Bending Nature's Rules to Pattern Nanostructures on Sticky Surfaces

Researchers form patterned nanowires by adapting a versatile technique used to self-assemble clusters on surfaces.

An important objective in surface science and modern technology is the development of simple recipes for fabricating nanostructures such as quantum dots, wires, and thin films. What makes the project challenging is that Nature places strict constraints on how atoms and surfaces interact. In general, you want the things you build on surfaces to stick. But you also want to move those same things into place. The first requires strong binding; the second, weak binding.

In 1998, John Weaver (University of Illinois, Urbana-Champaign) and collaborators resolved those conflicting requirements by developing a process that effectively replaces one surface with another. The process, buffer-layer assisted growth (BLAG), allows one to form assemblies of atoms on a weakly interacting buffer layer that can be evaporated afterward.[1] Using a buffer layer like solid xenon as a temporary proxy for the surface effectively changes the thermodynamics of the adatom–substrate system. Because atoms are weakly bound to the Xe layer through van der Waals forces, they spontaneously diffuse, bind to each other, and form three-dimensional clusters. Once formed at low temperature (20 K), the self-assembled aggregates can softly land on what may be a much more reactive surface when the buffer layer sublimates away as it warms to 80 K.

By combining this growth technique with laser-induced desorption—a process that selectively removes surface layers using the heat from a single laser pulse—Micha Asscher and his PhD student Gabriel Kerner, both from the Hebrew University of Jerusalem, have developed a new lithography method for patterning (potentially at nanometer resolution) almost anything on anything else. As proof of concept, they used the method to form submicron-wide wires of potassium on ruthenium.[2] The process, outlined in the figure, is simple.

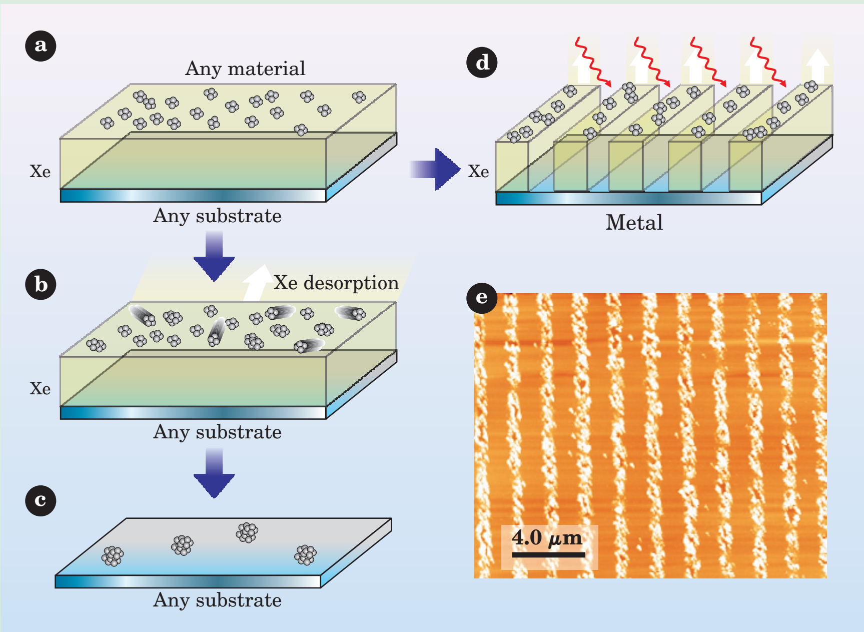
Making gratings

The Israeli researchers had originally set out to measure the diffusivity of potassium on other metals and metal oxides as part of an investigation into catalytic processes on clean, well-defined surfaces. Nonlinear reflection and diffraction methods are especially sensitive to monolayer changes at macroscopic scales. But to follow the diffusion, they first needed to create from the deposited potassium a thin periodic grating whose spatial order relaxes under the random diffusive motion of the potassium atoms.

Kerner used the interference of a split Nd:YAG laser pulse incident on the surface to make the grating, a technique originally introduced by Ron Shen (University of California, Berkeley). The 10-ns pulse heats the metal film to selectively break the surface bonds and desorb material. The trick is to avoid damaging the well-defined Ru surface. Potassium bonds strongly to Ru, but too high a laser power would change the surface from pristine and defect-free to roughened and pockmarked with lattice vacancies, dislocations, and steps—a change that would enormously influence the diffusion of surface atoms.

Kerner and Asscher realized that using a Xe buffer layer, though, would allow them to dial down the laser power to harmless levels, leaving strips of Xe coated with K clusters that line up along the interference fringes. Ulrich Höfer and coworkers had used a complementary approach in 1997 to demonstrate that a Xe template could control the sticking of hydrogen atoms on a silicon surface.[3] For the case of metal deposition on Xe, Asscher and Kerner found that it took at least 5–10 monolayers of Xe to create a clean pattern.

