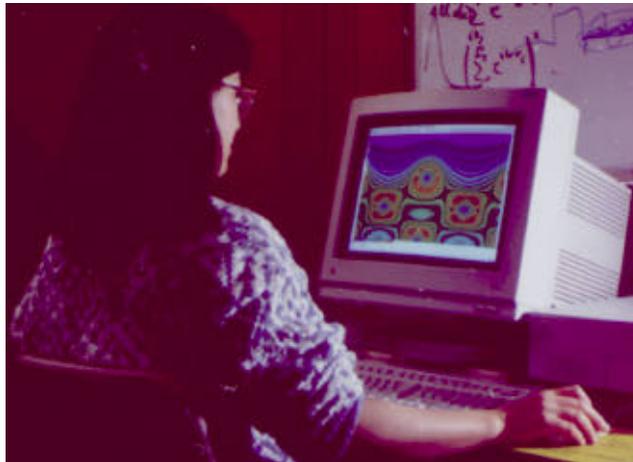


Toward Improved Understanding of Material Surfaces and Interfaces



Our atomic-level modeling of material surfaces and interfaces will impact the design of future materials.

THE surface of a material, whether it is a sheet of paper or a silicon wafer, defines the boundary of an object. Consequently, the properties of that surface determine how a second material will interact with it. For example, the words on this page result from a marking material, such as ink or toner, being deposited on the paper surface in specified patterns. For the printing process to be successful, the interaction between the marking material and the paper must be characterized by strong adhesion and minimal diffusion.

An understanding of surface properties and of how different materials interact has numerous other applications. Specifically, in the microelectronics industry, the complex integrated circuits that form the core

of a computer are built on the surfaces of semiconducting wafers, or chips. Chip fabrication involves adding thin layers of material to the surface, transferring the physical layout of the integrated circuit onto the chip, and selectively removing material to form circuit features. Combinations of these steps may be repeated hundreds of times to fabricate millions of transistors on these chips, which are often smaller than a few square centimeters. Features on individual transistors can be smaller than the wavelength of visible light (~ 415 nm), and they promise to become even smaller as technology advances. Consequently, an atomic-level (tens of nm) understanding of the surface properties of semiconductor devices is essential to their design and production.

The Field Advances

Surface science and materials engineering have made remarkable progress in recent years as a result of new atomic-scale deposition and diagnostic techniques. The deposition techniques, which allow atoms of one material to be added onto the surface of another, have given industry the ability to grow extremely thin films whose thickness can be controlled to within a single atomic diameter (~ 0.3 nm). New diagnostics, ranging from scanning tunneling microscopy to low-energy electron diffraction, can locate the positions of single atoms and can, therefore, provide unprecedented detail about the surfaces and interfaces of materials.

In addition to the development of these techniques, the close synergy between experimental and theoretical activities has demonstrated the power of computational methods to predict accurately the formation and structure of materials surfaces. The success of these methods may soon allow materials to be custom designed at the atomic scale.

The Laboratory Gets Involved

About five years ago, we began building new capabilities in atomic-level materials modeling. These capabilities were based on our previous work in computational and theoretical condensed-matter physics, which we traditionally used to provide data about materials properties to the Weapons Program. We have been very successful in transferring our expertise to industrial applications, as can be measured by our ability to partner with industry through the CRADA process. To date, we have four CRADAs with U.S. industry in materials modeling (see pp. 4–9), and we expect at least two more to begin in 1995.

Our work in computational and theoretical materials physics complements experimental work in surface science by providing insights into observed phenomena and by addressing issues that we cannot see or measure directly. Examples include:

- The atomic geometry and electronic structure of surfaces and interfaces.
- The attachment sites and binding energies of chemically adsorbed atoms and molecules on surfaces.
- The effects of defects and impurities on the physical and chemical properties of surfaces.
- The prediction of novel properties of multilayer materials.

As fabrication techniques become more sophisticated, atomic-level theory will play a critical role in the design

of new materials. By providing a framework for selecting from an ever-increasing number of possibilities, our calculations will focus experimental efforts along paths with the highest probability of success.

