Fabricating 2D Molecular Gradients with a Simple Mechanical Device

Scientists from North Carolina State University and the U.S. Department of Commerce's National Institute of Standards and Technology have used a silicon elastomer network in conjunction with a simple mechanical stretching device to produce two-dimensional molecular gradients for nanotechnology applications. The structure of these 2D molecular gradients was determined at the National Synchrotron Light Source. The research is described in the cover story of *Advanced Materials*, September 16, 2003.

Tuning the surface characteristics of materials has become of paramount interest in many fields of science and technology. While most applications involve surfaces that are chemically homogeneous, in other instances, surfaces are needed that comprise two or more chemically heterogeneous regions. Such heterogeneous structures can be applied as tools for chemical separations, substrates for selective adsorption, and specimens for lithography and other micro-fabrication technologies.

Authors (from left): Jan Genzer, Kirill Efimenko and Daniel Fischer

"We now see increased interest in generating and using 'gradient substrates,' in which the energy varies gradually across the sample surface," said Jan Genzer, a chemical engineer at North Carolina State and the lead author of the paper. "Numerous studies have shown that such structures offer a unique geometry for probing cell/substrate interactions, phase behavior in thin-liquid films, including those made of polymers, and directed motion of liquids. Recent reports also demonstrate that gradient substrates are useful in building molecular templates and exploring material characteristics using multi-variant approaches."

The scientists used a new synchrotron-based x-ray technique called combinatorial near edge x-ray absorption fine structure (NEXAFS) (cover story January 13, 2003, *Applied Physics Letters*) to map out the billionth-of-a-meter-thick molecular gradient with millimeter spatial resolution. According to Daniel Fischer, a physicist from the National Institute of Standards and Technology and co-author of the study, few techniques can be used to study the physical and chemical properties of chemically heterogeneous materials at the millimeter scale. In addition, most are limited in sensitivity, can damage the samples under study, or require special preparation protocols.

Said Fischer, "Combinatorial NEXAFS is non-invasive, does not require transparent samples, and provides simultaneous information about the chemical nature and orientation of the molecules on the surface. Also, we employed an in situ methodology, which is based on mechanical deformation of the substrate covered with a uniform array of grafted organosilane molecules."

Details of the Technique

A two-dimensional molecular gradient is produced by mechanically stretching a "dog bone"-shaped elastic poly(dimethylsiloxane) (PDMS) plastic sheet clamped in a simple screw-activated device (see figure).

As explained by Kirill Efimenko, a senior research associate at North Carolina State and a co-author of the study, turning the screw by hand stretches the PDMS sheet by 40 percent and produces a gradient of strains along the surface. The most strain occurs along the PDMS sheet that is continuous between the clamps. The asymmetrically stretched PDMS "dog bone" is then exposed to an ultraviolet ozone treatment, which sensitizes the PDMS, making it attractive to a gaseous organosilane monolayer deposited over the sheet's entire surface. After the monolayer deposition, the screw is turned backward, relieving the strain in the PDMS "dog bone." Doing so compacts the organosilane monolayer greatest at the position of highest original strain. The resulting 2D gradient in organosilane molecular density on the surface of the PDMS sheet was measured with combinatorial NEXAFS.

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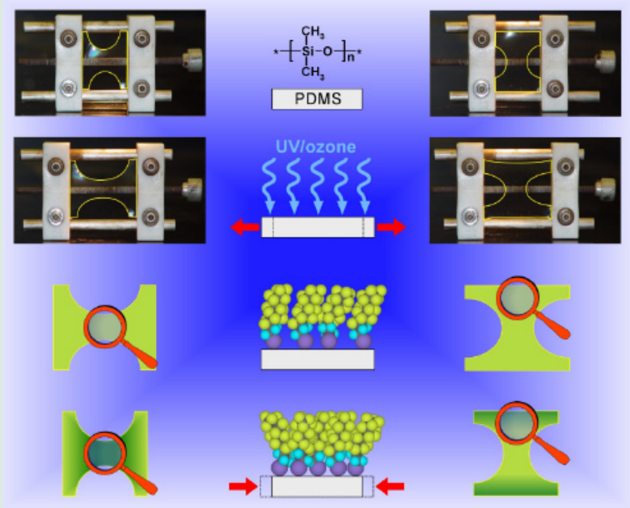
— Diane Greenberg



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