The pair also realized their patterning method has applications beyond its utility for diffusion studies. When metal atoms are first deposited on the Xe buffer, they diffuse to form small clusters, comprising, perhaps, 10–20 atoms. But when the surface warms and Xe evaporates, the motion



Recipe for buffer-layer growth. (a) Take any substrate and deposit a layer of cold xenon atoms on top. Follow that with atoms or molecules of your choice. Deposited on such a weak buffer layer, the atoms will interact almost entirely with just each other, as if on a skating rink. **(b)** Spontaneous diffusion produces three-dimensional nanoclusters. **(c)** Once allowed to warm, the Xe evaporates, which prompts clusters to further coalesce and softly land on the surface underneath. **(d)** The initial clusters can be patterned by using interference from a split laser pulse. The hot fringes ablate both the Xe buffer layer and metal clusters on top. Slow evaporation of the remaining Xe delivers the patterned clusters to the substrate, where they stick. **(e)** Experimental scanning force microscopy image of a gold grating (yellow) on ruthenium (orange), produced using this method. (Panels a–d adapted from ref. 5; panel e courtesy of Micha Asscher.)

and coalescence of the newly formed clusters can be profound—in principle, even producing clusters with tens of thousands of atoms. This makes the process an effective protocol for creating clusters of controlled sizes from practically any metal. By adjusting the buffer thickness, for instance, one can potentially tailor the size and density of the nanostructures that drop to the surface,[4] as well as the profile of the grating.

Clean lithography

To measure those grating profiles directly, Asscher and Kerner switched from potassium to gold films. The first scanning force microscopy images of Au on Ru show thin wires that consist of condensed clusters (panel e). Characterizing the properties of such wires (including their conductivity as a function of wire width) remains to be done. While initially diffusing on Xe, the clusters remain balled up, essentially out of contact with the Ru. But after landing, the extent to which clusters wet the substrate depends on their relative surface energies. And the thickness and coverage of molecules could be critical to the morphology of deposited material.

By adjusting the Bragg scattering angle and the laser's power density, Kerner has created patterns of lines that differ in widths and spacing. Because the desorption rate of ablated atoms depends exponentially on temperature, higher power densities sharpen the lines. Asscher points out that their method has the potential to form wires 30 nm wide and 5 mm in length—a 10^5 aspect ratio—using a single laser pulse.

In that respect, the work parallels conventional lithography: The laser wavelength accounts for how finely wires or circuit elements can be drawn. (Using an electron-beam or x-rays, even finer resolution is possible.) Columbia University's Tony Heinz argues that what really distinguishes patterning methods like Asscher's from more traditional photolithography is the chemical purity of the technique: "No one would claim traditional lithography is clean to the last monolayer. But this [method] is. . . . The xenon buffer layer vanishes without a trace."

Asscher envisions a time when vacuum chambers might replace clean rooms in lithographic facilities. But Heinz sees the technique's attractiveness more in terms of doing rigorous, well-controlled surface science. Fabricated in ultrahigh vacuum, for example, the patterned lines provide a template for studying carrier transport of simple molecules and exotic clusters in confined channels. But other projects come to mind as well: measuring crystal growth and diffusion of clusters of different sizes, or monitoring the reaction of one structure with another; in short, the kind of projects that prompted Asscher to develop the patterning method in the first place.

Mark Wilson

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Is Sedna's Strange Orbit the Shape of Things to Come?

A newly discovered distant minor planet may provide clues about the Sun's early environment.

According to Inuit legend, the goddess Sedna lives beneath the frigid Arctic seas. And so in late 2003, when Caltech's Michael E. Brown, working with Chadwick Trujillo of the Gemini Observatory and David Rabinowitz of Yale University, discovered an outer Solar System object whose surface temperature never rises much above 30 K, they proposed that it be named after the Inuit deity.[1]

The minor planet Sedna, whose official designation is 2003 VB_{12}, has a number of interesting properties. It is red like Mars, roughly 1500 km in diameter, and has a rotational period much longer than is typical for minor planets. But it is Sedna's record-breaking perihelion combined with its highly eccentric orbit that have planetary scientists most intrigued. If, as expected, other Sedna-like objects are soon found, the clues they leave promise to change scientists' view of the Solar System.

How orbits change

Since the autumn of 2001, Brown and colleagues have systematically observed the sky, searching for reasonably large and bright objects moving across the field of stars and galaxies. In any given observation, they train a 172-megapixel camera mounted on Palomar's Samuel Oschin telescope on a 10 square-degree section of sky. The camera, a mosaic of 112 charge-coupled devices (CCDs), takes three pictures over a three-hour period. By aligning the pictures so that the stars and galaxies overlap, Brown's team can look for moving objects. One such object was observed in the pictures taken on 14 November 2003, and Sedna's discovery was announced publicly on 15 March 2004. Although the idea behind the search is simple, the technology is not. It would have been extremely difficult to discover Sedna with CCDs and computing power from as recently as five years ago.

After they discovered Sedna, Brown and colleagues studied about three years of archival data to determine its orbit. Sedna lies well beyond the distant giant Neptune; it ventures no closer than about 76 AU from the Sun and its semimajor axis is about 480 AU. (The astronomical unit, or AU, is the mean Earth–Sun distance.) Having a semimajor axis greater than Neptune's, though, is hardly a mark of distinction. Planetary scientists now know of some 800 objects in the outer Solar System lying in the so-called Kuiper belt; the most famous of these is Pluto (see the article by Brown in PHYSICS TODAY, April 2004, page 49).

Some Kuiper belt objects—the ones with relatively circular orbits—may have formed in place. The higher-eccentricity objects, it is believed, had their orbits perturbed by gravitational interactions with Neptune or other giant planets. In many cases, that interaction is a scattering process. Scattered Kuiper belt objects have perihelia of about 30 AU, which corresponds to the radius of Neptune's orbit. Other Kuiper belt objects were resonantly captured by Neptune and locked into orbits whose period is a simple rational multiple of Neptune's. The most distant resonance is at 55 AU. The Kuiper belt has an edge at around 50 AU in the sense that all Kuiper belt objects, even if they occasionally stray well beyond 50 AU, lie on orbits with perihelia within that limit. Sedna is the only known object