Computational Methods

We use several computational methods to address issues in surface science. The most rigorous are known as first-principles, or *ab initio*, electronic structure methods. These are based on the local-density approximation model, and they rely solely on quantum-mechanical principles. The only input to these calculations is the chemical identity of the atoms that comprise the surface or interface. (For a more detailed description of these methods, see the article on pp. 33–38.) Calculations done with these methods can reveal the locations of the atomic nuclei at equilibrium as well as the energies and spatial distribution of the material's electrons. These methods can also be used to determine the forces exerted on the atoms, from which we deduce the motion of the atoms using the laws of classical physics.

Molecular dynamics is the general computational method used to track the positions and velocities of individual particles (atoms or groups of atoms) in a material as the particles interact with each other and respond to external influences. The motion of each particle is calculated by solving Newton's equation of motion, $\text{force} = \text{mass} \times \text{acceleration}$, where the force on a given particle depends on the interactions of the particle with other particles. (For more details on molecular-dynamics methods, see the article on pp. 13–24.)

To determine the forces on the atoms in molecular dynamics calculations, we employ one of two methods: *ab initio* methods, or model force laws. With *ab initio* methods,

the rearrangement of the local electron density must be calculated each time the atoms move a very small distance. Because of the speed limitations of present-day computers, we can track the motion of only a few hundred atoms for a short period of time.

For larger-scale calculations, we use model force laws to approximate the forces among the atoms. These force laws, which have been validated by a limited set of experimental data and by results from *ab initio* calculations, allow us to perform molecular-dynamics calculations more efficiently than is possible with *ab initio* methods. If the force laws are accurate, the calculations can yield valuable insights into the dynamic processes that occur at surfaces, but they do not yield information about the electronic properties of those surfaces. Ultimately, we choose the method that best balances the amount of time required to perform the calculation against the accuracy and nature of the information required.

Surface and Interface Formation

We follow three steps to model how surfaces and interfaces form. First, we calculate the structure of a chemically pure, or clean, surface at equilibrium. We next determine the reaction of the surface with additional atoms deposited on top of it. If the atoms bond, an interface will form, and we then determine the structure and properties of this interface.

Surface Relaxation

The first step in the calculational process is to determine the structure of a clean surface of a material. As a convenient starting point, we can imagine slicing a crystal in half between two planes of atoms. Initially, the atoms on the surface occupy the same positions as in the original

Understanding Tantalum Surfaces

Tantalum, like all crystalline materials, is composed of a number of atoms arranged in a regular pattern that is repeated throughout the material. In tantalum, the atoms form a body-centered cubic pattern, with one atom at each corner of a cube and one atom at the center of the cube. If we arrange these body-centered cubes side by side and top to bottom so that the face of any given cube coincides with the face of one of its neighbors, we can form a crystal of tantalum.

