

distribution. These characteristics of carbon led to better filling of carbon into the zeolite nanochannels, which are shown by nuclear magnetic resonance analysis.

Since the highly ordered structure suggested the absence of mesoporosity, the researchers concluded that one possible carbon structure may be "a curved graphene structure...accommodated to the curved inner surface of the zeolite nanochannels."

KINSON C. KAM

Theories of Polymer Crystallization Challenged by Molecular Simulations

A team of researchers at the University of Massachusetts has demonstrated their modeling results on polymer crystallization from solution in which entropic barriers control the initial lamellar thickness by initiation of crystal nuclei. The nuclei then grow by chain absorption at the crystalline interface, and the lamellae thicken in a cooperative process requiring mobility of all chains in the crystal. These results challenge the conventional Lauritzen-Hoffman (LH) theory and its generalizations.

In contrast to the crystallization of small molecules, the crystallization of polymers from solution is still poorly understood. Polymer molecules can participate in different initial nuclei, which leads to entropic frustration and incomplete crystallization, in which the polymer chains fold back and forth to form crystalline lamellae. So far, thermodynamics estimates have failed to predict the initial lamellar thickness, and all estimates are about 2 orders of magnitude higher than the 10 nm observed. There is also some controversy about the growth mechanism of the lamellae. As reported in the November 19, 2001, issue of *Physical Review Letters*, the group used Langevin dynamics simulations to reinvestigate these problems.

The results of the dynamics simulations show that the initial crystallization from solution does not occur by spinodal dynamics, but through a nucleation and growth mechanism, in which the initial lamellar thickness is dictated by free-energy barriers. The initial thickness is spontaneously selected, and the chains thicken by negotiating free-energy barriers before asymptotically approaching a thickness that is much smaller than the thermodynamically predicted extended chain limit. Chain growth occurs by simultaneous adsorption and crystallographic registry of diffusing chains at the growth front. In contrast to the LH model, this step is not hindered by an energy barrier. The chains then rearrange to form stems that are commensurate with the

crystal thickness at the growth front.

M. Muthukumar, Barrett Professor in the Department of Polymer Science and Engineering, said, "Our results suggest that the definitions of quench depth and equilibrium melting temperature, which depend on the equilibrium lamellar thickness, need to be redefined. This opens up 40 years of accumulated data for re-analysis."

CORA LIND

Hypersensitization Improves Performance of Rare-Earth-Doped Active Waveguides

The photosensitivity of optical waveguides has been enhanced in the past with the addition of hydrogen. The price for such sensitivity-enhancement includes thermal instability, additional absorption due to hydrogen-induced bands, lower gain, and out-diffusion issues during device fabrication. J. Canning and K. Sommer of the Optical Fibre Technology Centre at the University of Sydney have resolved these issues by using hydrogen hypersensitization in active optical waveguides.

Typically, waveguides are patterned by UV irradiation. To effectively demonstrate the advantages of hypersensitized fibers as compared with untreated and hydrogen-loaded fibers, a total of six specimens were measured for small signal gain and lifetime according to the following plan, as reported in the December 1, 2001, issue of *Optics Letters*. Two different types of fibers were used in the experiments. The first batch, consisting of three samples, was 12% germanosilicate fibers doped with 0.1 mol% Er^{3+} . The second batch, consisting also of three samples, was 17% phosphosilicate fibers doped with 0.3 mol% and 3 mol% of Er^{3+} and Yb^{3+} , respectively. In addition, three pre-irradiation treatments were applied to the samples. Two samples, one from each batch, were not modified. Two samples—again, one from each batch—were fully loaded with hydrogen at 200 atm, 80°C, for four days. The remaining two samples were hypersensitized samples; that is, hydrogen was introduced and the samples were given a preliminary exposure before the hydrogen was allowed to out-diffuse. Gratings in the fibers were subsequently written with a 244-nm (germanosilicate fibers) and a 193-nm (phosphosilicate) UV laser. The small-signal gain coefficient was measured using a tunable laser and a 980-nm pump. A chopper and an oscilloscope were used to measure the excited-state lifetime.

