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Localized Atomic Reactions Imprint Molecular Structures

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Adding a tool to the collection of procedures for nanoscale patterning, researchers in Toronto have demonstrated a technique for imprinting structures of molecules on underlying substrates. The study advances understanding of fundamentals in chemical reaction dynamics and may lead to methods for fabricating nanowires and other microscopic structures needed in the emerging field of molecular electronics.

As the drive continues toward further miniaturization of electronic devices, researchers in many disciplines are looking for ways to construct logic and computational circuits, sensors, and other types of sophisticated hardware in microscopic size. But rather than scaling down today's already small microelectronics machinery, investigators in molecular electronics take a bottom-up approach, building their components from just a handful of molecules--or fewer.

Getting molecules to line up precisely where they are needed is one piece of the puzzle. Molecular self-assembly and other methods are being studied for that task. But convincing aligned molecules to stay put can prove tricky. Some assemblies of molecules hold onto solid surfaces rather weakly. And although such molecules may order themselves into neat patterns that represent tiny circuit elements, the little structures may begin to unravel and fail as soon as electrical current starts flowing through them.

Polanyi: producing predictable patterns

Postdoctoral associates Ping-He Lu and Duncan Rogers and University of Toronto chemistry professor John C. Polanyi have now shown by scanning tunneling microscopy (STM) that isomers of dichlorobenzene self-assemble at preferred atomic sites on a silicon crystal. The molecules can be induced to dissociate, producing patterns of tightly bound chlorine atoms whose positions within the surface unit cell are determined by the location and structure of the parent molecules [*J. Chem. Phys.,* **112,** 11005 (2000)].

"The work illustrates in a very powerful way the benefit of probing reactions of single molecules on an atomic scale where ensemble averages can be avoided," remarks University of Texas, Austin, chemistry professor J. M. White.

"More and more, the chemistry community is moving toward investigating synthesis and characterization of large length-scale systems," White comments. At the same time, other areas, such as microelectronics, for example, are moving aggressively toward ever smaller submicrometer device features, he notes. "The critical length scales of these two fields are merging."

White adds that Polanyi's team shows how molecular properties incorporated during synthesis (in this case, structural differences among isomers) can be selectively imprinted onto the surface of the workhorse material of microelectronics--silicon.

Working under ultrahigh vacuum, the Toronto researchers prepare a pristine silicon specimen with an exposed (111) crystallographic face. Forces acting upon the crystal's surface cause the outermost layers of atoms to rearrange themselves relative to bulk silicon, adopting a geometry referred to as a 7 x 7 reconstruction.

Silicon (111) 7 x 7 is described as having a diamond-shaped unit cell consisting of 12 atoms and is widely studied because of its technological importance. Six of the atoms lie in the "faulted" half of the unit cell and the other six lie in the "unfaulted" half. The halves of the unit cell, which may be distinguished with STM, derive their name from a crystallographic feature known as a stacking fault.

Comparing the silicon surface chemistry of 1,2-dichlorobenzene to 1,4-dichlorobenzene, Polanyi and coworkers carry out successive experiments in which they coat the specimen with less than one molecular layer of the organic compounds, examine the surface with STM, illuminate the surface with 193-nm light, and then reimage the crystal surface.

The laser light causes the adsorbed molecules to photodissociate, sending pairs of chlorine atoms in search of new bonding sites, the group reports. And although the isomers are nearly identical in most regards, the researchers observe key differences in the final resting spots of the liberated atoms.

"We find a statistical distribution showing a most probable separation of 8 Å between adjacent chlorine atoms for 1,2-dichlorobenzene and a 14-Å separation for 1,4-dichlorobenzene," Polanyi says.

Offering a straightforward explanation to account for these differences, the Toronto chemist proposes that as the molecules fall apart the carbon-chlorine bonds extend roughly linearly from the phenyl rings. Both isomers steer their chlorine atoms toward near-neighbor sites where they can react with silicon dangling bonds (unsatisfied valencies). But the smaller angle between carbon-chlorine bonds in the 1,2-isomer compared with the 1,4-isomer leads to smaller separations between pairs of newly bonded chlorine atoms.

This simple interpretation seems intuitively clear. But in other chemical systems, the researchers point out, alternative events can occur. For example, molecular fragments may end up attached to a surface but well separated from other fragments or from the parent molecule. Or in many cases, fragments are ejected from a surface.

Polanyi, who won the 1986 Nobel Prize in Chemistry for work in reaction dynamics, explains that the present study follows an investigation in which his group showed that chlorobenzene can also be made to dissociate--depositing its chlorine atom on a silicon site immediately adjacent to the parent molecule. In that study, the group found that the fragment's preference for the faulted half of the unit cell was identical to chlorobenzene's preference [*J. Chem. Phys.,* **111,** 9905 (1999)]. Both studies show examples of what the team labels "localized atomic reactions"--concerted events in which bond breaking and bond making occur at adjacent positions.

In addition to helping extend the use of STM to probe reaction dynamics, the recent studies, which Polanyi describes as "demonstrations using simple molecules," offer possibilities for printing patterns of complex molecules on surfaces. "Self-assembly is sure to play a part in molecular electronics," he says, "and localized atomic reactions can help ensure that the molecular ink does not bleed but prints truly."

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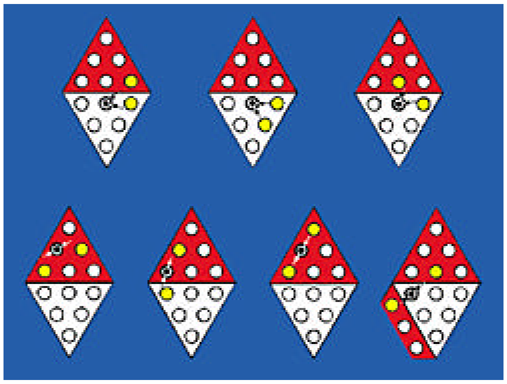
Reactions pin products to specific surface sites



Depicting photoreaction scenerios within the diamond-shaped unit cell of a silicon crystal surface, University of Toronto researchers show that localized atomic reactions place chlorine atoms (yellow) immediately adjacent to the molecules (black) from which they are derived (top = 1,2-dichlorobenzene, bottom = 1,4-dichlorobenzene) but that the differences in the structure of the parent molecules lead to differences in product spacings. Analyzing large numbers of samples shows that the most probable separations are roughly 8 Â for the 1,2-isomer and 14 Â for the 1,4-isomer.

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