Nanoscale "Glass-Blowing" Yields Nanopores with Single-Nanometer-Diameter Precision

Membranes with nanometer-sized pores are becoming important for many applications such as the detection and characterization of biomolecules. The fabrication of such nanopores is a challenging proposition. At Delft University of Technology, A.J. Storm and colleagues in C. Dekker's group have demonstrated a technique to fine-tune the size of pores in silicon dioxide with 1-nm precision using the electron beam in a transmission electron microscope (TEM). This level of control is at least one order of magnitude better than that achievable with conventional electron-beam lithography. They report this technique in the August issue of *Nature Materials*.

State-of-the-art silicon technology and silicon-on-insulator (SOI) wafers were used to fabricate 70 μm × 70 μm free-standing silicon membranes. These were thermally oxidized to create 40-nm-thick SiO_2 layers on both sides. Subsequently, electron-beam lithography, ion-beam etching, and anisotropic KOH wet etching were used to yield a membrane with a number of pyramid-shaped holes of various dimensions. The membrane was placed in the TEM and subjected to an electron beam with an intensity in the range of 10^5–10^7 A/m^2. This caused pores with diameters of ≤50 nm to shrink. The shrinkage of the pores could be precisely controlled by adjusting the beam intensity or by blanking the beam to stop the process. The TEM allowed for direct visual feedback during this process. At these electron beam intensities, the pores closed at a rate of 0.3 nm/min, which allowed the researchers sufficient time to easily control the final pore size. Conversely, the process caused pores of ≥80 nm diameters to expand, suggesting a dependence of the dynamics on initial pore size, according to the researchers.

The shrinking of the pores can be explained in terms of surface-tension effects in the silicon dioxide material. The electron irradiation softens the glassy silicon dioxide and induces viscous flow. This allows the oxide to deform slowly, driven by surface tension. The researchers compare this process to glass-blowing on the nanoscale.

The technique can be broadly applied to pores with initial diameters in the 50 nm range, which is achievable using standard lithographic processes or even a focused electron beam. Again, with TEM it is then possible to visually fine-tune the size of the pores as they shrink. Once the final size is reached, which is theoretically limited by the resolution of the TEM, the beam intensity is dropped, and the specimen quenches to its initial glassy state. In addition, the composition of the material around the pores does not change, and the pores are found to be stable at ambient conditions and in water. The researchers also used a higher electron-beam intensity (>10^8 A/m^2) to drill 6-nm-diameter holes in the membrane, and then slowly closed the holes using a lower beam intensity. The researchers anticipate that this technique will increase the level of control in a wide range of nanotechnology applications.

GOPAL RAO

Block Copolymer Organized by Directed Self-Assembly

Researchers at the University of Wisconsin's Center for Nanotechnology and Materials Research Science and Engineering Center on Nanostructured Materials and Interfaces have demonstrated a hybrid technique that combines photolithography and block copolymers, a self-assembling material, to produce defect-free patterns, oriented and registered with the underlying substrate, over arbitrary large areas. Block copolymers, which are compounds composed of two or more long polymer chains connected at the ends, tend to organize themselves into spots, cylinders, or broad, swirling patterns. For technological applications, ordered structures are needed.

Team leader Paul Nealey and colleagues used photolithographic techniques to chemically alter the surface of a standard silicon wafer. By employing extreme ultraviolet light (λ = 13.4 nm), which has a much shorter wavelength than the light used in conventional lithography, and interference techniques, the researchers were able to lay down an alternating pattern of straight, parallel, chemically activated stripes 20–30 nm wide. As reported in the July 24 issue of *Nature*, the researchers washed the patterned silicon surface with a solution containing the block copolymer. In this case, it was a compound containing just two component polymers: one that had a chemical attraction to one type of stripe, and another that preferred the opposite type of stripe. By manipulating parameters such as the spacing of the stripes and the length of the two polymers, the researchers achieved a precise balance of forces. As a result, the copolymer organized itself on top of the nanoscale stripes, with no evidence of swirling or other undirected behavior (see figure). Potential applications include nanoscale integrated circuits, using the copolymer patterns as templates for etching the underlying silicon.

