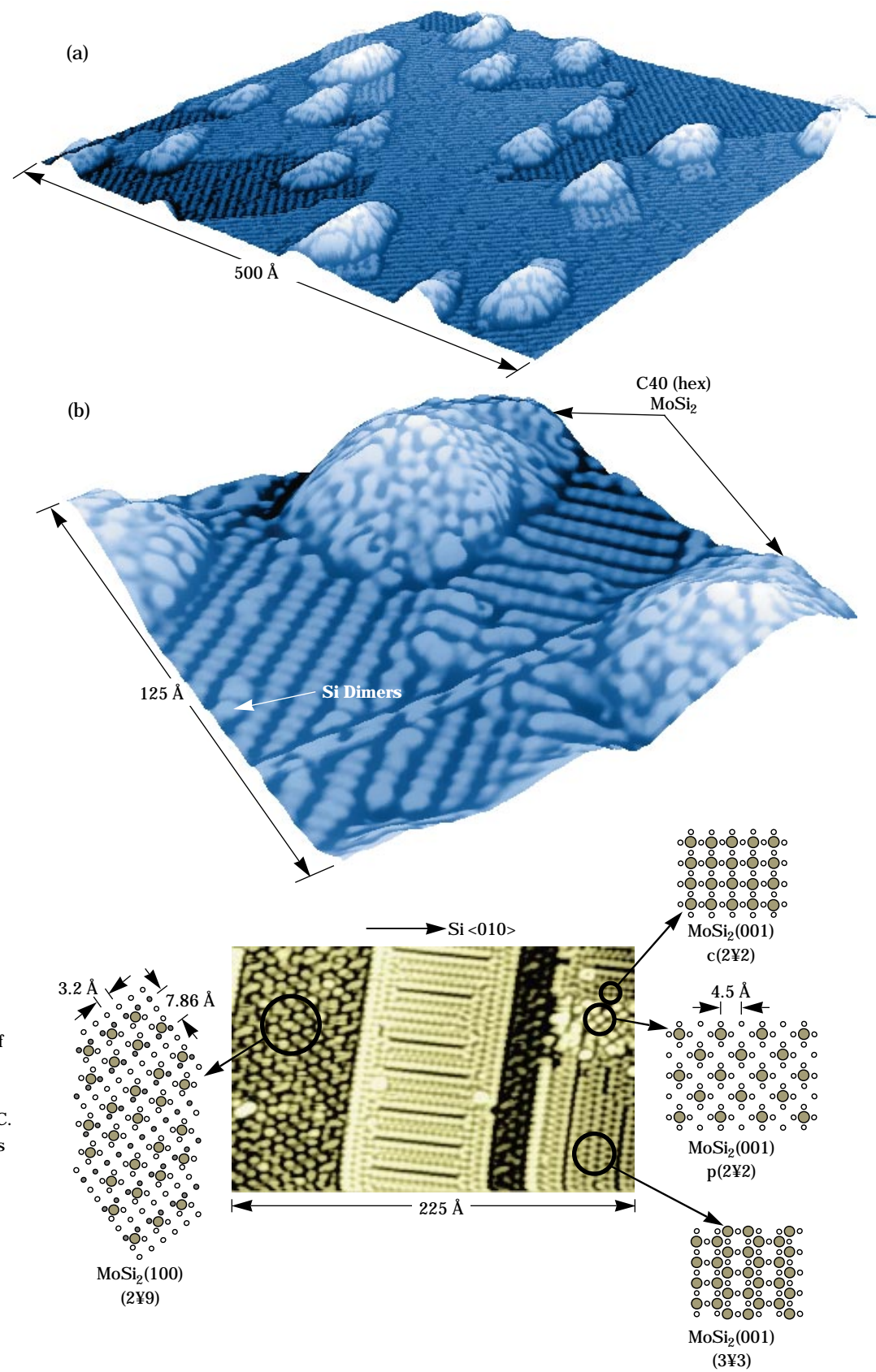
The third regime of disilicide growth occurs above 750°C. When molybdenum is deposited at 770°C, tetragonal MoSi<sub>2</sub> is formed. Figure 6, an STM image of the resulting surface, displays plateaus with large, flat terraces. Despite the variety of atomic arrangements observed in this image, each superstructure suggests a simple relationship to the periodicity (ordered, repeated atomic arrangement) of a

specific face of tetragonal MoSi<sub>2</sub>. The crystal face visible in the image then specifies the orientation of growth of the specific grain, which is preferentially oriented with respect to the silicon substrate.