In the germanosilicate samples, small signal gain was reduced with the intro-

duction of hydrogen throughout the 1520–1560-nm range, according to the researchers. They reported that the hypersensitized sample fared better than the fully loaded samples. Hydrogen caused little deviation in the upper excited-state lifetime, they said.

Small signal gain in the hypersensitized phosphosilicate fiber was comparable to that of the unmodified fiber. Lifetime in the hypersensitized fiber was slightly lower than that of the untreated fiber. The fully loaded fiber suffered significantly in both signal attenuation and excited-state lifetime.

The researchers concluded from this set of experiments that hypersensitization is a readily available method for improving stability, reliability, and efficiency of optical fibers and waveguides.

JUNE LAU

Molecules Designed to Mimic Bone at the Nanolevel

A research team at Northwestern University led by Samuel I. Stupp, the Board of Trustees Professor of Materials Science, Chemistry, and Medicine, has designed molecules that self-assemble into a three-dimensional structure that mimics the key features of human bone at the nanoscale level. These features include collagen nanofibers that promote mineralization and mineral nanocrystals. Collagen is found in most human tissues, including the heart, the eye, blood vessels, skin, cartilage, and bone, and gives these tissues their structural strength.

As reported in the November 23, 2001, issue of *Science*, the researchers created self-assembled nanofibers (~8 nm in diameter) that resemble the collagen fibrils of real bone in shape and size. When the nanofibers were exposed to solutions containing calcium and phosphate ions, the fibers became covered with hydroxyapatite crystals. These thin, rectangular mineral wafers grew on the nanofibers in a direction parallel to the fiber's length, mimicking hydroxyapatite-crystal growth on collagen in the formation of real bone.

According to the researchers, the assembly of the nanofibers themselves can be reversed by changing the pH level of the fibers' environment. The fibers also can be polymerized or cross-linked by oxidation to give them additional strength, a process that also can be reversed. The researchers said that the versatility of the nanofiber system offers the possibility of using the organic fibers as "cargo carriers," possibly for drug delivery to a specific point in the body. Natural enzymes found in the body can disassemble the fibers so that their cargo can be released.

To recreate bone's nanostructure in the laboratory, Stupp and his team designed a cone-shaped molecule, a peptide-amphiphile, that is bulkier and hydrophilic on one end (a peptide) and slimmer and hydrophobic on the other (an alkyl group). When in water at low pH, the molecules assemble themselves like spokes on a wheel, with the hydrophobic greasy tail directed to the center, leaving the peptide to face the exterior aqueous environment. This basic structure is repeated so that a long nanofiber is formed, similar to an insulated copper wire where the insulation is the peptide and the wire is the alkyl group. The synthetic fibers orient the growth of the hydroxyapatite crystals so that they mimic the structure found in natural bone.

The researchers engineered their peptide structure to attract bone cells, but the chemistry of the peptide is customizable, said Stupp, and can be changed to attract different cells to the fibrous scaffold, such as neurons, cartilage, muscle, liver, and pancreas cells.

Stupp said, "We've mimicked this for bone, but we have offered a strategy that would work for other tissues of the human body, or to create materials inspired by bone that could be useful in electronics or photonics."

Electrical Conductivity of Single-Molecule Wires Accurately Measured

Researchers from Arizona State University have determined a method for creating through-bond electrical contacts with single molecules, enabling them to achieve reproducible measurements of the molecules' conductivity. ASU chemistry professor Devens Gust said, "Progress in the field has been hampered by two problems. The first has been in making robust, reproducible electrical connections to both ends of molecules. After this has been achieved, the next problem is knowing how many molecules there actually are between the electrical contacts."

As reported in the October 19, 2001, issue of *Science*, the researchers began with a uniform atomic layer of gold atoms and attached octanedithiol insulator molecules to it through chemical bonds, forming a coating of aligned molecules. Using a solvent, they removed some of the insulators and replaced them with molecules of 1,8-octanedithiol, a molecule that is similar but capable of bonding with gold at both ends and acting as a molecular "wire."