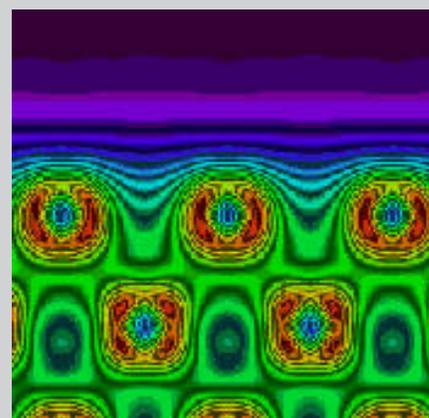
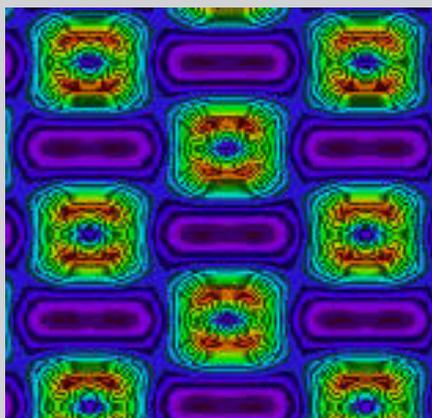
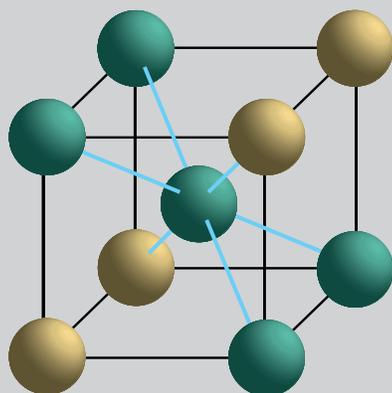
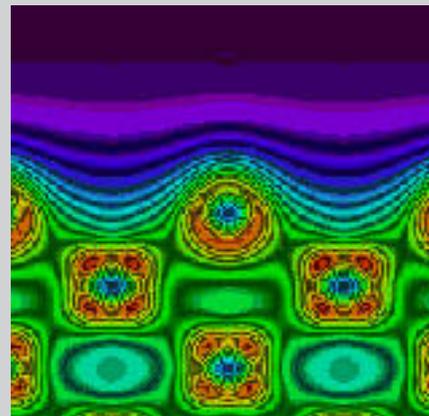
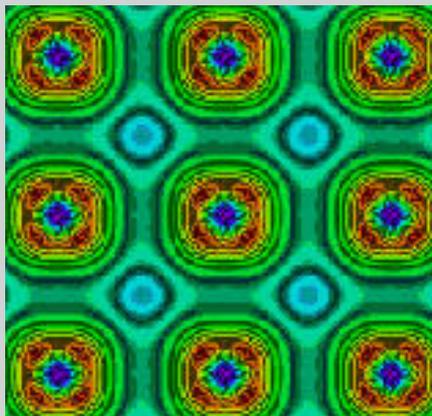
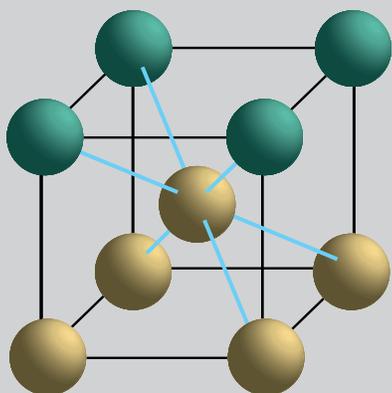
We can form many different tantalum surfaces depending on where we slice the crystal. If we slice the crystal between the planes of atoms parallel to one of

its cubic faces, we have a surface such as the one shown at top left. Slicing through the body of the cube along the face diagonal would produce a surface like that shown at bottom left. In both cases, the green atoms would become the atoms in the topmost layer of the surface.

The electron-density distributions of the relaxed surfaces are shown from the top and from the side for both surfaces. The top layer of atoms on both surfaces is pulled downward, so the separation between it and the second layer of atoms is reduced. For the surface shown at top left, the separation is reduced by 12%; for the surface shown at bottom left, the separation is reduced by only 2%.

Top views

Side views



crystal, but they will tend to move because they will no longer feel the forces of the atoms that were above them. After new equilibrium positions for these atoms are established, the surface is said to be “relaxed.” The goal of our calculations is to predict the structure of the relaxed surface in order to develop a microscopic understanding of chemical bonding at surfaces.

We use *ab initio* methods to calculate the atomic geometry of clean surfaces. This geometry, however, can vary widely depending on the planes of atoms between which the crystal was sliced. There can also be large variations in the nature of the surface relaxation among different classes of materials because of different bonding mechanisms. For example, in simple metals, the electrons responsible for bonding are distributed almost uniformly throughout the crystal. In contrast, the electrons in semiconductors are not as uniformly distributed and tend to pile up between

pairs of atoms to form highly directional covalent bonds.

Atom Deposition and Interface Formation

After we understand the structure of a clean relaxed surface, we introduce additional atoms onto that surface. Atom deposition is a more complicated problem to model because atoms generally react differently at different surface sites. The structure of an atom overlayer will depend not only on the chemical nature of the surface and on the surface temperature, but also on the density of the additional atoms. Sometimes atoms will react with the surface to create a chemical species that is no longer strongly bound to the surface. In this case, some of the substrate material will eventually vaporize, resulting in an etched surface. If the atoms bind with the surface, continued deposition will eventually form an interface.

To simulate atom deposition and interface formation, we use molecular-

dynamics calculations with model force laws. In our calculations, we first simulate several layers of atoms in a relaxed surface. We then project additional atoms one at a time toward the substrate, calculating the trajectories of these atoms and all the atoms in the substrate. After a number of atoms have built up on the surface of the substrate, we compare the structure of the simulated interface with experimental results.