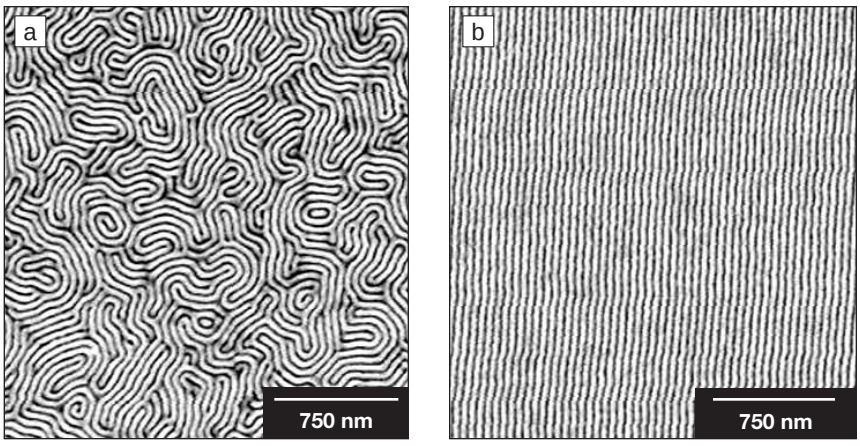

Figure. (a) Domain structure of a block-copolymer film on a homogeneous surface; (b) domain structure of a block-copolymer film after epitaxial assembly on a chemically patterned surface.

Ceria-Based Mixed Metal Oxides Assist in Clean Hydrogen Oxidation

Unfavorable thermodynamics makes the dehydrogenation of alkanes to alkenes an energetically expensive process. An efficient solution would be to derive the required energy from the oxidation of the hydrogen by-product. This requires the selective oxidation of hydrogen from a mixture of hydrogen and hydrocarbons. While supported oxides of *p*-block metals (i.e., metal elements in Groups IIIA–VIIIA with a valence-electron configuration of ns^2, np^{1-6}) have shown some selectivity toward hydrogen, they have several disadvantages, primarily due to liquefaction at the high reaction temperatures. University

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of Amsterdam researchers G. Rothenberg, E.A.B. de Graaf, and A. Bliek have developed a cerium tungsten oxide catalyst that is able to cleanly and selectively oxidize hydrogen while maintaining excellent thermal stability. Moreover, the catalyst can be readily regenerated with oxygen and serve as an oxygen "reservoir."

As reported in the July 28 issue of *Angewandte Chemie*, Rothenberg and coworkers doped ceria with Bi, La, In, Mo, Pb, Sn, V, W, Y, and Zr to make 10 ceria-based bimetallic oxides by using a parallel synthesis technique based on boiling molten mixtures of nitrate precursors followed by calcination. The extent of substitution of Ce ions was limited to 10% so as to retain the cubic fluorite crystal structure. As the redox chemistry of substituted ceria is sensitive to induced structural defects and stresses in the crystal lattice, the researchers expected to see varied oxygen mobility, which would produce different levels of catalytic activity and thermal stability in these systems.

Rothenberg said, "We had an idea that similar cations will create 'small holes' in the fluorite lattice, without causing too much disturbance. This way, you keep the oxygen-exchange properties of the ceria, but also, hopefully, tune the selectivity so that the new material will oxidize hydrogen selectively."

The catalysts were screened in cyclic redox experiments with a gas mixture that simulates the effluents from an ethane dehydrogenation process. While the lanthanum-, indium-, and zirconium-doped systems showed the highest activity, the tungsten-doped system showed >97% selectivity toward hydrogen. Moreover, this system showed excellent stability under sintering as well as negligible coke formation, properties that are of significance in commercial oxidative dehydrogenation reactions.

The mechanism of the hydrogen selectivity remains to be determined. Rothenberg thinks that the small hydrogen molecules may diffuse into the lattice, reacting with labile oxygen atoms that are unavailable to the bulky hydrocarbon molecules.

SARBAJIT BANERJEE

Titanium Nanotubes Serve as Hydrogen Sensors

Titanium nanotubes used as hydrogen sensors is an example of materials properties changing dramatically when crossing the border between real-world sizes and nanoscopic dimensions. Craig A. Grimes, associate professor of electrical engineering and materials science and engineering at The Pennsylvania State University, and colleagues have found that hydrogen entering an array of titanium nanotubes flows around all the surfaces, but also splits into individually charged atoms and permeates the surface of the nanotubes. These hydrogen ions provide electrons for conductivity. The change in conductance signals that hydrogen is present at a concentration above the background level.

The researchers report in the August 1 issue of *Sensors and Actuators B: Chemical* and an earlier issue of *Advanced Materials* (April 2003) that because the nanotubes are in close contact with each other (see figure), the contact points become highly conductive relative to the rest of the nanotube.

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