Gold 2-nm particles were then added to the solvent, where they bonded to the free ends of the 1,8-octanedithiol mole-

cules, thus creating a bonded metallic contact at either end of the conducting molecules. A gold-coated conducting atomic force microscope probe was then run across the surface and conductivity was measured when it made contact with the gold particles.

When electrical measurements were made on over 4000 gold particles, virtually all measurements fell into one of five groups of distinct conductivity curves, according to the researchers. The conductivity curves were distinct whole-number multiples of a single, fundamental curve, they said.

The researchers said that the fundamental curve represents conduction by a single molecule of octanedithiol attached to the two gold contacts. When more than a single molecule was bound, each additional molecule increased the current capacity by the single unit amount of current that could be carried by one molecule. When the probe encountered octanedithiol insulator molecules, which could not bond with a gold particle, a much higher electrical resistance was recorded.

Gust said, "The molecule becomes a much better conductor when it is 'soldered' into the circuit by the bonds to gold at each end. This suggests how we can wire single-molecule components into a molecular circuit board, and lays some important groundwork for doing practical molecular electronics."

Cubic ZnMgO Alloys Offer Alternative to III-Nitride Wurtzite Structure

Jagdish Narayan and his associates at North Carolina State University have synthesized ZnMgO alloys that have a cubic sodium chloride structure, which may provide an alternative to III-nitrides of wurtzite hexagonal structure. When ZnO is alloyed with MgO, it can be controlled to produce either a hexagonal (wurtzite) or cubic (sodium-chloride) structure, they said. The cubic structure can be grown epitaxially on Si(100) by domain-matching epitaxy, where four lattice constants of the silicon match with three of the substrate. In addition, ZnO and its alloys have a higher exciton binding energy (60 meV) as compared with III-nitride counterparts (25 meV), which results in less trapping of carriers and luminescent efficiencies, they said.

ZnO, a II-VI semiconductor with a bandgap of 3.27 eV at 300 K, compares very closely with GaN of III-V systems. To vary the bandgap of ZnO, it can be alloyed with MgO (8.2 eV) to increase the bandgap or with CdO (2.0 eV) to decrease it. This is similar to the III-nitride system,

Narayan said, where GaN is alloyed with AlN (6.2 eV) to increase the bandgap or with AlN to decrease it. These III-nitride alloys have a hexagonal (wurtzite) structure, which can be grown epitaxially only on substrates of hexagonal symmetry. These substrates include α -Al₂O₃, (III)Si, 6H-SiC, and ZnO. The epitaxial growth on 6H-SiC and ZnO(0001) substrates occurs by lattice-matching epitaxy due to a small misfit. On the other hand, Narayan said, the epitaxial growth of III-nitride on α -Al₂O₃ and (111)Si occurs by means of domain-matching epitaxy, where an integral multiple of major planes/lattice constants of the film match with the substrate. For example, six (0110) planes of the film match with the seven ($\bar{1}2\bar{1}0$) planes of the substrate after a 30°/90° rotation in the basal plane, he said.

The ZnMgO alloys can be used to produce any color, including the three primary colors needed for white light-emitting devices that would be more durable and consume less power than conventional incandescent bulbs or fluorescent lamps, Narayan said.

"The shorter wavelength can also be focused more tightly, leading to a substantial increase in storage capacity of magnetic and optical disks," he said.

The researchers anticipate further applications for their U.S. patented alloy in the field of spintronics, biosensors, and optical communications.

Nanosphere Converted to Nanoprism, Offering Different Properties

Scientists at Northwestern University have been able to create triangular nanoprisms. They reported the method used to produce triangular nanoprisms in large quantities, using commercially available silver nanospheres, soap, and visible light, in the November 30, 2001, issue of *Science*.

In nanotechnology, most of the bulk preparatory methods are for spheres and rods, said Chad A. Mirkin, director of Northwestern's Institute for Nanotechnology, who led the experimental portion of the study.

In their experiments, the researchers found that when they placed common nanospheres made of silver in a solution containing soap molecules and irradiated the mixture with room light for three days, the spheres were converted into triangular prisms 15 nm thick.

The light induced the nanospheres to break up into silver atoms, which then fed the growth of the nanoprisms, a process called ripening. The conversion process could be arrested at any point by