For example, the sets of small circles in the three diagrams on the right-hand side of Figure 6 represent the atomic arrangement of the [001] planes of tetragonal MoSi<sub>2</sub>. The large, shaded circles represent atomic sites in a superstructure that would correspond to the periodicity observed in the regions of the STM image. In the diagram on the left-hand side, the small, white circles represent silicon atoms in [100] planes, and the small, dark circles represent molybdenum atoms in those planes. The large shaded circles then constitute a superstructure that would correspond to the periodicity in the indicated region of the image rotated approximately 37 deg with respect to the neighboring regions. Such rotation would be required to achieve alignment between a disilicide crystallite growing



**Figure 4.** Filled- and empty-state STM images showing a 120-Å detail of the region shown in Figure 3. Each spot corresponds to a single surface atom. Various atomic arrangements are indicated with arrows.



**Figure 5.** (a) A 500-Å STM image of Si(100) following deposition of one monolayer of molybdenum at room temperature and annealing at 640°C. (b) 125-Å detail showing individual silicon dimers and silicide islands.

**Figure 6.** A 225-Å STM image of the surface resulting from the deposition of four monolayers of molybdenum on Si(100) at 770°C. The spacings between the atoms are indicated in the diagram.

along its <100> axis and one growing along its <001> axis. Both orientations of tetragonal MoSi<sub>2</sub> relative to the Si(100) substrate are consistent with those reported previously for thicker disilicide films. Neither the existence of these superstructures nor their relative prevalence was accessible from measurements used in previous analyses of the molybdenum/silicon system.

By associating specific microstructures with the temperatures at which they are processed, we are now equipped to determine the best procedure for synthesizing thin films that have the microstructures necessary for particular applications. For example, the temperature stability of multilayers used in x-ray mirrors is known to be related strongly to the microstructure of the interfaces between individual molybdenum and silicon layers.<sup>6</sup> The deliberate promotion during fabrication of one or another of the regimes of Mo/Si interfacial structure that we have identified above may therefore lead to multilayers with internal structure engineered for enhanced thermal stability.

With the advanced capabilities of STM, the Laboratory can evaluate how processing parameters affect the atomic structures of interfaces, identify surface defects that have a critical influence on film growth, and control their occurrence, which will lead to improved new materials with better performance characteristics.

**Key Words:** atomic ordering, disilicide, interface, molybdenum/silicon, nanoengineer, scanning tunneling microscopy, silicide, surface physics, thin film.

**Notes and References**

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**About the Scientist**



**PETER BEDROSSIAN** came to Livermore in 1992, when he joined the Chemistry and Materials Science Department as a Staff Physicist. He also works with the Advanced Microtechnology Program. In his short career here, he was a collaborator with a group at Sandia National Laboratories, Albuquerque, that received the 1994 Materials Science Award for Sustained Outstanding Research in Metallurgy and Ceramics from the U.S. Department of Energy. He has published 20 papers in the field of atomic-scale physics, including a number of articles in scanning tunneling microscopy.

Bedrossian received his A.B., A.M., and Ph.D. in Physics from Harvard University in 1985, 1987, and 1989, respectively. Prior to coming to Livermore, he worked at Sandia National Laboratories, Albuquerque, in the Surface Science Division from 1991 to 1992 and was a Humboldt Research Fellow at Forschungszentrum Jülich, Germany, in 1993.