Current Research

We are currently involved in a number of research efforts in modeling material surfaces and interfaces. Work in this field promises to revolutionize such areas as microelectronics and manufacturing through the development of new materials and fabrication processes.

Etching Tantalum with Chlorine

We are currently collaborating with the Wilson Center for Research

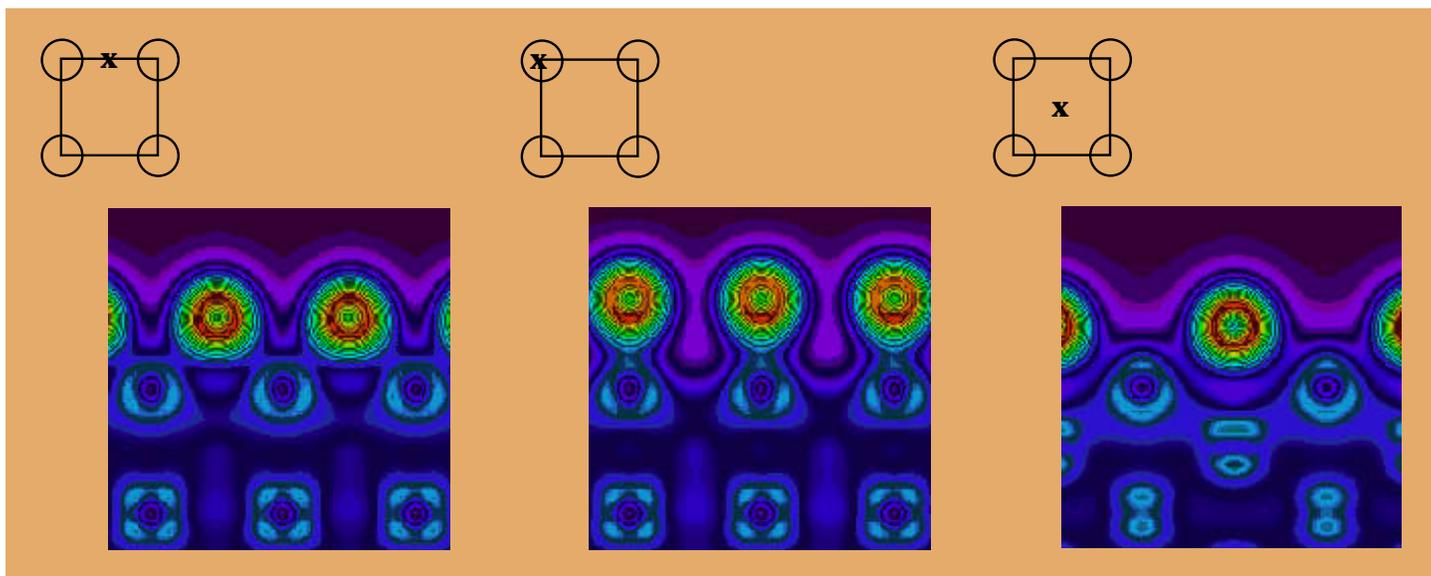


Figure 1. Adsorption of chlorine atoms at three binding sites on a relaxed tantalum surface. (This surface is illustrated in the top figure on p. 27.) The sketches above the figures are top views of tantalum atoms; an “x” indicates the location of the deposited chlorine atom. The figures, which are side views of the tantalum surface with chlorine atoms on top, indicate the electron-density distribution. The density is highest near the atoms, and the accumulation of electrons between the atoms is indicative of bond formation. We used this information to determine the preferred binding site of chlorine (shown in left-most figure).

and Technology of Xerox Corporation to model the etching of tantalum with chlorine. Tantalum has applications in thermal ink-jet printers and flat-panel displays, and the ability to etch tantalum selectively is key to the fabrication of such devices. Chlorine is a potential candidate for etching, although the interactions between chlorine atoms and tantalum surfaces are not fully understood at the microscopic, quantum-mechanical level. An ideal etchant would react strongly enough with the tantalum atoms to remove them from the surface, but not so strongly that it would damage those portions of the surface that are not to be etched.

Our first goal is to understand the structure of clean tantalum surfaces. Fortunately, tantalum surfaces relax in very simple ways. When a tantalum surface is exposed, the relative positions of the atoms in the surface plane do not change. Rather, the whole layer simply moves vertically until the forces are balanced. Using *ab initio* calculations, we modeled the relaxation of two tantalum surfaces and discovered that the degree of vertical movement varies considerably with the crystalline orientation of the surface (see the box on p. 27 for a description of these surfaces).

