which is very close to the experimentally observed characteristic length of 280 nm. Buehler developed a new theoretical framework that provides a quantitative treatment of the nanomechanics of collagen fibrils.

Buehler used large-scale computer simulations that begin at the atomistic scale, treating individual chemical interactions based on quantum mechanical calculations to obtain results consistent with his theory. Previous models of collagen typically involved empirical parameters and lacked a rigorous connection between quantum chemistry, molecular structure, material properties and collagen's physiological function. Buehler's model provides a first-principles-based materials representation. Furthermore, the model provides a basis for understanding the effects of diseases "caused by defects in the molecular structure of collagen altering the intermolecular and molecular properties due to genetic mutations, which modifies the mechanical behavior of collagen fibrils."

Collagen, an extracellular matrix protein, plays an important role in defining the infrastructure of physiological tissues under load or strain, and is critical to tissues within the skeletal, muscular, and cardiovascular networks. Improved understanding of nature's design criteria will help guide materials and biomedical engineers to develop enhanced biomimetic polymers. Buehler's work could contribute to research that may one day develop cures for collagen-related diseases such as the Ehler–Danlos syndrome, joint hyperextensibility, or scurvy.

"We are currently extending our models to describe the deformation mechanics of other structural proteins and more complex materials such as bone," said Buehler. "For example, the smallest building blocks of bone are mineralized collagen fibrils, which can be modeled using similar concepts."

Combination of Top-Down and Bottom-Up Approaches Allows Fabrication of High-Aspect-Ratio 2D $KTiOPO_4$ Photonic Crystals

In many applications where optoelectronic modulation of light is needed, it would be very useful to have micro- or nanostructures fabricated from materials with large electro-optic coefficients such as the ones found in many inorganic nonlinear crystals. Unfortunately, when top-down procedures are applied to such materials to produce, for instance, two-dimensional (2D) photonic crystals, they are not as effective as when they are applied to semiconductors. A. Peña of the Universitat Rovira i Virgili, S. Di Finizio from the ICFO-Institut de Ciencies Fotoniques, J. Martorell and A. Rodriguez of the Universitat Politecnica de Catalunya, Spain, and their colleagues have obtained 2D photonic crystals by growing microrods of $KTiOPO_4$ inside the air holes of an ordered macroporous silicon membrane closely bound to a $KTiOPO_4$ substrate (see Figure 1).

As reported in the September issue of *Advanced Materials* (DOI: 10.1002/adma.200502566), the researchers prepared the silicon membranes by computer-controlled light-assisted electrochemical etching of a patterned *n*-type <100> silicon wafer, with which they control the growth, size, depth, and quality of the pores. A *c*-oriented $KTiOPO_4$ substrate was bound to the sili-

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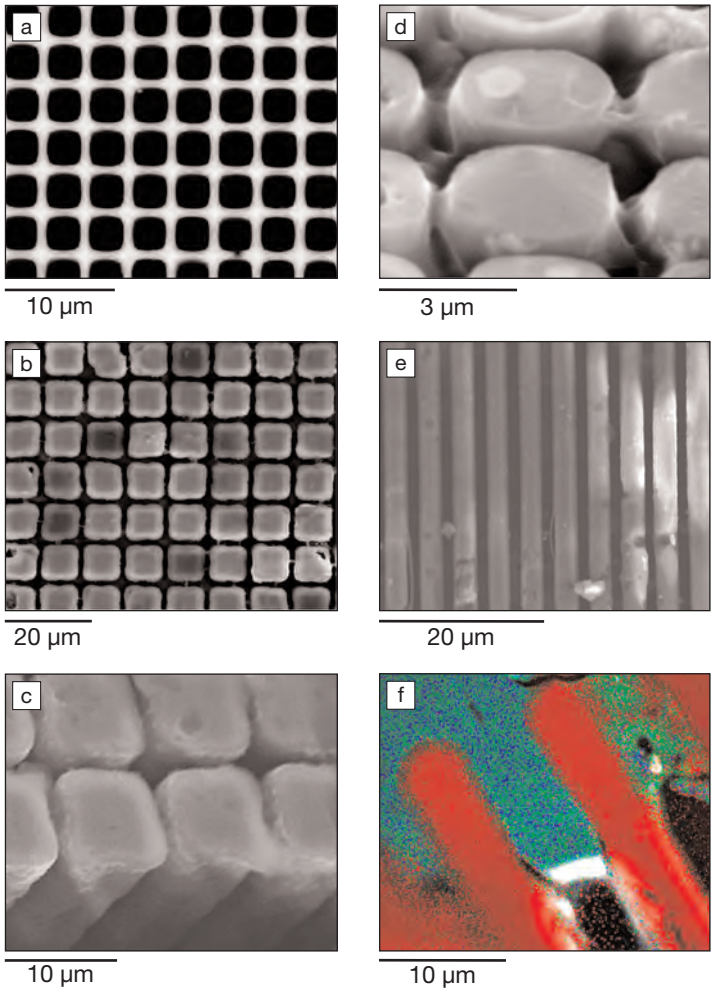

