

relative stability of the *cis* and *trans* isomers and the energy barrier between them. In one example (Figure b), with a *meta* linkage and a total of six hydrogen bonds per azobenzene in the *trans* state, ΔH increased by 260% over gas-phase azobenzene and E_a increased by 20%, giving a half-life for the photoexcited state of the azobenzene-CNT fuel of greater than one year, a marked improvement over gas-phase azobenzene.

Kolpak and Grossman said that their azobenzene-CNT fuel will be water soluble due to the hydroxyl groups on the solvent-accessible surfaces. Increased solubility can be achieved with substitution of additional polar groups at positions in contact with the solvent, which should not affect ΔH or E_a , so that formation of highly concentrated solutions is possible. The researchers estimated that the temperature of the heat released by their azobenzene-CNT fuel to be 620 K, but said that even higher temperatures could be achieved by lowering the heat capacity of the fuel.

Kolpak and Grossman said, “In addition, our results suggest that one can generalize the concept of hybrid photoisomer-substrate nanostructures to other photoactive molecules, different substrates, and different linker chemistries, potentially leading to a wide range of novel degradation-resistant, high-stability, and high-energy density solar thermal fuels.”

Steven Trohalaki

dicted volumetric energy density equal to that of Li-ion batteries, by covalently bonding photoactive azobenzene derivatives to carbon nanotubes (CNTs).

As reported in the June 10 online edition of *Nano Letters* (DOI: 10.1021/nl201357n), Kolpak and Grossman used density functional calculations to show that the CNT facilitates a close-packed, crystalline arrangement of azobenzenes—see (b) in figure. The packing interactions and the symmetry-breaking of the azobenzenes (a consequence of

their attachment to the CNT) both contribute to a large increase in ΔH . In the packed state, the researchers found that the position at which the azobenzenes were attached to the CNT (*para*, *meta*, or *ortho* with respect to the azobenzene nitrogen double bond) could be used to alter the value of ΔH . By also substituting hydroxyl groups for phenyl hydrogens, and thereby enabling the formation of hydrogen bonds between adjacent azobenzenes, the researchers found that they could simultaneously increase the

Nano Focus

Triblock polymers make square arrays with long-range order

Block copolymers exhibit rich self-assembly behavior which has been exploited to generate a wide range of periodic structures in bulk and in thin film form. Self-assembly of diblock copolymer thin films has been widely exploited to generate sub-10 nm microdomain patterns without the necessity for costly lithographic processing, and has yielded geometries based on parallel lines and close-packed arrays of dots.

Three component triblock terpolymers extend the range of geometries which can be generated to include square arrays of dots, but thin films of triblock terpolymers suffer from the drawback that the patterns are usually broken up into small regions with only short-range order. Overcoming this problem, a team of researchers has now demonstrated that much longer range order can be imposed upon these triblock terpolymer structures through the selective application of surface topography and polymer brush coatings.

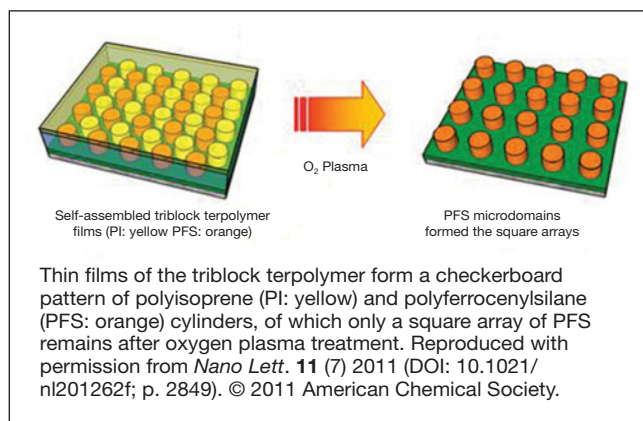
As reported in the July 13 issue of

Nano Letters (DOI: 10.1021/nl201262f; p. 2849), C.A. Ross from the Massachusetts Institute of Technology, I. Manners from the University of Bristol, and their co-workers used a blend of polyisoprene-block-polystyrene-block-polyferrocenylsilane (PI-b-PS-b-PFS) and 15% polystyrene homopolymer to create cylinders of PI and PFS arranged in alternating square arrays within a PS matrix. Coating sufficiently thin films (~32 nm) of this material onto silicon wafers covered with short polymer chains (a polymer brush) caused the cylinders to orient themselves perpen-

dicular to the surface. The extent of order in the resulting checkerboard pattern was honed by carefully adjusting the film thickness, the type of polymer brush, and solvent annealing. Swelling the film with the appropriate amount of chloroform allowed a relatively hydrophilic polyethylene oxide (PEO) brush to be used, whose similar interaction with all three components promoted large ordered domains of up to 1.75 μm in size. The films were then etched with an oxygen plasma, which preferentially removes the PS and PI regions to leave only a square pattern of PFS posts which etch more slowly due to their iron and silicon content.

The long-range order of the pattern was further improved by forming the block copolymer film on substrates which had been pre-patterned with walls

and posts using electron beam lithography. The substrate pattern then acted as guiding surface features. While a more neutrally interacting flat surface promotes order, these vertical features are most beneficial when selectively interacting with the PFS block, and so were coated separately with a PFS brush. In this way, posts placed sparsely throughout the grid act as surrogate PFS cylinders and enforce order on the pattern over longer distances. Square arrays



such as these are useful as etch masks through which a Cartesian grid can be transferred onto functional materials, providing a layout for minute circuitry or other nanoscale devices.

Tobias Lockwood

Two-state dynamics achieved on amorphous silicon surface

Amorphous silicon (α -Si) is widely used in the semiconductor industry for a range of device applications due to its low cost and because it is much easier to form flexible thin films than crystalline silicon. In an effort to settle the continuing debate over whether α -Si is a glass or simply an amorphous solid, M. Grubele, J. Lyding, G. Scott, and S. Ashtekar from the University of Illinois at Urbana-Champaign have attempted to observe the two-state dynamics of α -Si clusters which is characteristic of glass.

As reported in the June 10 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.106.235501), the researchers used low energy ion implantation and chemical vapor deposition (CVD) to create an amorphous silicon surface from a Si substrate, generating the two-state dynamics. A scanning tunneling microscope (STM) was utilized to directly observe the hopping between the two states at a temperature of 295 K (see figure). This temperature lies above the tunneling regime and below the glass transition temperature of α -Si as reported at 900 K, a universal observation of glassy behavior.

Since α -Si surfaces are normally grown with hydrogen incorporated into the structure, the researchers passivated the α -Si surfaces with 1% hydrogen. With the addition of hydrogen, a two-state motion was not observed, which was attributed to the fact that hydrogenation quenches the two-state dynamics by relaxing the surface to lower energy structures. Hydrogen passivation caps the most strained, least-bonded Si atoms to lower the surface free energy, thereby reducing two-state dynamics. Furthermore, the surface showed signs of crystallization including larger clusters, cracks, and highly structured patches. Cracks indicate that the density of the remaining α -Si surface increased, as expected if strain is relieved. The crystalline patches ranged from just a few atoms to hundreds of atoms in surface area, consistent with a Si(111) surface structure, the lowest energy surface

structure for Si. Blobs observed on the surface indicated the merging and undercutting of the surface structure as a result of a reaction with hydrogen. Thus hydrogen passivation has major structural and dynamical consequences.

This research provides an improved understanding of the glassy behavior of amorphous silicon. Although two-state dynamics hopping has been pre-