Next, we calculated the properties of six chlorine-binding sites on two tantalum surfaces. Figure 1 shows our results for one of these surfaces. In addition to finding the preferred binding sites, we are also constructing a model force law that can be used in molecular-dynamics simulations. This force law will allow us to predict the behavior of chlorine atoms that come into contact with a tantalum surface (see also the article on p. 9).

Metal-Semiconductor Interfaces

Understanding the interface between a metal and a semiconductor is critical to the microelectronics industry. In an integrated circuit, thin metallic films

are deposited on semiconductor surfaces. If the number of metal atoms deposited on the insulating surface of a semiconductor is so small that they are isolated from one another, no electric current can flow along the surface. However, if the number of metal atoms surpasses a critical value, the metal atoms in the overlayer will start to interact and become conducting. In advanced microelectronic devices, the electrical properties of the metal-semiconductor interface are critical elements in the design process.

Simple models predict that the transition from insulating to conducting behavior will occur when the separation between metal atoms is nearly equal

to that in a normal conducting wire of the same material. In such a case, the transition would depend only on the nature of the metal atoms and would be independent of the surface properties of the substrate. To test this model and to determine the threshold at which a metal overlayer becomes conducting, we performed *ab initio* calculations for gold and sodium atoms deposited on a semiconductor commonly used for optoelectronic applications, gallium arsenide.

Figure 2 shows the electron-density contours for low and higher coverages of gold atoms on the surface of gallium arsenide. At low coverage, the electrons are localized near individual gold

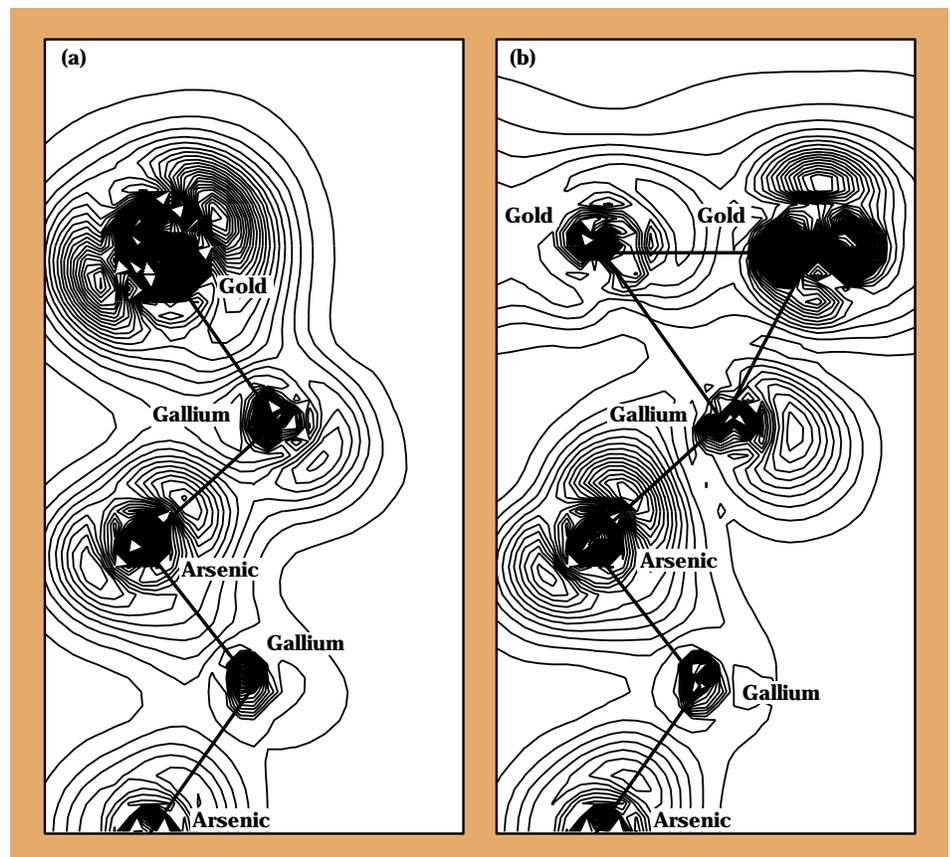


Figure 2. Side views of the electron-density contours for gold atoms deposited on a gallium arsenide surface. At low coverage (a), the electrons are localized near individual gold atoms, and the surface is insulating. At higher coverage (b), the electrons are more uniformly distributed in the gold overlayer, and the surface becomes conducting.

atoms and cannot move easily along the surface. At higher coverage, the electrons are more evenly distributed along the surface, as in a metal, and can move easily to conduct electrical current. We find that the gold overlayer becomes conducting near the ideal coverage, as predicted by simple models.

