ORGANIC CHEMISTRY ON SILICON SURFACES

A growing repertoire of simple procedures adds organic function to semiconductors

MITCH JACOBY, C&EN CHICAGO

One way to make today's advanced electronic devices even more versatile is to endow them with the rich variety of function associated with organic molecules. The ability to absorb and emit light, sense molecules, or recognize biological entities, for example, could bring additional sophistication to microelectronics. To capitalize on the potential, scientists are working on ways of introducing organic chemistry to semiconductor technology. For some researchers, the focus is on building a repertoire of organic reactions on a foundation of silicon--literally.

"Silicon is the ideal substrate on which to bind organic molecules because of its ubiquity in chip technology and integrated-circuit manufacturing processes," says Jillian M. Buriak, a chemistry professor at the University of Alberta, Edmonton.

Similar views are expressed by other researchers who work in the field. "Silicon is arguably the most important material in modern technology," says Matthew R. Linford, an assistant chemistry professor at Brigham Young University in Provo, Utah. "Anything we can do to modify silicon and alter its properties has important implications for the enormous semiconductor industry."

Several reactions and techniques for forming bonds between organic molecules and solid surfaces are already well established and have been used for years to modify silicon, germanium, and other semiconductor materials (C&EN, April 17, 2000, page 32). But in contrast to some methods that require high-vacuum, inert environments, or elaborate equipment, a number of simple procedures that require little or no specialized tools can be performed in the open air have been reported recently.

In one example, Linford's research group has shown that silicon surfaces can be patterned and functionalized with a large variety of organic molecules using a straightforward wet chemical mechanical-based approach.
"It's easy and it works in the open lab," Linford stresses enthusiastically. "You simply take a silicon wafer, clean it using standard procedures, rinse it off and dry it, pour a liquid on it, and then just write. Wherever you write, you functionalize."

**IN ONE VERSION** of the procedure, the "writing" is carried out with a diamond-tipped tool in the presence of liquid alkenes or alkynes. Scratching the angstrom-thick oxide coating typically found on the surface of silicon wafers breaks Si2Si bonds and exposes bare silicon, which reacts quickly with the unsaturated organic species. The method leaves behind robust monolayer films of alkyl chains after the unreacted reagents are washed away.

Linford points out that although the procedure is quick and simple, the patterns formed with the diamond tool tend to be irregular and lead to features that are on the order of 100 µm wide and 5 µm deep.

The Brigham Young group found that somewhat finer features could be produced by reducing the force on the tip. But the team sought to make patterns with even smaller dimensions. So Linford, graduate student Yit-Yian Lua, postdoctoral associate Travis L. Niederhauser, and coworkers modified the procedure, replacing the diamond tip with a tiny tungsten carbide ball. Using that variation of the technique, the group can prepare silicon surfaces with patterns measuring roughly 20 µm wide and just 10–20 Å deep [*Langmuir*, 19, 985 (2003)]. Still finer features (30 nm wide) can be "written" using an atomic force microscope (AFM) tip in yet another version of the method that was developed in collaboration with Brigham Young physics professor Robert C. Davis [*Appl. Phys. Lett.*, 82, 808 (2003)].

The method isn't limited to alkenes and alkynes. Linford's group has also used the technique with alkyl halides, alcohols, and aldehydes, and just recently, they reported patterning surfaces with mixed layers of epoxides and diepoxides. In that study, the researchers found that the mixed-epoxide monolayers react with amines, which opens the door to protein-coupling reactions and even more possibilities for controlled functionalization of silicon [*Angew. Chem. Int. Ed.*, 42, 4046 (2003)].

Linford notes that recently his group began investigating chemo-mechanical patterning of germanium, glass, quartz, and polymer surfaces. They have also begun focusing on a number of applications including targets for matrix-assisted laser desorption-ionization (MALDI) mass spectrometry and arrays of samples for multiple surface experiments.

To make sample arrays, the group prepares surfaces with checkerboard patterns written with a hydrophobic material, such as a long-chain olefin. Individual compartments within the checkerboards can be filled with tiny water droplets containing DNA, semiconductor quantum dots, or other analytes by dipping the patterned material into the aqueous solutions or using microliter dispensers. The hydrophobicity of the checkerboard lines traps the water droplets, which then evaporate and deposit their solutes.

Another example of a straightforward technique for
functionalizing and patterning silicon surfaces is being developed by the University of Alberta group led by Buriak, who also serves as a senior research officer in Canada's National Institute for Nanotechnology. The Alberta method is based on an electrografting reaction in which an atomic force microscope is used to pattern silicon surfaces with nanometer-thick lines of alkyne molecules. Buriak notes that other researchers have used related techniques to completely coat (not selectively pattern) silicon surfaces with organic molecules.

In the electrografting procedure, a conducting AFM tip, such as platinum, serves as one electrode in an electrochemical cell, and the silicon surface serves as the other electrode. By applying a potential difference across the interface between the probe tip and the silicon surface and then dipping the tip into liquid alkyne, Buriak's group is able to covalently bond the organic molecules to atoms in the semiconductor surface and form patterns arbitrarily.

Demonstrating the procedure, Buriak and coworkers decorated hydrogen-capped silicon surfaces--in air--with lines of alkynes measuring roughly 40 nm in diameter. The lines were prepared from 1-octadecyne, 1-dodecyne, and 1,4-diethynylbenzene (J. Am. Chem. Soc., 125, 11334 (2003)). Buriak conducted the study with chemists Patrick T. Hurley and Alexander E. Ribbe at Purdue University, where she moved from recently.

TO EXAMINE the properties of the pattern lines, Buriak's group used an AFM again, but this time with an oxide-coated silicon tip in an imaging configuration and a friction-measuring mode. The measured heights match closely with the calculated lengths of the molecules, the group reports, indicating that the films are just one molecule thick (but slightly compressed). And friction measurements also give the expected results: The hydrophilic tip interacts less with the hydrophobic monolayers than with the surrounding silicon surface.

Buriak notes that the electrografting technique has the potential to be applied broadly. Many of the molecular wires that have already been synthesized contain terminal alkyne functions, she says. In addition, a large number of alkynes are available commercially and many more can be synthesized readily. In principle, the method can be used to attach a great variety of molecules directly to silicon. If so, "the surface characteristics of silicon can be tailored at will," Buriak says. In addition, she says that the ability to pattern surfaces with conjugated species "may provide the ideal electrically active interface to silicon microcircuitry."

With a growing collection of procedures for forming strong and stable silicon-carbon bonds, researchers are starting to apply the enormous number of molecular transformations in organic chemistry to semiconductor surfaces. The possibilities seem boundless. On paper, chemists tend to draw simple structures--molecular wires, conjugated polymers, and unsaturated molecules with unspecified R-groups. But as Buriak points out, "Those R-groups are limited only by your imagination."
TINY ART A simple chemo-mechanical technique can be used to draw thin (1- to 2-nm), sharp patterns with organic molecules on silicon as shown here in a secondary-ion image that measures a few hundred micrometers on a side (left) and a close-up atomic force micrograph (right). IMAGES COURTESY OF MATTHEW R. LINFORD