Putting Semiconductor Theory on a More Solid Basis

Theorists now can predict what experiment finds

By DIETRICK E. THOMSEN

Forty years ago there really was no scientific discipline known as solid-state or condensed-matter physics. What was known of the structure of solids then was likely to occupy one chapter in a textbook on quantum mechanics. Today, according to Marvin Cohen of the University of California at Berkeley, solid-state is the largest branch of physics in numbers of persons engaged in it. Much of that development is due to semiconductors, which provide both interesting physics and practical devices that have miniaturized electronics almost to the vanishing point and so have engendered revolutionary changes in the way the world uses electronic circuitry.

Back in the 1930s the basic problem in describing the structure of solids was solved in principle by Schrödinger's equation, says John Northrup of the Xerox Palo Alto Research Center in Palo Alto, Calif. Schrödinger's equation describes the interaction between an atomic nucleus and an electron (with emphasis on the singular). For hydrogen atoms, which have one proton and one electron, the solution is not too difficult. For more complex systems there are serious problems. A solid, says Northrup, is a system of something like 10^{23} atoms and electrons. "Exact solutions are impossible." For decades solid-state theory lagged very far from experiment. In the '50s, Cohen says, when theorists tried to calculate the electronic structure of solids from first principles, semiconductors came out to be metals, and metals came out semimetals.

Now all that has changed. Developments of the last few years have brought theory and experiment very close together. According to a number of participants, this close relationship was one of the striking differences between the recent 17th International Conference on the Physics of Semiconductors, held in San Francisco, and previous meetings of the same group.
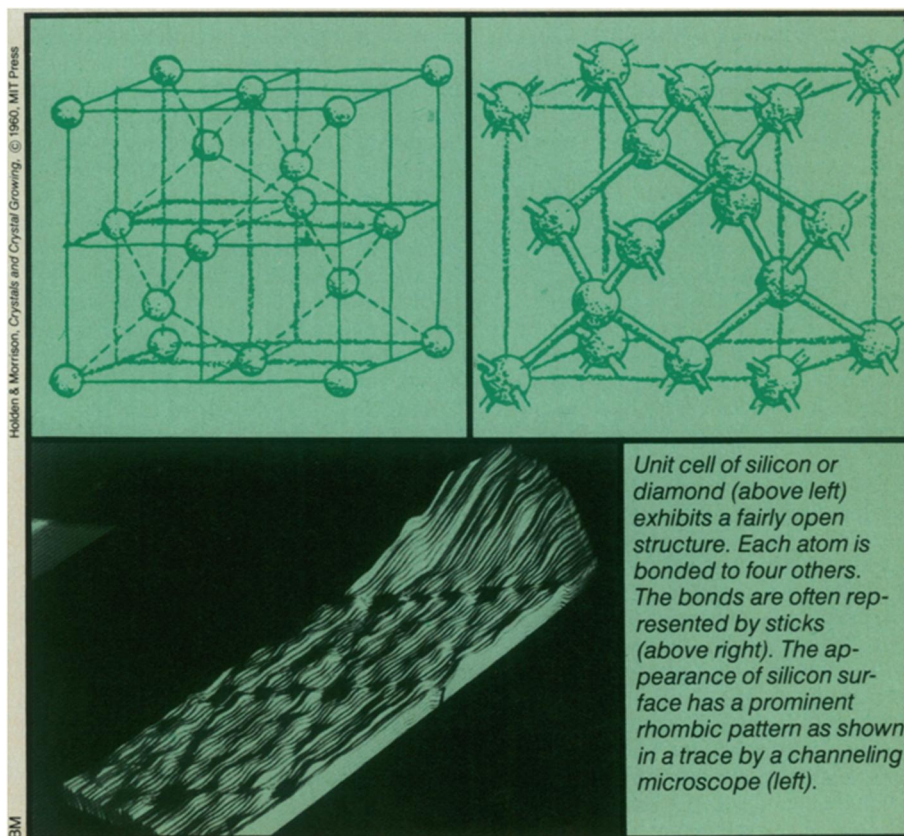
Several factors have figured in the change. One of the most important is the calculational power of modern computers — it is possible to say that silicon has helped physicists to understand silicon. Another is the adoption of what is called a pseudopotential approach.

A potential is a mathematical expression from which energies and forces may be calculated. For instance, a gravitational potential for the solar system would enable calculation of the forces on a given planet in a given position. From it one might also calculate the total energy of the solar system with the planets in such-and-such a configuration. In a solid the potential is concerned with the configuration of atoms and electrons, the forces among them and the total energy of different arrangements.

Exact solutions are still impossible, however, so the theorists turn to a pseudopotential. This is not a false potential (the terminology, though standard, is a bit unfortunate) but rather a simplified or approximate potential. Theorists arrive at it by ignoring parts of the interaction that don't interest them and calculating only the ones that do.

For example, silicon, the most studied and most used semiconductor, has a nucleus with 14 positive electric charges surrounded by 14 electrons. The interaction between the nucleus and the electrons is a very strong one and so hard to calculate. But for the purposes of electronics only four of the electrons are interesting. These are the valence electrons, which a silicon atom can share with other atoms in the formation of chemical bonds. The other 10 electrons are tightly bound to the nucleus. So, instead of trying to calculate the nucleus-electron interaction, the theorists calculate the interaction between the core — which consists of the nucleus and 10 electrons and has a net positive charge of four — and the four valence electrons. This is much simpler, but it still takes powerful computers.