However, calculations for sodium indicate that the nature of the transition can depend on the strength of the electronic interactions between the gallium arsenide surface and the additional atoms. **Figure 3**, which compares the bonding of sodium and gold atoms at equal coverage on a gallium arsenide surface, illustrates this difference. The sodium atoms are

pulled much closer toward the surface of the gallium arsenide than are the gold atoms, indicating that sodium interacts more strongly with the surface than does gold. Contrary to the simple model, we find that sodium only becomes conducting on the gallium arsenide surface at coverages twice that of gold.

Molybdenum-Silicon Multilayers

Being able to simulate the relationship between particle deposition and interface formation is particularly important when dealing with multilayer structures made of alternating layers of different materials. Multilayer structures, some with layers as thin as 5 nm, have applications in advanced

lithographic techniques for transferring circuit layouts onto semiconductor chips. One multilayer structure in which we have particular interest is that composed of molybdenum and silicon. This multilayer structure is used in highly reflective x-ray mirrors, whose performance depends on the sharpness of the interfaces and on the layer thicknesses.

Interestingly, when molybdenum atoms are deposited on top of silicon layers, the interfaces formed are far less abrupt than those formed when silicon atoms are deposited on top of molybdenum. To investigate this asymmetry, we performed two molecular-dynamics simulations (see **Figure 4**). For one, we deposited molybdenum atoms on a silicon slab; for the other, we reversed the process. Although the force law that we used for these simulations was approximate, the calculations nevertheless shed some light on the reason for the structural asymmetry of the interfaces.

Each atom in a bulk crystal of the metal molybdenum is surrounded by 14 closely neighboring atoms, whereas each atom in the semiconductor silicon is covalently bonded to only 4 neighboring atoms. When a molybdenum atom is atop a silicon substrate, it will have only a few neighbors, so it will attempt to surround itself with more neighbors by burying into the substrate. A silicon atom, in contrast, will remain atop the molybdenum surface because it already has a sufficient number of neighbors. The better we understand the microscopic mechanisms determining interface thickness, the better we will be able to guide the fabrication of high-performance mirrors.

Conclusion

LLNL has developed significant expertise in the field of atomic-level materials modeling and design. We

