

π -bonds surface in crystal debate

An elegant new spectroscopy technique has been used to tip the scales in favor of one theory, among several proposed over the last 20 years, that describes the mosaic arrangement of atoms on the surface of freshly cleaved silicon and germanium crystals. The results from this and other surface studies, experimenters at the recent American Physical Society meeting in Detroit said, are especially important to the design of very small integrated circuits, in which surface and interface properties can dominate and limit the operation of a device.

When a crystal is cleaved, the atoms on the newly formed surface re-arrange themselves in order to reach the lowest energy state. The earliest conception of the resulting surface atomic pattern in silicon, cut orthogonal to the so-called [111] direction (in three dimensions), was named the buckling model and calls for alternate rows of atoms to move perpendicular to the surface, either up or down.

In the competing "chain" model, proposed a few years ago, the bonds of surface atoms, left dangling by the cleavage, join up into what are known as π -bonds. To allow π -bonding to occur, the surface atoms form zig-zag chains on the surface, looking much like the neat rows of a freshly planted garden. Theoretical calculations of the energy required for different atomic geometries favor this latter π -bonded chain model.

Several different types of spectroscopic experiments have been done to determine which of the competing models, or their many variations, are correct. The results from these studies tend to support the chain theory in silicon. However, LEED (Low-Energy Electron Diffraction) analysis has produced conflicting data. In the case of germanium (which has the same bulk crystal structure as silicon), the picture is even less clear.

In addition, says Nabil M. Amer of the Lawrence Berkeley Laboratory in California, the conventional spectroscopic methods have some disadvantages. LEED, for example, requires detailed calculations of where the atoms reside in the first few layers beneath the surface. This extra input increases the uncertainty of the results.

Moreover, most methods suffer from relatively poor sensitivity because they are only able to indirectly measure the relatively weak signal coming from the surface. This is done by subtracting the signal originating from the bulk in samples with oxidized surfaces from the bulk-plus-surface spectra obtained when the surfaces are clean.

For these reasons, Amer and colleagues, working with Marjorie A. Olmstead, a Ph.D. candidate at the University of California at

Berkeley, devised a new spectroscopic technique called photothermal displacement spectroscopy. In this technique, a "pump" laser is aimed at the sample, which has been cleaved in an ultra-high vacuum. Following the absorption of the light, the surface thermally expands, creating a little bump. Another laser beam then probes the surface and is deflected by the bump. By measuring the angle of deflection, the researchers could determine how much light was absorbed from the pump beam.

As they changed the polarization of the pump beam, the investigators found that the intensity of the light absorbed parallel to the direction of the chains in silicon was 20 times greater than that measured when the light was polarized in the direction of the displaced atoms, as denoted in the buckling mode. Similar results were ob-

tained for germanium.

Because this technique relies on symmetry considerations alone, the researchers believe that this is an unambiguous test of the validity of the models, and strongly supports the chain theory. However, says Olmstead, "while this tells us about the symmetry of the surface, it does not indicate the exact position of the atoms."

The findings for silicon agree with results from another experiment performed by an Italian research group, which was able, for the first time, to polarize the light used in conventional difference reflectivity analysis. Both the Italian and Berkeley work on silicon appear in the March 26 PHYSICAL REVIEW LETTERS. The new germanium results have just been submitted by the Berkeley researchers to PHYSICAL REVIEW, B.
—S. Weisburd

A crystal route to optical purity

Separating chemical twins, when the only difference between the molecules is that one is "left-handed" and the other is "right-handed," as shown by their effect on polarized light, can be a tricky, delicate task. Producing only one instead of a mixture of these two mirror-image forms of a molecule is even more difficult. Now, as a result of a discovery by Herbert C. Brown and Bakthan Singaram of Purdue University in West Lafayette, Ind., chemists have a simple, versatile method for synthesizing optically pure organic compounds even when the starting materials contain a mixture of the two forms.

"This has major implications for synthetic chemistry and the manufacture of drugs," says Singaram. The ability to obtain optical purity may also provide more effective optically active pesticides, food additives and other organic compounds. He presented the research team's findings at this week's American Chemical Society meeting in St. Louis.

The starting material is α -pinene, which is the ingredient largely responsible for the pungent smell of pine trees. This substance is produced naturally in great quantities in either left-handed or right-handed forms, depending on the species of pine. Although individual trees generate only one of the forms, commercial methods for extracting the chemical generally process the material into a mixture of both types of α -pinene. Brown and Singaram found that when an α -pinene mixture dissolved in diethyl ether is treated with borane to produce diisopinocampheylborane, the product containing the more abundant form of α -pinene crystallizes out of solution, leaving the less abundant form still dissolved.

This result was a surprise, says Singaram. A few more steps convert the

crystalline product, now 100-percent optically pure, into a stock solution that can react with olefins (organic compounds containing double bonds between carbon atoms).

Reaction of the stock solution with an olefin creates a product that is also 100-percent optically pure when it crystallizes out of solution. Further treatment displaces the α -pinene so that it can be reused and leaves an alkylborane that can be converted readily into other organic compounds. By selecting an appropriate olefin, theoretically almost any optically active compound can be synthesized at 100-percent optical purity. "The method is very simple," says Singaram. "Just a single crystallization is enough to ensure optical purity."

The method is particularly attractive because it can be carried out easily on a large scale and because α -pinene is readily available commercially. In addition, Singaram notes, "By and large, organoboranes are among the most versatile reagents known so far."

One result of the research may be the manufacture of more effective drugs at lower cost in the future. Many drugs can exist in both left-handed and right-handed forms, but the two forms often vary greatly in their biological activity. Most existing chemical methods produce a mixture of the two forms. The new technique promises an economical way of producing optically pure drugs that would likely be more potent and have fewer side effects.

The Purdue researchers are now systematically studying these organoborane reactions to see which synthesis routes work best for creating specific organic compounds. "We have our work cut out for us," says Singaram. "We're going to open up a big, new field of chemistry."
—I. Peterson