Unit cell of silicon or diamond (above left) exhibits a fairly open structure. Each atom is bonded to four others. The bonds are often represented by sticks (above right). The appearance of silicon surface has a prominent rhombic pattern as shown in a trace by a channeling microscope (left).

Silicon naturally assumes the same crystal structure as diamond. The theorists calculate the total energy of a silicon crystal in this diamond configuration using varying amounts of distance between the atoms. For a certain distance the total energy will be a minimum. Nature tends to seek states of least energy, so this minimum-energy value of the distance should be the "lattice constant" of silicon, the natural distance between atoms. Experiment verifies the calculation.

Under pressure silicon can adopt other crystal structures. One of these is a hexagonal form that is found in some meteorites, and another is a structure that is the same as that of tin. This means, Cohen says, that under pressure silicon becomes a metal. Theory can calculate the amount of pressure needed: It should be 100 kilobars, give or take 10 kbar. Cohen says experimenters at first insisted that the pressure must be at least 300 kbar, but they are now down to 150, and Cohen expects they will eventually reach the predicted value.

In the not too distant past, theory could not predict numbers like this; they could only be determined empirically. The theory operates independently of experimentally determined numbers. The only input is one number, 14, the atomic number of silicon. On the basis of such calculations, Cohen and co-workers are preparing a paper predicting that under extreme conditions silicon will become a superconductor.

Recent advances in experimental techniques have simplified the apparatus for exerting pressures such as those that make silicon change its crystal structure. Years ago, Cohen says, it would have taken rooms full of equipment to do it. Today there is the diamond anvil cell. A small piece of the substance to be pressured is put between two tiny pieces of diamond. Because the diamond anvils are very small, a reasonable force on them will transmit tremendous pressure to the sample. Diamond anvil cells can be and have been carried in a pocket from one side of the United States to the other.

If silicon becomes a superconductor, it will probably be at an extremely low temperature. A few other semiconductors are known to become superconductors under pressure, but nothing has been done with them technologically because the required temperatures are impractical — less than a tenth of a degree above absolute zero. However, there is always the hope that this kind of work will find something that becomes superconducting at a reasonably high temperature, perhaps even 77 kelvins or above. That is the temperature at which nitrogen liquefies, and so such a superconductor could be refrigerated with liquid air, which is easy to obtain and need not be recycled. At lower temperatures the refrigerant must be liquid helium, which is scarce, or liquid hydrogen, which is flammable.

If theorists can find something that would become that kind of superconductor under pressure, it might not be necessary to leave the pressure on. Many substances that change crystal structure under pressure do not go back to the original when the pressure is released. Diamond is an example. Diamond is not the lowest energy configuration of carbon; graphite is. But nature makes diamonds under pressure deep in the earth, and when they are dug up, they remain diamonds. Cohen and co-workers are looking for a cheap way to make diamonds out of graphite. In addition to its present industrial uses, diamond is an excellent conductor of heat. It would be very good, Cohen says, for carrying heat away from electronic components, but, of course, gem diamonds are too expensive for such an application.

Pure crystals may be physically and even technologically interesting, but silicon gets its current electronic applications from the presence of defects. As Sokrates T. Pantelides of IBM's Thomas J. Watson Research Center in Yorktown Heights, N.Y., points out, "A pure semiconductor without defects would be useless." But John D. Joannopoulos of MIT adds, "There are good defects and bad defects." The good ones make diodes and transistors possible, and they make interfaces between different semiconductors that otherwise wouldn't match. There are two general classes of defects, Joannopoulos says: foreign atoms introduced into the substance, and atoms in the wrong place. Technologists have to know how defects are formed and what their properties are.

"To make devices," says Pantelides, "you have to arrange impurities in certain ways. Engineers can cope now without much microscopic understanding, but it will get worse. As devices get smaller, they have to get cleaner, and engineers have to know how to do it." Advances in experimental technique that allow greater accuracy of measurement are complementary to theoretical advances, he adds. Both he and Joannopoulos cite computers and the pseudopotential approach as the important advances — so many of these things can be calculated, and the only input is the atomic number.

Roberto Car of Stanford Electronics Labs in Stanford, Calif., refers to theoretical developments as a kind of microscope to see what happens. They can predict some things that are hard to see experimentally. "The limitation now," he says, "is the computer."

Interfaces and surfaces are where most of the action is. "All devices work because of interfaces," says Ross Bringans of the Xerox Palo Alto Research Center. He adds that "clean surfaces have no technological use as such," but they are studied as a step toward understanding the sort of interfaces — between two semiconductors or between a semiconductor and a metal — that are of technological interest.

A surface, Cohen says, is something between two and three dimensions. At a surface atoms have to adjust to the breaking of bonds that would normally extend through the surface, or they have to make connections to atoms of another substance. "Movement completely changes surface properties," he says. Until recently there was only one technique for studying surface configurations, low-energy electron diffraction, says Yves Petroff of the University of Paris XI at Orsay, France. People believed it gave the answers because it was the only technique. Today there are several techniques: photoemission, tunneling microscopes (SN: 8/18/84, p. 101), absorption of polarized light and probing with synchrotron radiation. Graduate student Marjorie A. Olmstead of the University of California at Berkeley uses polarized light to study cleaved silicon surfaces in vacuum. Her measurements of the electronic structure of such surfaces, what happens to dangling bonds, etc., are credited with supporting some of the latest theoretical calculations.

Surfaces will be even more important as devices get smaller, says Northrup. He credits the new theoretical developments, particularly the pseudopotential approach and the use of local density approximations, with simplifying the previously intractable problem of 10^{23} atoms and electrons and bringing a new element of realism to theoretical predictions. He judges that "theorists have caught up." □