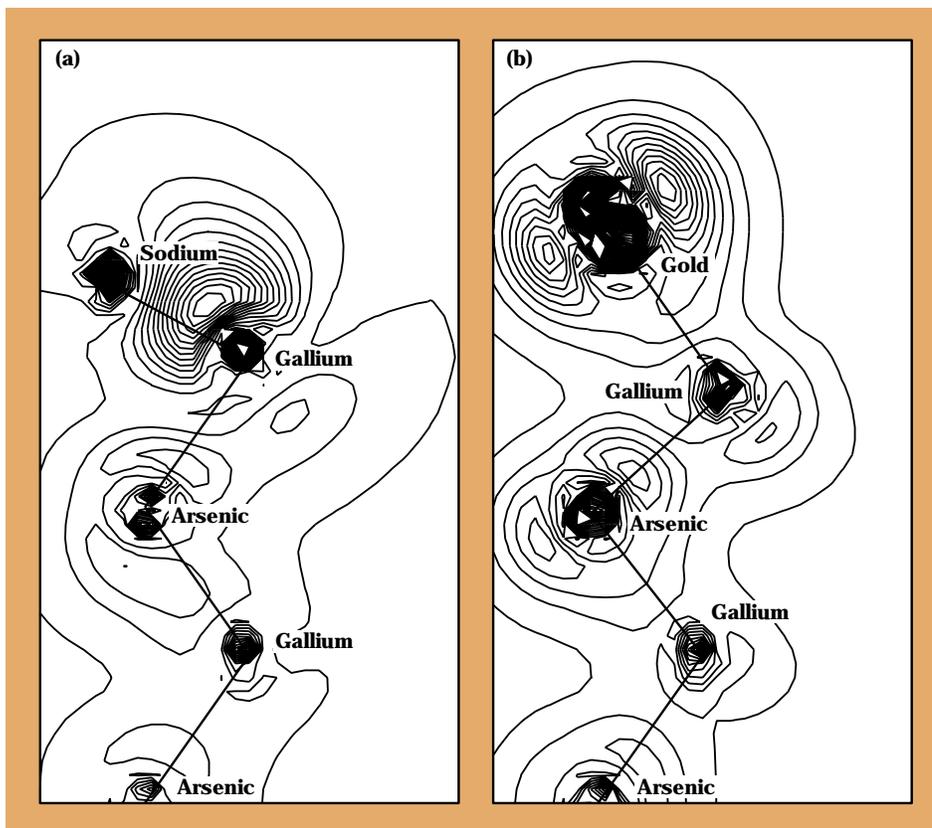


Figure 3. Side view of the bonding of sodium (a) and gold (b) atoms to a gallium arsenide surface. The sodium atom interacts more strongly with the surface than does the gold atom. As a result, the sodium overlayer becomes conducting at a higher coverage than for gold.

are currently involved in several exciting collaborative projects that promise to speed the development of novel materials for the microelectronics industry. As our calculational methods improve and as computers continue to grow in power and memory, the size and complexity of the materials design problems we can address at the atomic level will scale with them.

The emergence of massively parallel computing environments will eventually make simulations of realistic, complex systems routine. The opportunities provided will revolutionize atomic-level, quantum-mechanical simulations of materials and processes, making true atomic engineering of devices and products a reality.

Work funded by the Department of Energy's Assistant Secretary for Defense Programs and Director of Energy Research.

Key Words: atomic structure; bonding; computational methods—*ab initio*, model force laws, molecular dynamics; crystal structure; interfaces; materials modeling; semiconductors; surfaces.

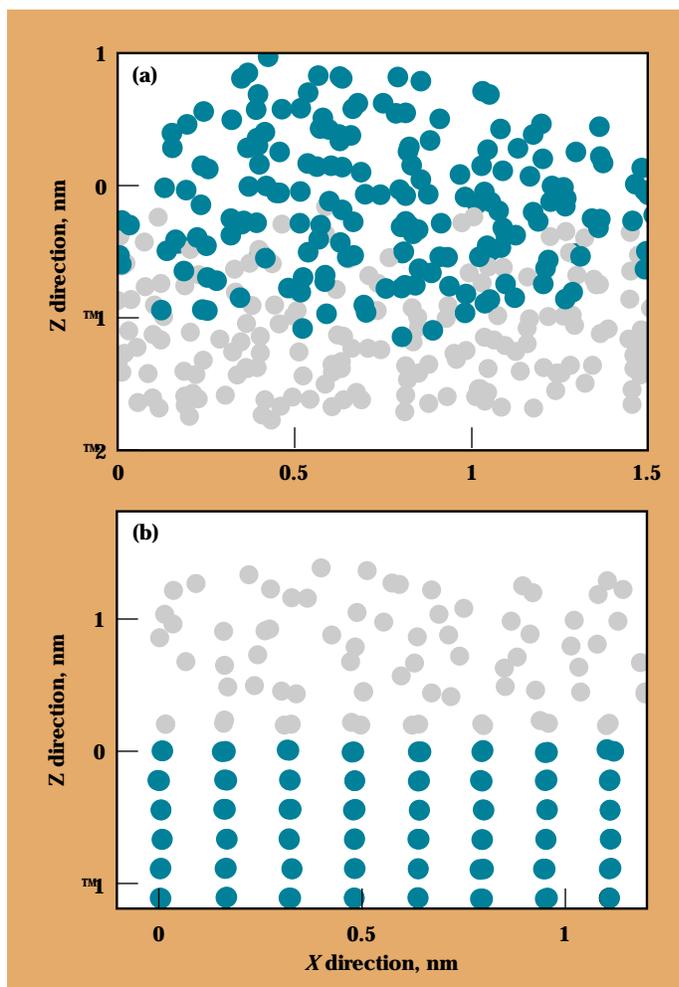
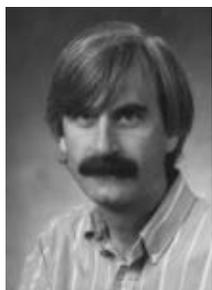