Figure 1. Scanning electron microscopy images of (a) a macroporous silicon two-dimensional (2D) square lattice membrane; (b) top surface of a 2D $KTiOPO_4$ (KTP) photonic crystal after polishing and partial etching of the silicon mask; and (c) side view of the 2D KTP photonic crystal, where the silicon template has been selectively etched from the KTP. (d) Detailed view of a 2D KTP crystal with a period of 4.5 μm, which was also used for the optical measurements. (e) Side view of a plane of columns of a 2D KTP photonic crystal lattice. (f) Energy-dispersive x-ray analysis of the KTP columns grown within the air holes of the silicon matrix: red areas indicate the presence of silicon, green areas indicate potassium, and bluer areas indicate titanium. Images (b), (c), and (e) were taken without the deposition of a gold layer, so that the samples could be used for later optical measurements. (Images reproduced with permission from Advanced Materials*, DOI: 10.1002/adma.200502566; © 2006 Wiley-VCH.)*

con membrane and the template/substrate set was dipped into a supersaturated growth solution of $KTiOPO_4$, removed, and slowly cooled to avoid thermal stresses that might produce cracks in the grown columns. After removing the composite material from the growth solution, polishing its surface to optical quality, and partially removing the silicon template by selective chemical etching, the researchers obtained a 2D photonic crystal consisting of squared $KTiOPO_4$ rods with 4.5 μm lattice parameters and 80 μm rod lengths.

These photonic structures showed a high degree of crystallinity, with the axis of the $KTiOPO_4$ rods perfectly oriented with the $KTiOPO_4$ substrate. The researchers demonstrated the photonic-crystal

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properties of the 2D structures by measuring the specular reflection of light as a function of the wavelength of the incident field, observing a dip at 1100 nm, corresponding to the third-order Bragg reflection band. The researchers also demonstrated the potential of the 2D array of $KTiOPO_4$ rods to host an efficient nonlinear interaction by measurements of the diffracted light at the second-harmonic frequency of the incident wave.

This procedure enables control over the direction of growth relative to the orientation of the 2D structure. For any given application, it will then be possible to use the most appropriate combination of nonlinear or electro-optic coefficients of the material, something which is not always possible in bulk $KTiOPO_4$, given the limited material birefringence. Such newly developed photonic crystals, which should be easily integrated in silicon-based devices, may find applications in generating light more efficiently at higher frequencies, in the electro-optic modulation of light, and in obtaining backward parametric amplification and oscillation.

Submicrometer Technique Etches Curvilinear Silicon and Glass Patterns with HF-Saturated Hydrogel Stamps

Applications in micro-optics, microfluidics, and microelectronics call for micrometer-sized devices with curvilinear or multilevel surface topographies. Casting elastomers against rigid masters is a parallel process that can rapidly create such architectures, but the resulting polymeric devices possess low resistance to mechanical wear, are permeable to gases, and often swell when exposed to organic solvents. Durable inorganic substrates, with better mechanical and chemical properties, may be patterned by expensive techniques such as reactive ion etching, laser ablation, or micromachining, but the throughput rate of these serial processes is low. In the July 16 issue of *Advanced Materials* (p. 2004; DOI: 10.1002/adma.200600716), followed by a recent publication in *Chemistry of Materials* (p. 4722; DOI: 10.1021/cm061468p), researchers at Northwestern University, led by B.A. Grzybowski, have presented a novel, inexpensive, direct-printing technique that is suitable for rapid prototyping of multilevel reliefs in a variety of rigid substrates. The technique boasts a lateral resolution (in silicon) of several hundred nanometers, and it can pattern several square centimeters at a time.

