

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 $70\ \mu\text{m} \times 70\ \mu\text{m}$ 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 – $10^7\ \text{A}/\text{m}^2$. This caused

pores with diameters of $\leq 50\ \text{nm}$ 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 $0.3\ \text{nm}/\text{min}$, which allowed the researchers sufficient time to easily control the final pore size. Conversely, the process caused pores of $\geq 80\ \text{nm}$ 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 ($>10^8\ \text{A}/\text{m}^2$) 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 ($\lambda = 13.4\ \text{nm}$), 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 – $30\ \text{nm}$ 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.

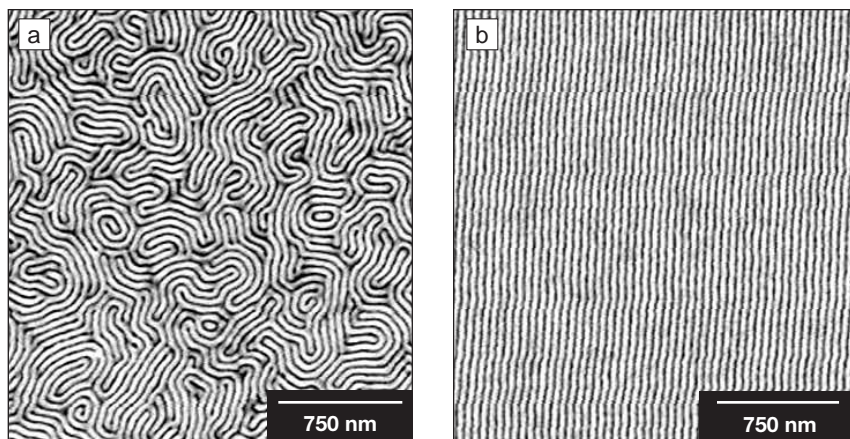


Figure. (a) Domain structure of a block-copolymer film on a homogeneous surface; (b) domain structure of a block-copolymer film after epitaxial assembly on a chemically patterned surface.

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