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SURFACE SCIENCE

Surface Bonding Reconsidered

Study blurs the line between thermal and electronic processes in desorption

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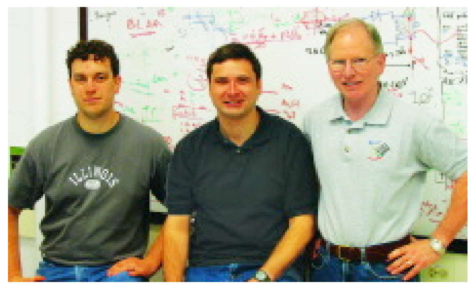
Conventional descriptions of the way chemical bonds at surfaces are formed and broken may need to be reevaluated, a new study indicates. Researchers have shown that fundamental events generally thought to be uninvolved in certain types of bonding processes may, in fact, play a key role.



GROUP EFFORT UIUC surface scientists Trenhaile (from left), Antonov, and Weaver take a break.

COURTESY OF JOHN WEAVER

The findings blur the lines used for classifying reaction mechanisms and show that commonly held assumptions regarding bonding may not always be valid.

Mechanisms for breaking bonds are generally classified as thermal or electronic in nature. According to classic textbook descriptions, in the thermal process, energy is pumped into a vibrational mode--a stretching motion, for example--causing a chemical bond to stretch, weaken, and eventually break.

In an alternative scenario, energy from an impinging electron, photon, or other source excites an electron in a bound state, causing it to undergo a sudden transition to an unstable, unbound state, which leads to bond breaking.

The bond-breaking processes are characteristically different from one another. For example, the timescales are distinct because the motions of atoms (in thermal processes) are sluggish compared with the relatively instantaneous reconfiguration of electrons (in electronic processes). The timescale difference forms the basis of the Franck-Condon principle, a simplifying assumption that is widely used in computations. In addition, electronic transitions generally require more energy than is available in thermal processes.

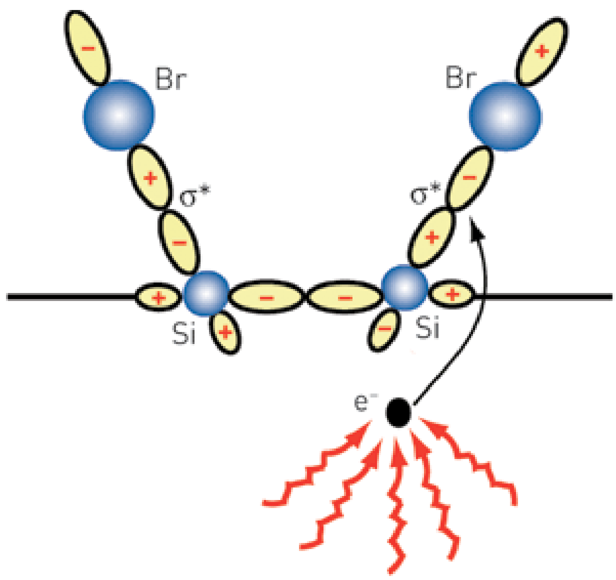
Now, researchers at the University of Illinois, Urbana-Champaign (UIUC), have shown that in the case of a bromine-coated silicon crystal, low-energy thermal vibrations of atoms in the lattice (known as phonons) can pool their energy and excite an electron at the Si-Br interface into an antibonding state, thereby breaking a bond and causing bromine to desorb (*Surf. Sci.*, published online April 14, dx.doi.org/10.1016/j.susc.2005.03.053).

On the basis of temperature-dependent scanning tunneling microscopy and kinetics analysis, John H. Weaver, a professor of materials science and physics; grad students Brent R. Trenhaile and Vassil N. Antonov; and coworkers determined that occasionally 10 or more phonons can "gang up" on an electron and stimulate desorption.

In a commentary in *Surface Science*, Robert J. Hamers, a professor of chemistry at the University of Wisconsin, Madison, notes that the "surprising" and "important" results show that the distinction between thermal and electronic mechanisms "is clearly violated" in this case, and it's the "breakdown of the Franck-Condon principle that makes the reaction possible." Hamers adds that "multiphonon processes are quite common, but their crucial role in controlling chemistry at surfaces has not been previously recognized."

Hamers points out that the desorption study has implications for adsorption (bond formation) and may lead to new types of selective masks and procedures for semiconductor processing.

Although the crucial step in the desorption process is a rare event, Hamers says the investigation shows that bonding "involves a complex interplay between lattice vibrations and electronic transitions, thereby breaking down the difference between thermal and electronic processes."



BREAKING BONDS Ordinarily weak crystal-lattice vibrations (phonons, wavy lines) sometimes work in concert to promote an electron in a bromine-coated silicon surface to an antibonding state (σ*), which leads to bromine desorption.

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