Using soft lithographic techniques, Grzybowski and co-workers created a flexible hydrogel stamp by first patterning a reusable micropatterned master with the desired topography, then casting high-gel-strength agarose against it. They "inked" the agarose stamp by soaking it for 4 h in a 0.6 M aqueous solution of hydrofluoric acid, with 0.1 vol% Triton X-100 surfactant.

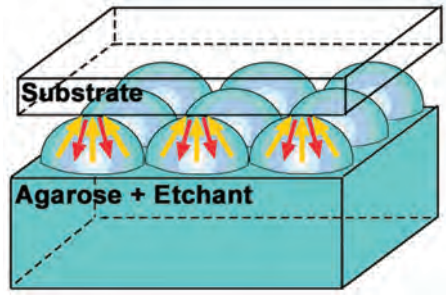

Figure 1. Schematic illustration of the experimental procedure for reaction-diffusion microetching.

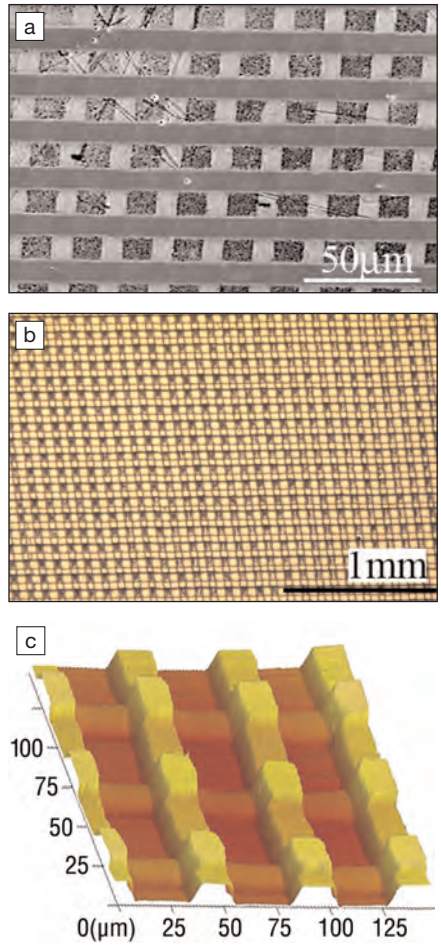

Figure 2. Three-dimensional (3D) architecture fabricated by sequential application of arrays of parallel lines along perpendicular directions. Pattern in GaAs: (a) scanning electron microscope image, (b) large-area optical micrograph, and (c) atomic force microscope image of a 3D structure showing trenches 0.7 μm and 0.4 μm deep. (Reprinted with permission from Chemistry of Materials ***18*** *(20) (October 3, 2006) p. 4722; DOI: 10.1021/cm061468p; © 2006 American Chemical Society.)*

The researchers laid the saturated stamp, feature side up, in light mineral oil, which confined the etchant to the raised features and reduced evaporation. Next, they placed the solid substrate to be patterned (e.g., a glass slide or a silicon wafer) directly upon the stamp, and ensured intimate contact by resting a small weight on top. Depending on the material system and the desired feature depth, the subsequent isotropic etching takes from several minutes to several days. The scientists then cleaned the etched surface using a piranha solution. The scheme is summarized in Figure 1.

The bulk agarose gel acts as a two-way "pump" that supplies fresh etchant and efficiently removes reaction products through diffusive transport. The etch rate is reaction-limited and is approximately constant. More concentrated acid solutions etch faster (which is helpful when making high-aspect-ratio features) but have detrimental effects on the stamp.

This easy-to-use, reliable method is reminiscent of woodcut printing, but on a submicrometer scale. The scientists have demonstrated the versatility of the technique by fabricating several difficult devices using their technique, including an array of convex/concave microlenses and a multilevel passive microfluidic mixer in glass.

"By exploiting other interfacial chemistries," Grzybowski said, "we have used the reaction-diffusion microetching process to pattern other materials, including zinc oxide and gallium arsenide." An example is shown in Figure 2.

RICH LOUIE

Nanocrystalline, Flexible Photoelectrochromic Films Display Quick Response Time

Changes in the optical properties of chromogenic materials occur by electric, thermal, or photo activation—for example, electrochromic "smart" windows that display switchable glazing. The change in color of photoelectrochromic (PEC) materials results from light absorption and application of an electric field. For example, a previously reported PEC device is based on an inorganic electrochromic film combined with a dye-sensitized semiconductor electrode. Recently, G. De Filpo and co-researchers at the Department of Chemistry, University of Calabria, Italy, developed a PEC film that uses a polymer-

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