Figure 4. Molybdenum-silicon interfaces. (a) Side view of a silicon slab (gray dots) after 192 molybdenum atoms (blue dots) were deposited on it. The delineation between the molybdenum and silicon is not abrupt because many of the molybdenum atoms intermix with the silicon. The atoms that were deposited last begin to form a layer of pure molybdenum. (b) Side view of a molybdenum slab upon which 80 silicon atoms were deposited. Here, the interface between the molybdenum slab and the silicon layer is abrupt at the atomic level.



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properties of a material can be tailored by introducing defect levels inside the fundamental band gap. Accidental defects can also degrade the performance of a scintillator. At present, no one can calculate defect

excitations accurately, so we have to generalize the quasiparticle method to handle this problem. The first application of this method, to a chlorine vacancy in lithium chloride, yielded an accurate estimate of the

frequency of light absorbed by this defect. Eventually, it should be possible to predict defect properties for a wide range of materials, thereby advancing the development of new scintillators.

Work funded by the Department of Energy's Assistant Secretary for Defense Programs.

Key Words: electrons; local-density approximation; pseudopotentials; quasiparticles; radiation detection; scintillators.

Notes and References

1. All research on fullerene solids had been completed as of the date of this writing, but a document describing the work has not yet been published. For more information on fullerene solids, contact Eric Shirley (301) 975-2349.

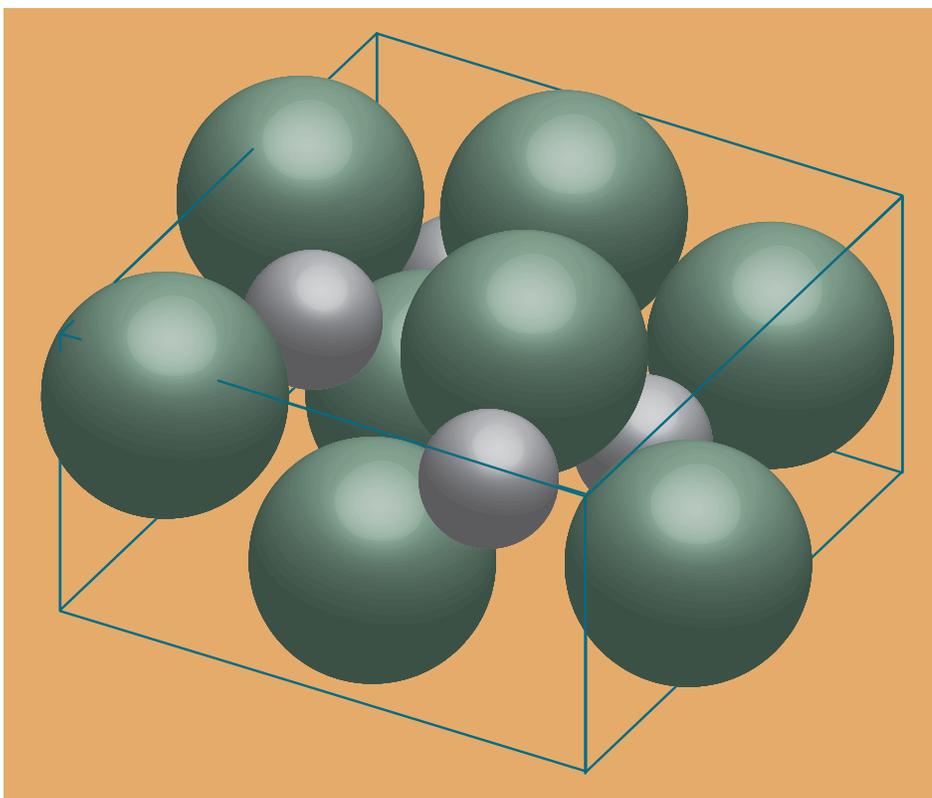


Figure 5. Unit cell of the orthorhombic phase of lead fluoride, which has potential scintillator applications. The connecting lines that define the box enclosing the fluorine (green) and lead (gray) atoms are intended only as a guide.



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